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Kinetics and impacting factors of HO_2 uptake onto submicron atmospheric aerosols during a 2019 air quality study (AQUAS) in Yokohama, Japan

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Abstract

HO_2 uptake kinetics onto ambient aerosols play pivotal roles in tropospheric chemistry but are not fully understood. Field measurements of aerosol chemical and physical properties should be linked to molecular level kinetics; however, given that the HO_2 reactivity of ambient aerosols is low, traditional analytical techniques are unable to achieve this goal. We developed an online approach to precisely investigate (i) the HO_2 reactivity of ambient gases and aerosols and (ii) HO_2 uptake coefficients onto ambient aerosols (γ) during 2019 air quality study (AQUAS) in Yokohama, Japan. We identified the effects of individual chemical components of ambient aerosols on γ. The results verified in laboratory studies on individual chemical components: transition metals play a key role in HO_2 uptake processes and chemical components indirectly influence such processes (i.e., through altering aerosol surface properties or providing active sites), with smaller particles tending to yield higher γ values than larger particles owing to the limitation of gas phase diffusion is smaller with micrometer particles and the distribution of depleting species such as transition metal ions is mostly distributed in accumulation mode of aerosol. The modeling of γ utilized transition metal chemistry derived by previous studies, further confirming our conclusion. However, owing to the high NO concentrations in Yokohama, peroxy radical loss onto submicron aerosols has a negligible impact on O_3 production rate and sensitivity regime.

1 Introduction

As an important atmospheric trace gas, the hydroperoxyl radical (HO_2) links many of the key oxidants in the troposphere, including the hydroxyl radical (OH), nitrate radical (NO_3^-), ozone (O_3), and hydrogen peroxide (H_2O_2) (Logan et al., 1981; Chen et al., 2001; Jaeglé et al., 2000; Sommariva et al., 2004; Jacob, 2000). However, its observed concentration in field measurements has not yet been fully explained by sophisticated models (known as the "HOx dilemma") (Stone et al., 2012; Creasey et al., 1997; Kanaya et al., 2007b; Whalley et al., 2010; Millán et al., 2015), although it can be mostly solved in the conditions of clean marine air or stratospheric air where NO concentration is low or aerosol

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loading is low enough to make the heterogeneous reaction of HO_2 not important (Sommariva et al., 2004; Kanaya et al., 2007a). Owing to the short atmospheric lifetime of HO_X(=OH+HO_2+RO_2), the HOx reactivity measurement can provide a robust test of its complex chemistry (Heard and Pilling, 2003). The HO_2 uptake kinetics of ambient aerosols, including HO_2 reactivity (k_a) and the HO_2 uptake coefficient (γ), influence many atmospheric processes, including ozone formation rates and their sensitivity to NO_X (Sakamoto et al., 2019), H_2O_2 formation thus aerosol properties (Thornton et al., 2008). With $\gamma > 0.1$, HO_2 concentration can also be influenced under conditions such as low [NO] or high aerosol loading (Lakey et al., 2015; Mao et al., 2013b; Martínez et al., 2003; Tie et al., 2001, Jacob, 2000; Matthews et al., 2014). These effects make the HO_2 uptake kinetics of ambient aerosols indirectly influence human health and climate change.

From laboratory, field, and modeling studies (Taketani et al., 2012; Taketani et al., 2008; Bedjanian et al., 2005; Thornton et al., 2008; George et al., 2013; Lakey et al., 2016a; Lakey et al., 2016b; Matthews et al., 2014; Cooper and Abbatt, 1996; Hanson et al., 1992; Thornton and Abbatt, 2005; González Palacios et al., 2016; Mozurkewich et al., 1987; Remorov et al., 2002; Jaeglé et al., 2000; Loukhovitskaya et al., 2009; Stone et al., 2012), HO_2 uptake coefficients onto different types of aerosol can span several orders of magnitude (~0.002–1), which can be affected by many parameters, such as droplet/particle size and composition, the presence of dissolved reactive gases (Mozurkewich et al., 1987), and environmental conditions (i.e., relative humidity (RH), pH, and T). In the absence of metals, the uptake of HO_2 by ambient aerosols is believed to occur *via* the acid–base dissociation of HO_2 (pKa = 4.7), followed by electron transfer from O_2^- to HO_2 (aq), producing H_2O_2 (Jacob, 2000; Thornton et al., 2008; Zhou et al., 2019b). However, laboratory studies have shown that certain transition metals (i.e., Cu(II) and Fe(II)) can act as catalysts and accelerate HO_2 uptake rates onto many chemical compounds (Thornton et al., 2008; Taketani et al., 2008; Taketani et al., 2012, Cooper and Abbatt, 1996). Owing to the sufficiently high metal concentrations in tropospheric aerosols, as shown in previous field measurements (Hofmann et al., 1991; Wilkinson et al., 1997; Guieu et al., 1997; Manoj et al., 2000; Halstead et al., 2000; Siefert et al., 1998; Sedlak and Hoigné, 1993; Guo et al., 2014), recent studies have proposed that γ may be dominated by metals contained in the aerosol. This can lead to the

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HO_2 destruction (Mao et al., 2013a; George et al., 2013), forming H_2O_2, HO_2–water complexes, or water and sulfate (Mozurkewich et al., 1987; Cooper and Abbatt, 1996; Gonzalez et al., 2010; Loukhovitskaya et al., 2009; Mao et al., 2010; Macintyre and Evans, 2011), which are important in the evolution of the chemical composition and physical properties of particles (George and Abbatt, 2010; George et al., 2008). The available data concerning HO_2 uptake kinetics onto ambient aerosols are insufficient for quantitative consideration owing to the much lower k_a value, as compared with the HO_2 reactivity of ambient gases (k_g). Therefore, they are below the detection limits of the current instruments.

To our knowledge, aside from us, only one study has measured γ, using an offline method that integrated ambient aerosols over size and time (Taketani et al., 2012). Considering that the offline method may distort γ, we developed an online approach to evaluate HO_2 uptake kinetics onto ambient aerosols. This method was successfully applied in Kyoto, Japan, in summer 2018, using a versatile aerosol concentration enrichment system (VACES) and a technique combining laser-flash photolysis with laser-induced fluorescence (LFP–LIF) (Zhou et al., 2019b). The obtained average γ value (~0.24) was comparable with the previous values used for modeling studies (~0.2) (Stadtler et al., 2018; Jacob, 2000). However, the large standard deviation (± 0.20, 1 σ) of γ along with the measurement time suggest that many other parameters might play a role, e.g., the measurement setup, aerosol characteristics, T, and RH.

In this study, we chose Yokohama (Japan), a coastal city with higher pollutant levels than Kyoto and different properties of the air masses from mainland Japan and the coast, as the measurement site. This is part of the Air QUAlity Study (AQUAS) campaigns. The chemical and physical properties of ambient aerosols were quantified in real-time. To test their influence on k_a and γ, we conducted correlation matrix analysis coupled with the bootstrap method and classified the arriving air masses from different directions. Further, the main mechanism of γ was investigated by comparing the real-time quantified γ values with the modeled values. The impact of the peroxy radical's loss onto ambient aerosols on air quality is evaluated through their impact on ozone formation rates and their sensitivity to NO_X. The results obtained here will for better estimation of the heterogeneous reaction between HO_2 and ambient aerosols in sophisticated air quality models.

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2 Materials and methods

2.1 Sampling sites

The measurement campaign was conducted at Yokohama Environmental Science Research Institute in Yokohama, Japan (location: 35°28'52.8"N, 139°39'30.3"E), from July 24 to August 03, 2019. The sampling ports of the instruments were placed approximately 25 m above the ground. Figure S1 shows the air mass directions during the campaign, which can be classified into two categories: (i) from the sea to the north, toward Yokohama City (~19% of the experimental period: from 12:00 July 25 to 12:00 July 27, 2019) and (ii) from the mainland toward Yokohama City (~81% of the experimental period). This classification was intended to distinguish the chemical properties of aerosols arriving from the mainland and the ocean, and to consequently quantify their impacts on k_a and γ.

2.2 Measurement strategies, instrumentation, and related data analysis

LFP–LIF and VACES In situ ambient air HO_2 reactivity was measured using LFP–LIF, which was adapted from a laser-induced pump and probe OH reactivity measurement technique. This approach has been successfully employed for gas and aerosol phase HOx (=OH+HO_2) reactivity measurements (Sadanaga et al., 2004; Miyazaki et al., 2013; Sakamoto et al., 2018). Further details concerning the HO_2 reactivity measurements are described in the Supporting Information (SI). To compensate for the relatively low ambient aerosol concentrations and thus the low k_a, a setup with VACES and an auto-switching aerosol filter was used before LFP–LIF. The enrichment factor of the ambient aerosol surface area (E) was calculated from the difference between the surface areas measured before and after VACES by two scanning mobility particle sizers (SMPSs) (see SI).

HO_2 reactivities in ambient air caused by two modes were measured: (a) the gas phase mode with aerosol filter on, the HO_2 reactivities are represented as k_g, and (b) the gas + enriched aerosol phase mode with aerosol filter off, the HO_2 reactivities are represented as k_g+Ek_a, where E represents the enrichment factor of k_a, Ek_a represents the total HO_2 reactivities caused by enriched ambient aerosols, the usage of Ek_a is based on the assumption that HO_2 uptake with aerosol particles follows the pseudo-first-order rate law. We modeled k_g in both modes using a theory identified previously (see SI: HO_2

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reactivity of ambient gas phase) (Zhou et al., 2019b) and compared it with the measured values. The differences between measured and modeled k_g in mode (a) enabled us to establish their interrelationship and to check instrument stability. The differences between (k_g+Ek_a) and the modeled k_g in mode (b) are considered as the enriched aerosol phase HO_2 reactivity (Ek_a). The total HO_2 reactivity decay profile follows single-exponential decay:

$$HO_2 = [HO_2]_0 \exp\left(-(k_g + Ek_a + k_{bg})t\right) \quad (1)$$

where k_{bg} denotes the zero air background obtained by injecting zero air with the same RH as the real-time ambient value into the reaction cell every 24 h for 30 min. The RH was controlled by passing some of the zero air through a water bubbler. The value of k_{bg} was subtracted separately on each day. The variability of k_{bg} (i.e., the reproducibility of the laser system) was calculated as the standard deviation of the response of repeated measurements on different days. It was found to be ~4%, which is slightly higher than the instrument precision (3%). A 30-min average calculation was applied to the data to reduce data fluctuation. The observed HO_2 uptake coefficients onto ambient aerosols (γ_{obs}) can be calculated from the dependence of Ek_a on γ_{obs}:

$$Ek_a = \frac{\gamma_{obs}\omega_{HO_2}ES}{4} \quad (2)$$

where ES and ω_{HO_2} represent the enriched surface area of ambient aerosol after VACES (~12.5) and the mean thermal velocity of HO_2 (~437.4 m s^{-1}), respectively. Therefore, the HO_2 reactivity of ambient aerosol (k_a) can be obtained from Ek_a by dividing by the enrichment factor E.

High resolution–time of flight–aerosol mass spectrometry (HR–ToF–AMS) A field-deployable HR–ToF–AMS (Aerodyne Research Inc.) (DeCarlo et al., 2006) was used for the characterization of the non-refractory aerosol mass with a time resolution of ~3 min. The HR-ToF-AMS measured the total organic aerosol (OA), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-), and the two most dominant oxygen-containing ions in the OA spectra, i.e., mass-to-charge ratios of m/z = 44 (Org44, mostly CO_2^+) and m/z = 43 (Org43, mainly $C_2H_3O^+$ for the oxygenated OA and $C_3H_7^+$ for the hydrocarbon-like OA) (Ng et al., 2011). The fractions of Org44 and Org43 in OA are represented as f_{44} and f_{43}, respectively. Ambient air was sampled through a critical orifice into an aerodynamic lens, which

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efficiently transmitted particles between 80 nm and up to at least 1 μm. Particles were flash-vaporized by impaction on a resistively heated surface (~600 ºC) and ionized by electron ionization (70 eV). The m/z values of the resulting fragments were determined using a ToF mass spectrometer. Data were analyzed using the ToF–AMS software SQUIRREL and PIKA. Data were not corrected for lens transmission efficiency. Standard relative ionization efficiencies (RIE) were used for organics (RIE = 1.4), nitrate (RIE = 1.1), chloride (RIE = 1.3), sulfate (RIE = 1.12), and ammonium (RIE = 4). Concentration data were obtained from background-subtracted stick-mass data (low-mass-resolution-base mass concentration data, which are calibrated using ammonium sulfate particles) and determined assuming a collection efficiency (CE) of 0.5.

Filter-based photometer Real-time measurement of the equivalent black carbon (eBC) was performed using a 5-wavelength dual-spot absorption photometer (MA300, AethLabs, San Francisco, CA, USA), which performed an online correction for possible artefacts resulting from filter loading and multiple scattering (Drinovec et al., 2015). In this study, eBC data obtained from light attenuation at a wavelength of 880 nm were used to avoid possible contributions from brown carbon; the time resolution was ~1 min.

Trace elements Fourteen trace elements (Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Ba, and Pb) were measured using an offline method at two-day intervals from 21 July to 5 August 2019. The suspended particle matter (SPM) was collected onto 623.7 cm^2 size quartz fiber filters (Pallflex Tissuquartz 2500QAT-UP), which had an available collecting area of 405.84 cm^2, using a high-volume sampler (1000 L min^{-1}). Approximately 2 cm^2 of each filter was cut into pieces and placed into a polytetrafluoroethylene (PTFE) pressure digestion tank with 1 mL 49% hydrofluoric acid (HF) and 5 mL 69% nitric acid (HNO_3). A Thermo Fisher X2 Series inductively coupled plasma mass spectrometer (ICP–MS) was then used to determine metal concentrations. By assuming that the metal fractions were the same in SPM and PM_1 (aerosol particles with aero-dynamic diameters less than 1 μm), the concentrations in PM_1 were estimated according to the tested metal concentrations in SPM and the ratio between SPM and PM_1 measured in-situ.

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Water-soluble inorganic species NR-PM_1 water-soluble inorganic species (including Na^+, SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Ca^{2+}, K^+, Mg^{2+}) used for *the ISORROPIA-II model* were also measured using offline method, as described above. For extraction, we cut 1/4 of a 47 mm filter punched from the original collected filter and placed it in 10 mL of ultrapure water (18.2 MW cm^{-1}) in a centrifuge tube. This was followed by 15 min of ultrasonication in a 30ºC water bath. The solution was then vortexed (Vortex Genie 2, Scientific Industries, USA) for 1 min to ensure homogeneity and filtered through syringe filter with pore size of 0.45-μm (Advantec Dismic-25, PTFE). An Ion Chromatograph (IC, ICS1600, DIONEX, USA) was employed to determine the concentrations of these inorganic ions in the extracted solution.

Scanning Mobility Particle Sizers (SMPS) Particle mass and surface area before and after VACES were determined using two SMPSs (model 3936L72 and 3936L75, TSI, Shoreview, MN, USA) that measured particle size distribution at 14.1–736.5 nm and 14.6–661.2 nm at 5-min intervals.

Gas phase monitors NO_2 was measured by cavity attenuated phase shift (CAPS, Aerodyne Research, USA, at 1-s intervals), NOy－NO by chemiluminescence (Model 42i-TL, Thermo, at 10-s intervals), CO by Thermo CO analyzer of nondispersive infrared spectroscopy (Model 48i-TLE, Thermo Scientific, USA, at 10-s time intervals), and O_3 by UV absorption (Model 1150, Dylec, AMI Co., Ltd, at 10-s time intervals). HCHO was determined by high performance liquid chromatography (HPLC; 1260 Infinity, Agilent Technologies Inc, USA) from 14:00 July 29, to 12:00 August 3, 2019. An average value of ~2 ppb was used for the data analysis.

ISORROPIA-II model NR-PM_1 water-soluble inorganic species (including Na^+, SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Ca^{2+}, K^+, Mg^{2+}) and meteorological parameters including temperature and RH were used to calculate the aerosol pH and liquid water content based on the *ISORROPIA-II* model (Fountoukis and Nenes, 2007). We ran *ISORROPIA-II* in "reverse" mode and the particles were assumed to be deliquescent, i.e., in metastable mode (Hennigan et al., 2015). The thermodynamic equilibrium of the NH_4^+- SO_4^{2-}- NO_3^- system case was used for modeling.

3 Results and discussion

3.1 The HO_2 uptake kinetics onto ambient aerosols

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The measured total HO_2 reactivities were compared against the modeled gas phase HO_2 reactivity under the experimental conditions both with and without the aerosol phase. Without the aerosol phase, the modeled k_g values are calculated according to the description in Sect. 2.2, which are not statistically different with the measured k_g values (Fig. 1a second panel, T-test, p = 0.49, with alpha = 0.05), indicating that HO_2 loss in the reaction cell was dominated by its reaction with NO_2 in the LFP-LIF system. With the aerosol phase, the measured (Ek_a+E_g) and modeled values ($\approx E_g$) were significantly different (see Fig. 2b, first panel, T-test, p = 0.04, with alpha = 0.05). The differences were considered to be the HO_2 reactivities of enriched ambient aerosols (Ek_a). Ek_a ranged between 0.01 s^{-1} (25th percentile) and 0.1 s^{-1} (75th percentile), with an average value of 0.066 ± 0.062 s^{-1}, the corresponding k_a, calculated by dividing Ek_a by E, ranged between 0.001 s^{-1} (25th percentile) and 0.08 s^{-1} (75th percentile), with an average value of 0.005 ± 0.005 s^{-1}. The error for Ek_a was estimated as ~ 0.05 s^{-1}, calculated as the propagated errors from k_g+Ek_a (equals to the systematic error of the instrument, ~0.05 s^{-1}) and the modelled k_g in mode (b) (~ 0.001 s^{-1}). Accordingly, the errors for k_a was estimated as ~ 0.004 s^{-1} (from the obtained error of Ek_a by dividing by the enrichment factor E). The corresponding γ, calculated from Eq. 2, ranged from 0.05 (25th percentile) to 0.33 (75th percentile), with an average value of 0.23 ± 0.22. The gas-phase diffusion effects on γ were estimated to be less than 1% (i.e., negligible) (further details are given in the SI).

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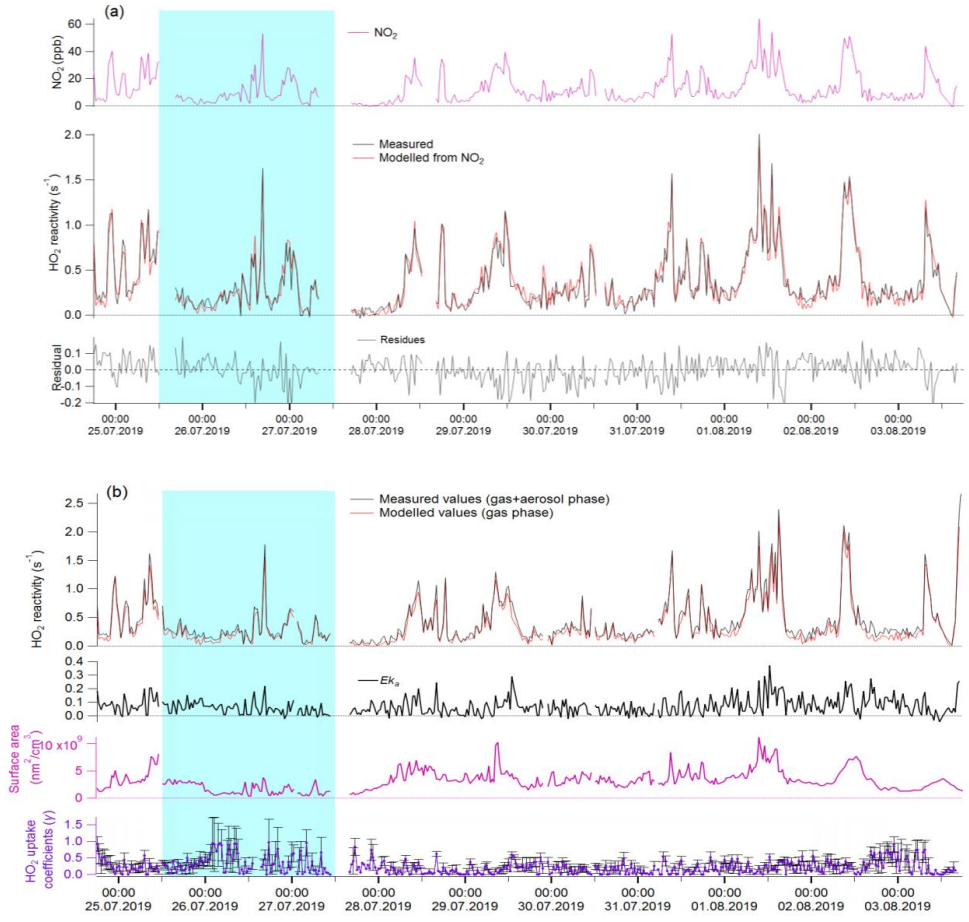

228

229 Figure 1: Temporal variation of parameters under different experimental conditions. (a) Without aerosol phase:
230 1st panel: measured NO_2 concentrations (ppb); 2nd panel: measured (red line) and modeled (black line) k_g; 3rd panel:
231 fitting residues of modeled k_g values, ranging from −0.04 (25 percentile) to 0.05 (75 percentile), which are
232 considered to be the systematic error of the LFP–LIF instrument. (b) Gas + aerosol phase: 1st panel: measured
233 total HO_2 reactivity (k_g+Ek_a) and modeled k_g; 2nd panel: Ek_a, calculated from the difference between the measured
234 and modeled values from the 1st panel; 3rd panel: the surface area of the enriched ambient aerosols (ES); 4th panel:
235 γ calculated from Ek_a and ES according to Eq. 2. The blue shaded area represents the air masses from group i
236 (from coast), the remainder is from group ii (from mainland). The errors for γ were estimated as the propagated
237 errors of k_a (~0.004 s^{-1}) and the surface area (~8%), based on the systematic errors of the instrument.
238
239 Statistical significance analysis showed that the average γ value of group i (0.35 ± 0.28) is significantly
240 higher than that of group ii (0.21 ± 0.16) (calculated p = 4.9E-5; Mann-Whitney), indicating that the air
241 masses from the ocean yield higher γ values than the air masses from mainland Japan. This difference
242 maybe influenced by many factors, for example, the mass accommodation coefficients (α^{HO_2}), which
243 are driven by the physical and chemical properties of the aerosols. Studies have shown that α^{HO_2} are

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typically ~ 0.2 and 0.5 for organics and inorganics, respectively (Lakey et al., 2016b, 2016a; Taketani et al., 2008, 2009; Thornton et al., 2005; Moon et al., 2018; George et al., 2013; Mozurkewich et al., 1987), while for aerosols with transition metals, γ values could be limited only by α^{HO_2} (Mozurkewich et al., 1987). Thus we will discuss such differences in the aerosols arriving from the ocean (group i) and the mainland (group ii) in the following sections (more details can be found in Sect. 3.4 and Table S1). The average value of k_a at Yokohama (0.005 ± 0.005 s^{-1}) was much higher than that found for Kyoto city (0.0017 ± 0.0015 s^{-1}) (with calculated $p < 0.05$; Mann-Whitney), this may due to many differences in aerosol properties in Kyoto and Yokohama city. We list some of them as follows: 1) mass composition, the aerosols in the coast city tend to contain more sea salts thus increased k_a, 2) particle size distribution, smaller particles tending to yield higher γ values than larger particles owing to the limitation of gas phase diffusion is smaller with micrometer particles, and the distribution of depleting species (e.g., transition metal ions) are mostly distributed in accumulation mode of aerosol, 3) the water content and the metal concentrations, this will highly influence the HO_2 uptake capacity of the ambient aerosols. However, the average HO_2 uptake coefficient onto ambient aerosols (γ) in Yokohama (~0.23) was comparable with previous measured (~0.24–0.25) (Zhou et al., 2019b; Taketani et al., 2012) and modeled (~0.20) values (Stadtler et al., 2018; Jacob, 2000). The large standard deviation (± 0.21, 1σ) of the values along with the measurement time may be due to the instantaneously changed chemical and physical properties of ambient aerosols, indicating that a large bias may exist if a constant γ value is used for modeling.

3.2 Bulk chemical composition of ambient aerosols

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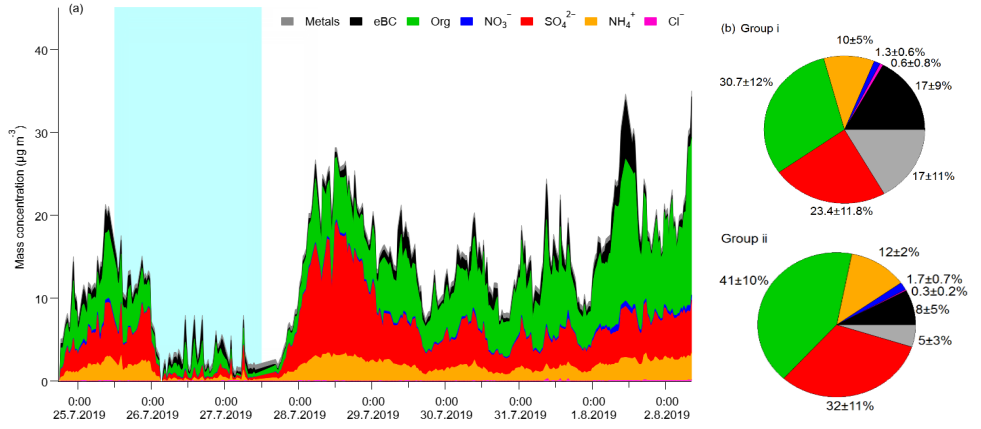

Figure 2: (a) Concentrations of non-refractory chemical components plus eBC in Yokohama, Japan (July 24 to August 02, 2019). The blue shaded area represents group i from coast and the remaining areas represent group ii from mainland. (b) Average contribution fractions of different chemical components of groups i and ii.

Figure 2a shows the time series of the mass concentrations of OA, SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, and eBC in PM_1 in Yokohama from July 24 to August 02, 2019, which is ~1.5 days less than for the LFP–LIF data. During this period, PM_1 ranged from ~1 to 35 μ g m^{-3} (average ≈ 13 μg m^{-3}) and was dominated by OA, SO_4^{2-}, and NH_4^+, with contributions of 39 ± 11%, 30 ± 12%, and 12 ± 4%, respectively; these were followed by eBC and metals, with contributions of 10 ± 7% and 8 ± 8%, respectively. Cl^- contributed < 1% in both groups, which is similar to that reported for an urban area in winter in Bern (Switzerland) (Zhou et al., 2019a). However, NO_3^- contributed much less (~2 ± 0.7%) compared with that reported for Bern (~19 ± 4%), which may be due to the reverse reaction of NH_4NO_3 converting to HNO_3. Since Yokohama is a coastal city, and HNO_3 is easy vaporized in summer, gaseous HNO_3 may sink with sea salt particles by forming $NaNO_3$ through heterogeneous reactions (Finlayson-Pitts and Pitts, 2000).

Figure 2b shows the average contribution fractions of different components of group i and group ii. The main differences in the components between these two groups are the fractions of OA, BC, SO_4^{2-}, and metals. The OA fraction was ~1.8 and ~8.4 times higher than that for the metals in groups i and ii, respectively. As OA can cover the surface of the particles and thereby decrease γ (Lakey et al., 2016a; Takami et al., 2013), the difference between the OA and metal fractions in these two groups may partially explain the much higher γ values of group i (vs. group ii). Previous studies have shown quite

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low HO_2 uptake coefficient on BC (~ 0.01) (Saathoff et al., 2001; Macintyre and Evans, 2011), which in contrast to the results obtained here. This may due to the much higher fraction of eBC in group i (vs. group ii) may also provide active sites thus facilitating the physical uptake of HO_2. We also observed slightly higher Cl^- and BC fraction in group i (from ocean) than that of group ii (from mainland), which may due to the effects of sea salt and the ship emissions, respectively. From the average diurnal patterns (Figs. S5 and S6), the trends in k_a follow the trends in chemical composition, whereas γ shows a contrasting trend with both variables in both groups. For group ii, SO_4^{2-} and OA exhibited higher values whereas γ exhibited lower values during the daytime than those during nighttime, indicating that secondary aerosol formation resulting from photochemical reactions may decrease γ. To identify the influence of each individual chemical component of ambient aerosol on k_a and γ, we further performed correlation matrix analysis.

3.3 Influence of individual chemical components of ambient aerosol on k_a and γ

For the ambient aerosol with multiple components, k_a and are influenced by many factors, and those factors also have mutual effects to each other, for example, the transition metal Cu and Fe contained in ambient aerosols can be chelated by organics (Lakey et al., 2016b). The direct correlations between transition metals and γ may give us some hints about the interactions of different chemical components in ambient aerosols and their effects to γ. Therefore, we produced a Pearson correlation matrix of all the testing chemical composition factors in Yokohama city. To exclude the effects of the different fractions of chemical components in groups i and ii, the bootstrap method, which is based on the creation of replicate the inputs by perturbing the original data through resampling, was employed. The resampling was performed by randomly reorganizing the rows of the original time series such that some rows of the original data were present several times while other rows were removed. The final results were obtained by running the data for 1000 bootstrap replicates. The average values of these 1000 bootstrap replicates are listed in Fig. 3.

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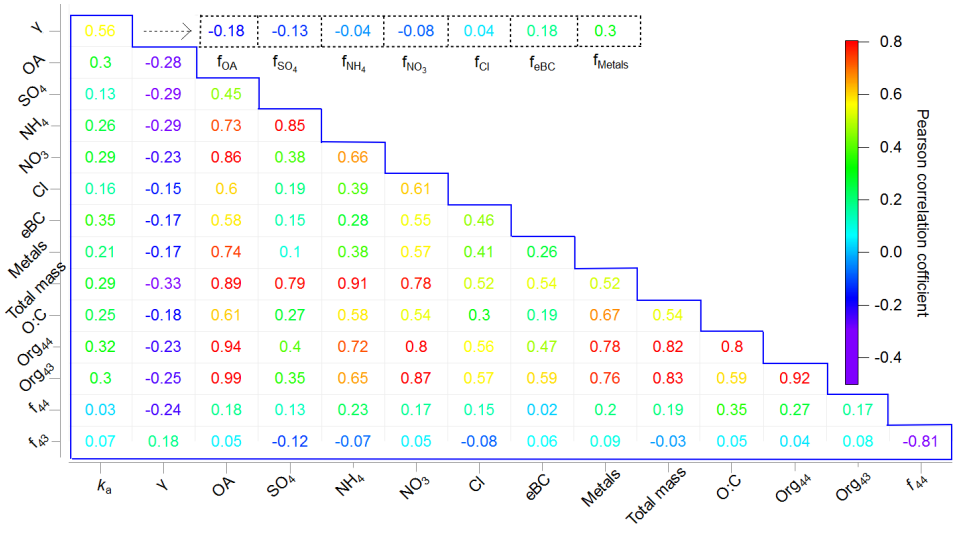

Figure 3: Correlation matrix showing Pearson's r values for the chemical compositions, k_a, and γ during the corresponding measurement periods (in the blue box), as well as the Pearson's r values for the chemical composition fraction *i* (represented as *fi*, *i* = OA, SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, eBC, and metals) and γ (in the dashed line box).

Most of the chemical components had strong or moderate Pearson correlation coefficients with each other (Fig. 3), although k_a and γ showed only a moderate correlation with each other (0.56). As γ can be correlated with the qualitative, rather than quantitative, properties of the aerosols, we further investigated the Pearson's r values between the chemical composition fractions and γ. The results show that k_a was positively correlated with total mass and the individual chemical components, whereas γ showed only a weak positive correlation with *f*metals (0.30) and f_{eBC} (0.18). This indicates that the metals may act as a catalyst, thus accelerating the depletion of HO_2 (Mao et al., 2013a) (chemical reaction), and that BC may provide the active sites for HO_2 radical interaction with ambient aerosols (physical uptake). The very weak correlation of γ with f_{Cl^-} (0.04) may be related to Cl^- chemistry, for example, HO_2(g) can react with NaCl(g) and produce NaOH and Cl_2(g), thus cause a decrease in the HO_2 concentration, which in turn indirectly effects γ (Remorov et al., 2002). Interestingly, when considering the Org44 and Org43 fractions in total OA separately, γ is positively correlated with f_{43} (0.18) but negatively correlated with f_{44} (−0.24). This is consistent with the conclusion from Lakey et al. (2016b), i.e., that more oxidized organic aerosols tend to be highly viscous and thus decrease HO_2 uptake coefficients (Lakey et al., 2016b). In summary, γ was dominated by the free forms of transition

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metals that can act as catalysts of HO_2 uptake onto ambient aerosols, and was indirectly affected by chemical components that might alter the properties of ambient aerosols, e.g., oxygenated OA can cover the aerosol surface and alter the viscosity of ambient aerosols, thereby decreasing γ (Lakey et al., 2016a; Lakey et al., 2016b; Takami et al., 2013), whereas BC may provide active sites and thereby increase γ though physical uptake. This is further confirmed by the classification of the air masses, i.e., the air mass from the ocean (group i), which had a higher HO_2 uptake capacity, contained less OA and more metals than that from mainland Japan (group ii). We further compared the measured γ values with the modeled γ values using previously proposed mechanisms, as shown below.

3.4 Possible mechanism of HO_2 uptake onto ambient aerosols

Two mechanisms of HO_2 uptake onto aqueous ambient aerosols have been proposed, for which equations have been derived from a previous study (Thornton et al., 2008): (i) HO_2-only chemistry and (ii) chemistry with transition metals playing a role. In this study, the liquid content of the total ambient aerosol mass ranged from 70% to 88%, as obtained from the *ISORROPIA-II model*. As the solubility of Fe is rather small in ambient aerosol, the reaction rates of Fe/Mn for liquid phase HO_2 in aerosol is ~ 100 times slower than it is for Cu, thus the influence of Fe and Mn on HO_2 uptake can be neglected compared to Cu or scaled as equivalent [Cu^{2+}] (Fang et al., 2017; Hsu et al., 2010; Baker and Jickells, 2006; Oakes et al., 2012; Song et al., 2020), therefore, we use the soluble Cu as surrogate for transition metals in ambient aerosols to assess the influence of transition metals to γ in ambient aerosols. The Cu solute mass fraction in the liquid content of the ambient aerosols was estimated as (3.5–30) × 10^{-4} mol L^{-1} according to our offline filter test (Sect. 2.2), and the activity coefficient for total Cu was assumed to be 0.1 (upper limit) based on a study of $(NH_4)_2SO_4$ particles at 68% RH (Ross and Noone, 1991). Using copper ions as a surrogate metal for transition metal ions (TMIs), the potential HO_2 loss onto aqueous ambient aerosols via mechanisms involving TMIs was estimated as (Hanson et al., 1994):

$$\frac{1}{\gamma^{\mathrm{TMI}}} = \frac{1}{\alpha^{\mathrm{HO_2}}} + \frac{\omega}{H_{eff} RT \sqrt{k^I D_{aq} Q'}} \quad (3)$$

where $\alpha^{\mathrm{HO_2}}$ is the mass accommodation coefficient of HO_2, ω is the mean HO_2 molecular speed (cm s^{-1}), H_{eff} is the effective Henry's Law coefficient, R is the gas constant (J K^{-1} mol^{-1}), and T the temperature

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(K). k^{I} is the pseudo-first-order rate constant equal to k^{II}_{TMI}[TMI], where k^{II}_{TMI} is the second order rate constant for aqueous phase reaction with HO_2/O_2^- and TMI. Q' accounts for aqueous-phase diffusion limitations and is expressed as

$$Q' = [\coth(q) - \frac{1}{q}]; q = r_p\sqrt{\frac{k^{I}}{D_{aq}}} \quad (4)$$

Table S1 shows more details of the parameters used for modeling. γ^{TMI} with α^{HO_2}=0.2 (typically for organics) and 0.5 (typically for inorganics as explained in Table S1) are plotted in Fig. 4a along with the measured γ values; the much lower variation of the modeled values may due to the low time resolution (~2 days) of [Cu]. The measured γ values (averaged value: ~ 0.23) are significantly lower than the modelled γ^{TMI} with α^{HO_2}=0.5 (averaged value: ~ 0.32), but significantly higher than the modelled γ^{TMI} with α^{HO_2}=0.2 (averaged value: ~ 0.16), both with calculated p<0.05 (t-test), indicating that the chemical components may be internally mixed, as proposed by Takami et al. (2013), which influences the aerosol surface tension and the activity of the free form of the copper ion (i.e., OA and BC) to constrain γ^{TMI}; however, this is not considered in this model. No linear correlation was found between γ^{TMI} and γ. Further classification of measured $\gamma \geq 0.4$ and $\gamma < 0.4$ shows that γ^{TMI} has a weak correlation with measured γ values when $\gamma \geq 0.4$ (Fig. S7), which may due to the higher fraction of metals in the total mass at measured $\gamma \geq 0.4$ (~12%) than at < 0.4 (~7%); therefore, the impact of the other chemical components is much lower. The γ values obtained here are comparable with those in previous ambient aerosol studies (Taketani et al., 2008; Zhou et al., 2019b) (Fig. 5b). When compare with single-compound aerosols obtained from laboratory studies, γ values were generally higher than the HO_2 uptake coefficients onto organic species (Lakey et al., 2015), soot particles (Bedjanian et al., 2005), and the dry state of inorganic aerosols (i.e., $(NH_4)_2SO_4$, NaCl, and H_2SO_4), but comparable or lower than aqueous and copper-doped aqueous phases of inorganic species (Fig. 5b) (George et al., 2013; Lakey et al., 2016b; Taketani et al., 2008; Thornton and Abbatt, 2005). This may indicate the collective effects of the individual chemical components of ambient aerosols to γ, and the significant influence of RH to aerosol states of single-component particles thus their HO_2 uptake coefficients.

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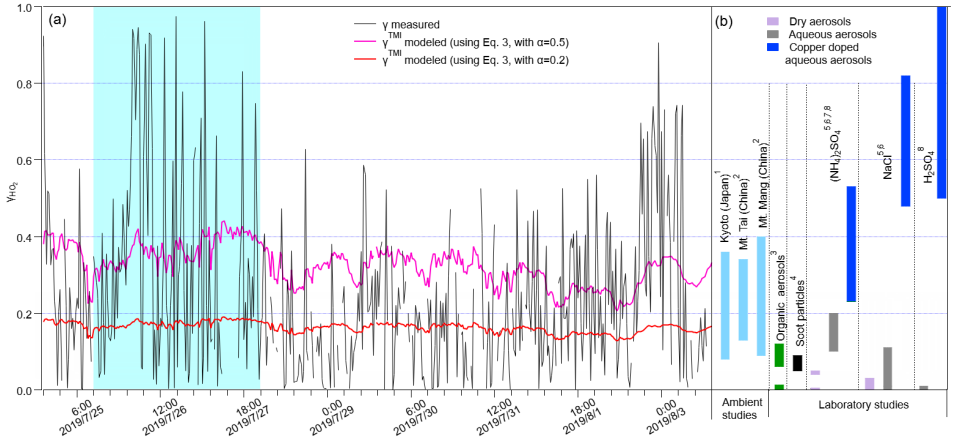

Figure 4: (a) Measured and modeled γ values along with measurement time. The blue shaded area represents group i; the remaining areas represent group ii. (b) HO_2 uptake coefficients onto different types of aerosol obtained from ambient and laboratory studies, the numbers indicate the related references from which the data were obtained: 1. Zhou et al., 2019b; 2. Taketani et al., 2012; 3. Lakey et al, 2015; 4. Bedjanian et al., 2005; 5. Taketani et al., 2008; 6. George et al., 2013; 7. Lakey et al., 2016b; 8. Thornton and Abbatt, 2005.

Other studies have shown that γ is strongly negatively temperature dependent (Remorov et al., 2002; Mao et al., 2010; Cooper and Abbatt, 1996; Hanson et al., 1992; Thornton and Abbatt, 2005; Gershenzon et al., 1995). Here, RH and T were stabilized by the VACES–LFP–LIF system, as compared with those in ambient air (Fig. S8). We noticed that k_a and γ showed no dependence on RH and T in the reaction cell (see Fig. S9), indicating that the instantaneous change of RH and T may not be dominating factors in terms of the variation of k_a and γ with measurement time. This suggests that the individual chemical components and physical properties of ambient aerosols may dominate γ variation during field campaign; both the metal-catalyzed reactions and the chemical components and their states should be considered to yield more accurate γ values. Results obtained here are in accordance with previous results on correlations between particulate H_2O_2 (which can be formed by the uptake of HO_2) and coarse particulate transition metals (Wang et al., 2010). Using an offline methodology to investigate the influence of RH and T by maintaining constant experimental conditions or chemical compositions will be the subject of future work.

3.5 Influence of the physical properties of ambient aerosols on k_a and γ

HO_2 heterogeneous loss rates are driven by the different particle sizes of different aerosol types (i.e., urban ambient aerosols and marine aerosols)(Morita et al., 2004; Guo et al., 2019; Jacob, 2000). In this

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study, k_a and γ showed no linear dependence on the mean ambient particle diameters (see Fig. S10). Identifying the fractional contributions of aerosols in different particle size ranges to k_a and γ is highly desirable in terms of understanding their influence. However, it seems that high γ values (> 0.8) occur when the surface area is < 2×10^{-6} cm^2 cm^{-3} and the mean particle diameter is < 110 nm. This is in accordance with a previous study showing that aerosols yield the highest fractional contribution to the total heterogeneous loss rate of HO_2 radicals of size < 0.1 μm (Morita et al., 2004) and that the mass accommodation process plays the determining role for small and medium sized aerosols in controlling HO_2 uptake. Guo et al. (2019) states the HO_2 radicals experience less loss upon diffusion onto large aerosols than do small droplets due to dilution effects make the larger aerosols having lower depleting species concentrations (Cu^{2+}). However, this was based on the assumption that the total mass of Cu^{2+} is constant during the hygroscopic growth of particles which is not always true in the ambient conditions. Further studies about Cu^{2+} content in particles with different size distribution are needed to fully understand the result here.

3.6 Significance of k_a to O_3 formation potential

In urban atmosphere, XO_2 (=HO_2+RO_2) fate is important to the photochemical production of ozone ($P(O_3)$). Here, the loss rates of XO_2 due to three factors were compared: (i) uptake onto the ambient aerosols (L_{P-XO_2} in Eq. 5), since no experiment or reference available for RO_2 uptake onto ambient particles, we assume the RO_2 reactivities caused by its interaction with ambient aerosols were the same as k_a, (ii) XO_2 self-reactions (L_{R-XO_2} in Eq. 6), and (iii) reaction with NO (L_{N-XO_2} in Eq. 7), which can produce NO_2, a precursor of O_3; therefore Eq. 7 can also be regarded as $P(O_3)$.

$$L_{P-XO_2} = k_a[XO_2] \quad (5)$$

$$L_{R-XO_2} = 2 * (k_{HO_2-HO_2}[HO_2]^2 + k_{HO_2-RO_2}[HO_2][RO_2]) \quad (6)$$

$$L_{NO-XO_2} = k_{NO-XO_2}[NO][XO_2] = P(O_3) \quad (7)$$

where $k_{HO_2-HO_2}$ and $k_{HO_2-RO_2}$ are the second-order rate constants of HO_2 self-reaction and its reaction with RO_2, respectively. k_{NO-HO_2} is the second-order rate constant of the reaction of HO_2 with NO. The HO_2 concentration was estimated from O_3 concentration using the method described by Kanaya et al.,

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(2007a). The RO_2 concentration is then estimated by assuming a steady state of HO_2 in the HO_X cycle; the reaction rates of HO_2 radicals are approximated as 0:

$$\frac{d[HO_2]}{dt} = P_{HO_2} - L_{HO_2} = k_{CO-OH}[OH][CO] + k_{H_2CO-OH}[OH][H_2CO] + k_{NO-RO_2}[RO_2][NO] - 2k_{HO_2-HO_2}[HO_2][HO_2] - k_{HO_2-RO_2}[HO_2][RO_2] - k_{NO-HO_2}[HO_2][NO] - ka[HO_2] = 0 \quad (8)$$

where k_{CO-OH} and k_{H_2CO-OH} are the second-order rate constants of the reactions of CO and H_2CO with OH, respectively. The different XO_2 loss rates described in Eqs. 5–7, along with the measurement times, are shown in Fig. 5a. Generally, L_{P-XO_2} is much greater than L_{R-XO_2}, indicating that the XO_2 taken up by ambient aerosols will compete with the XO_2 self-reaction, thus influencing XO_2 concentration. However, such an influence may have a negligible impact on $P(O_3)$ because L_{P-XO_2} is tens of thousands times lower than L_{NO-XO_2} owing to the relatively high NOx concentration in Yokohama. We further tested the impact of L_{P-XO_2} on ozone formation sensitivity regime, according to the method proposed by Sakamoto et al. (2019), in which L_N/Q is used as a new indicator:

$$\frac{L_N}{Q} = \frac{1}{1+\left(\frac{(2k_R[XO_2]+k_a')k_{OH-VOCs}[VOCs]}{(1-\alpha')k_{NO-HO_2}[NO]k_{OH-NO_2}[NO_2]}\right)} \quad (9)$$

where $k_{OH-VOCs}$ and k_{OH-NO_2} are the second-order rate constants of the reactions of OH with VOCs and NO_2, respectively. k_{NO-HO_2} is the second-order rate constant of the reaction of NO with HO_2. α' is the proportion of RO_2 in XO_2. L_N is the OH radical loss rate through its reaction with NO_2. (= $k_{OH-NO_2}[OH][NO_2]$), and Q is the total loss of the HOx radicals in the HOx cycle reaction (= $L_N + L_{P-XO_2} + L_{R-XO_2}$). The regime transition point can be expressed as

$$\left(\frac{L_N}{Q}\right)_{transition} = (1-\chi)\frac{1}{2} + \chi\frac{1}{3} \quad (10)$$

where $\chi = L_{P-XO_2}/(L_{P-XO_2} + L_{R-XO_2})$. The results indicate that both L_N/Q and $L_N/Q\_without\_aerosol$ (calculated with and without including k_a' in Eq. 9, respectively) were higher than $L_N/Q\_transition$, indicating that ozone formation was VOC-sensitive throughout the campaign and that the aerosol uptake of XO_2 (*k*a') showed no impact on the O_3 formation regime (see Fig. 5, here we only consider the daytime, when photochemical reactions occur). The plots of L_N/Q and $L_N/Q\_without\_aerosol$ as a

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function of NO concentration show the values were closer to $L_N/Q\_transition$ (~0.4) at lower NO concentrations (Fig. S11); therefore, aerosol uptake may play a more important role in the O_3 formation regime at NO levels lower than those observed in this study. The temporal variations in key factors used in this section are shown in Fig. S12.

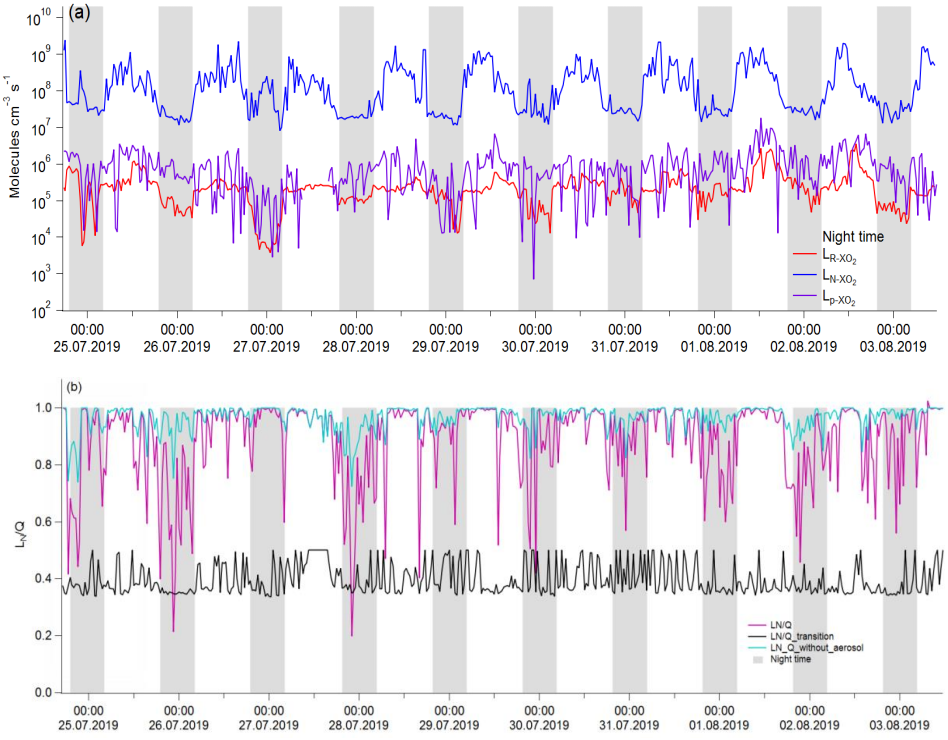

Figure 5: Temporal variations in (a) HO_2 radical loss rates and (b) L_N/Q (red line) and the regime transition threshold ($L_N/Q\_transition$, black line) used to assess the ozone sensitivity regime. The gray shaded areas represent nighttime (from National Astronomical Observatory of Japan) and are not discussed herein.

4 Conclusions

This study used a reliable online methodology to investigate HO_2 uptake kinetics onto in situ ambient aerosols (i.e., HO_2 reactivity of ambient aerosols k_a and HO_2 uptake coefficients γ) and discussed the impacting factors on such processes, i.e., chemical compositions and physical properties of ambient aerosols and experimental conditions. k_a ranged between 0.001 s^{-1} (25th percentile) and 0.005 s^{-1} (75th percentile), with an average value of 0.005 ± 0.005 s^{-1}. The corresponding γ, ranged from 0.05 (25th

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478 percentile) to 0.33 (75th percentile), with an average value of 0.23 ± 0.22, is comparable with previous
479 measured (~0.24–0.25) (Zhou et al., 2019b; Taketani et al., 2012) and modeled (~0.20) values (Stadtler
480 et al., 2018; Jacob, 2000). We noticed that k_a and γ showed no dependence on RH and T in the reaction
481 cell in this study, indicating that the instantaneous change of RH and T may not be dominating factors
482 in terms of the variation of k_a and γ with measurement time, and the large standard deviation of the γ
483 values along with the measurement time (± 0.21, 1σ) may be due to the instantaneously changed
484 chemical and physical properties of ambient aerosols, a large bias may exist if a constant γ value is used
485 for modeling.

486 We found that the individual chemical components of ambient aerosols may have collective effects
487 of to γ, through the analyses of 1) separating the air masses into two groups, group i from the ocean and
488 group ii from mainland Japan; 2) the average diurnal patterns; 3) the correlation matrix analysis of each
489 individual chemical component of ambient aerosol with γ; and 4) the modeling studies using previously
490 proposed mechanisms. All these effects clearly indicating that the transition metals contained in ambient
491 aerosols may act as a catalyst, thus accelerating the depletion of HO_2, however, they can be chelated by
492 OA. OA can also cover the aerosol surface and alter the viscosity of ambient aerosols, thereby
493 decreasing γ, and that more oxidized organic aerosols tend to be highly viscous and thus decrease HO_2
494 uptake coefficients. Results obtained here are in accordance to previous laboratory and modeling studies
495 (Mao et al., 2013a; Lakey et al., 2016b; Lakey et al., 2016a; Takami et al., 2013; Thornton et al., 2008;
496 Hanson et al., 1994), and that the chemical components of ambient aerosols may be internally mixed,
497 as proposed by Takami et al. (2013), which influences the aerosol surface tension and the activity of the
498 free form of the copper ion (i.e., OA and BC) to constrain γ. In contrast to previous studies saying that
499 BC may shrink HO_2 losses onto ambient aerosols (Saathoff et al., 2001; Macintyre and Evans, 2011;
500 Bedjanian et al., 2005), we found BC positively correlated with HO_2 uptake coefficients (0.18), this
501 may be owing to BC can provide active sites thus facilitating the physical uptake of HO_2. Here, we
502 observed higher γ values (> 0.8) when the mean particle diameter is < 110 nm, identifying the fractional
503 contributions of aerosols in different particle size ranges to k_a and γ is highly desirable in terms of
504 understanding their influence.

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In summary, the individual chemical components and physical properties of ambient aerosols may dominate γ variation during field campaign; both the metal-catalyzed reactions and the chemical components and their states should be considered to yield more accurate γ values. In future work, improvements to the time-resolution of metal measurements are needed for more precise analysis. For more detailed investigations of HO_2 uptake mechanisms, an offline methodology that can maintain constant chemical compositions or other experimental conditions (such as RH and T) will be useful. The HO_2 loss onto ambient aerosols was identified to have a negligible impact on the O_3 production rate and formation regime owing to the high NO_X concentrations in Yokohama. This process may play a more important role in O_3 formation under low NOx and high aerosol loading conditions. The results help us to understand the impacts of HO_2 uptake kinetics on chemical transformations in troposphere.

Appendix:

Air mass directions (Figure S1), measurement strategy (Figure S2), a technique combined laser-flash photolysis with laser-induced fluorescence (LFP–LIF), the enrichment of the ambient aerosols, HO_2 reactivity of ambient air, correction of gas-phase diffusion for HO_2 uptake coefficient, HO_2 reactivity of ambient gas phase (k_g), examples of HO_2 decay profiles (Figure S3), HO_2 reactivity calibration with different NO_2 concentrations (Figure S4), diurnal trends in individual chemical components of ambient aerosols (Figure S5), diurnal trends in k_a and γ(Figure S6), correlations between measured and modeled γ (Figure S7), time series of the averaged RH and T in ambient air and the reaction cell (Figure S8), dependence of k_a and γ on RH in reaction cell (Figure S9), dependence of k_a and γ on mean particle diameter (Figure S10), dependence of day time LN/Q and LN/Q_without_aerosol on [NO] (Figure S11), profiles of key factors determining XO_2 loss rates and $P(O_3)$ sensitivity (Figure S12), summary of equations and values used for γ modeling (Table S1), summary of equations and values used for XO_2 (=HO_2+RO_2) loss and O_3 formation sensitivity regime (Table S1).

Author contribution

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J.J., K.M., Y.S., and Y.K. designed the experiments and J.J. and Y.B. carried them out. J.J. did the data analysis and prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

Data availability

Data supporting this publication are available upon request for the corresponding author (junzhou@jnu.edu.cn).

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