Chemical characterization of oxygenated organic compounds in gas-phase and particle-phase using iodide-CIMS with FIGAERO in urban air

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Abstract

The characterization of oxygenated organic compounds in urban areas remains a pivotal gap in our understanding of the evolution of organic carbon under polluted environments, as the atmospheric processes involving interactions between organic and inorganic compounds, anthropogenic pollutants and natural emissions lead to the formation of various and complex secondary products. Here, we describe measurements of an iodide chemical ionization time-of-flight mass spectrometer installed with a Filter Inlet for Gases and AEROsols (FIGAERO-I-CIMS) in both gas-phase and particle-phase at an urban site in Guangzhou, a typical mega-city in southern China, during the autumn of 2018. Abundant oxygenated organic compounds containing 2-5 oxygen atoms were observed, including organic acids, multi-functional organic compounds typically emitted from biomass burning, oxidation products of biogenic hydrocarbons and aromatics. Photochemistry played dominant roles in the formation of gaseous organic acids and isoprene-derived organic nitrates, while nighttime chemistry contributed significantly to the formation of monoterpene-derived organic nitrates and inorganics. Nitrogen-containing organic compounds occupied a significant fraction of the total signal in both the gas and particle phases, with elevated fractions at higher molecular weights. Measurements of organic compounds in particle the phase by FIGAERO-I-CIMS explained 24±0.8% of the total organic aerosol mass measured by aerosol mass spectrometer (AMS), and the fraction increased for more aged organic aerosol. The systematical interpretation of mass spectra of the FIGAERO-I-CIMS in the urban area of Guangzhou provides a holistic view of numerous oxygenated organic compounds in the urban atmosphere, which can serve as a reference for the future field measurements by FIGAERO-I-CIMS in polluted urban regions.

1 Introduction

In urban air, atmospheric chemical processes are varied and complex, as the result of large emissions of both anthropogenic pollutants and biogenic volatile organic compounds, associated with strong interactions with each other (He et al., 2014; Karl et al., 2018; Shrivastava et al., 2019). Consequently, strong formation of secondary pollutants, e.g. ozone and secondary organic aerosol (SOA), are observed in urban and downwind regions (Huang et al., 2015; Zhang et al., 2014). Oxygenated organic compounds are not fully accounted for in some earlier studies, which may explain some of the discrepancies between observations and models for many unaddressed issues in atmospheric chemistry. Oxygenated organic compounds are supposed to be the top candidates for missing OH reactivity observed in various environments including pristine rainforests and urbanized areas (Noelscher et al., 2016; Yang et al., 2016, 2017). The photolysis of carbonyls serves as a critical radical source driving ozone formation in highly polluted industrialized areas (Edwards et al., 2014; Liu et al., 2012; Xue et al., 2016). Although it has been discovered a long time ago that oxygenated organic compounds make up a substantial fraction of submicron aerosol mass (Kroll and Seinfeld, 2008), enormous difficulty still exists in accurately predicting formation and evolution of SOA (de Gouw et al., 2005; Hodzic et al., 2010; Volkamer et al., 2006).

One of the biggest obstacles to ~~understand~~understanding the role of oxygenated organic compounds is the characterization of these extremely complicated and diverse chemicals which encompass tens of thousands of individual species spanning a wide range of volatility. Chemical ionization mass spectrometry (CIMS) is a powerful technique for the molecular-level characterization of oxygenated organic compounds because of the following advantages (Zhao, 2018): direct measurements and fast time response to capture the rapid temporal change of short-lifetime intermediates; soft ionization providing chemical information on molecular level; selective ionization ensuring measurements for specific classes of species. Iodide anion ionizes species mainly through adduction (Iyer et al., 2016) and is used for the detection of oxygenated organic compounds particularly organic compounds with 2-5 oxygen atoms (Lee et al.,

2014; Lopez-Hilfiker et al., 2016; Riva et al., 2019). It has been shown that I-CIMS is an excellent technique to investigate oxidation processes of volatile organic compounds (VOCs) and formation of SOA (Isaacman-VanWertz et al., 2018). Installed with a thermal desorption inlet that collects and heats aerosol to evaporate organic compounds, e.g. Filter Inlet for Gases and AEROsols (FIGAERO, Lopez-Hilfiker et al., 2014) and Micro Orifice Volatilization Impactor (MOVI~~-HRToF-CIMS~~, Yatavelli et al., 2012), the CIMS instruments are capable of analyzing particle-phase species and gas-particle partitioning in a semi-continuous way (Stark et al., 2017; Stolzenburg et al., 2018).

Although FIGAERO-CIMS has gained recent popularity in atmospheric chemistry research, much of the published work was done in chambers or in the laboratory (D'Ambro et al., 2017, 2018; Hammes et al., 2019; Lopez-Hilfiker et al., 2015). As for the applications in field campaigns, most work has been mostly performed in forest or rural areas (Huang et al., 2019; Hunter et al., 2017; Lee et al., 2016, 2018b), ~~and systematic analysis of~~ measurements in the urban atmosphere by FIGAERO-~~-~~CIMS is still limited (Le Breton et al., 2018b). ~~In this study, we present the measurement results using FIGAERO-I-CIMS during~~Meanwhile, a ~~coordinated campaign in Guangzhou, a megacity in the Pearl River Region of China. We provide an overview of gas-phase and particle-phase oxygenated species detected in the~~systematic analysis on mass spectra of FIGAERO-~~I-CIMS during the campaign.~~ CIMS in the ambient air is imperative, for a more holistic view in investigating emissions and chemistry of oxygenated organic compounds using FIGAERO-CIMS. In this study, we present the measurement results using FIGAERO-I-CIMS during a coordinated campaign in Guangzhou, a megacity in the Pearl River Region of China. We describe the experimental design, instrumentation setup, calibration and data processing for the FIGAERO-I-CIMS in the campaign. This work will provide a detailed interpretation of the mass spectra of oxygenated species in both gas-phase and particle-phase. The bulk chemical properties ~~of organic compounds in both gas phase and particle phase will~~ will also be discussed to provide an overview of organic compounds.

2 Methods

2.1 Measurement site and supporting data

Measurements were conducted during the coordinated campaign "Particles, Radicals and Intermediates from oxiDation of primary Emissions over the Great Bay Area" (PRIDE-GBA) in October and November 2018. The Great Bay Area (GBA) refers to a highly industrialized and urbanized area in southern China, including two Special Administrative Regions of Hong Kong and Macao, and nine cities surrounding the Pearl River estuary. Affected by the subtropical monsoon climate, the weather in the region was characterized by high temperatures and relative humidity (RH) as well as sufficient sunshine (~~global~~total solar radiation of the Pearl River Delta region in ~~Fall,~~the fall of 2016 was ~1200 MJ/m^2, Liu et al., 2018). The city of Guangzhou lies in the north of the GBA and south of the mountains. Therefore, the city is extensively influenced by both anthropogenic and biogenic emissions. The urban site was located at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (23.14°N, 113.36°E). Online instruments sampled from inlets set up in laboratories on the eighth-floor or ninth-floor (about 25 meters above the ground).

In addition to FIGAERO-I-CIMS discussed later, ~~measurements~~measurement data from a suite of other instruments were also used in this work. A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.) was deployed to provide chemical composition and many other parameters of ambient aerosol including f60, liquid water content (LWC), particulate organic ~~nitrates~~nitrate and elemental ratios (Hu et al., 2016, 2018). The parameter f60 is the ratio of the integrated signal at m/z 60 to the total signal of organic components and is used as a tracer for biomass burning emissions (Cubison et al., 2011). LWC of aerosol was taken as the sum of water contributed by inorganic components ~~which was~~ predicted by ISORROPIA II model and organic components ~~which was~~ calculated based on the organic hygroscopicity parameter (Fountoukis and Nenes, 2007; Guo et al., 2015). Based on AMS data, organic nitrate concentrations were determined by 2-3 times lower NO_2^+/NO^+ ratios for organic nitrate than inorganic nitrate (Fry et al., 2013). The calculation method of elemental ratios based on AMS data has been described

elsewhere (Aiken et al., 2007; Canagaratna et al., 2015). Detailed information about AMS measurements from the PRIDE-GBA campaign is forthcoming in a separate manuscript. An online GC-MS/FID (Wuhan Tianhong Instrument Co., Ltd) and a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytic GmbH) (Yuan et al., 2017) served as the analytical techniques for measuring isoprene and other VOCs (e.g. monoterpenes, aromatics and a few oxygenated VOCs) (Wu et al., 2020), respectively. Trace gases (CO, O_3, NO and NO_2) were measured by commercial gas monitors (Thermo Fisher Scientific Inc.) (Wang et al., 2020d). Photolysis rates were measured by PFS-100 photolysis spectrometer (Focused Photonics Inc.). Temperature and RH were measured by a Vantage Pro2 weather station (Davis Instruments Corp.). Time series and diurnal profiles of meteorological parameters, trace gases, the photolysis rate of NO_2 (j_{NO_2}) along with several important VOCs (isoprene, monoterpenes, toluene and benzene) are shown in ~~Figure~~Fig. S1. The temperature during the campaign was between 17 and 33°C with an average of 24°C and RH was between 27 and 97% with an average of 70%.

2.2 FIGAERO-I-CIMS

2.2.1 Experimental setup

Our instrument consists of a Filter Inlet for Gases and AEROsols (FIGAERO) and a time-of-flight chemical ionization mass spectrometer coupled with an iodide ionization source (Bertram et al., 2011; Lee et al., 2014; Lopez-Hilfiker et al., 2014). The FIGAERO is a multi-port inlet assembly following a two-step procedure alternating between gas mode in which online measurements of gases and semi-continuous sampling of particle-phase species are conducted, and particle mode in which particulate composition is investigated via thermal desorption (Lopez-Hilfiker et al., 2014; Thornton et al., 2020). Iodide source is a “soft” ionization technique with little ionization-induced fragmentation and selective detection towards multi-functional organic compounds, providing elemental compositions for thousands of oxygenated compounds in the atmosphere (Hyttinen et al., 2018; Iyer et al., 2016; Lee et al., 2014; Riva et al., 2019).

The sample air was drawn into the ion molecule reaction (IMR) chamber where it intersected and reacted with ~~the iodide~~primary ions generated by flowing 2 mL/min 1000 ppm methyl iodide in 2.4 L/min N_2 through an X-ray source. The pressure in the IMR chamber was maintained at 370-390 mbar. Equipped with a long time-of-flight mass analyzer, our instrument was configured to measure singularly charged ions up to 603 Th with a mass resolving power of 10000-11000 (m/Δm at 50% height) during the campaign (Fig. S2).

Ambient air was continuously sampled through two inlets protruding about 1.5 meters out of a window on ninth-floor of a building. One was a 3-meter PFA tubing (1/4-inch OD) for gas phase sampling, through which roughly 9 L/min air was drawn, and 2 L/min was directly taken into the instrument for gas measurements without removing particles, resulting in an inlet residence time of 0.24 seconds. The gas sampling line inside the room was covered by heat insulation associated with a heating cable to minimize condensation on the tubing surface. The other inlet for particle phase was a 3.8-meter metal tubing (3/8-inch OD) fitted with a $PM_{2.5}$ cyclone and a Nafion dryer (Perma Pure, model PD-07018T-12MSS) to reduce water content in the sampled air. The particle phase inlet was drawn by a laminar flow at ~8 L/min (Reynolds number of ~1500), 3.8 L/min of which was collected on PTFE membrane filters (Zefluor®, Pall Inc., USA). The residence time was 1.3 seconds for the particle phase sampling line. Semi-volatility and low-volatility compounds tend to interact with wall surfaces of both ~~inlet~~inlets and the IMR and thus extend response time (Krechmer et al., 2016). As accurate correction for wall losses remains impossible, no wall loss correction was performed in this study.

The FIGAERO worked in a cyclical 1-hour pattern with two modes (Fig. S3): measuring gas for the first 24 minutes while simultaneously collecting particles on the filter; and then analyzing the particle-phase collection for another 36 minutes. In every 24-minute gas mode, ambient air was measured for the first 21 minutes, followed by 3-minute gas background by overflowing zero air at 5 L/min through a pinhole just in ~~the~~ front of the IMR. The background measurements ~~for CIMS~~ are inevitably influenced by wall interactions, especially for "sticky" species. Recently, Palm et al. (2019)

proposed a new way to determine gas background ("fast background") by fast switching between ambient air and background, which greatly improves accurate determination of CIMS background. In the remaining 36 minutes, the components of the collected particles were thermally desorbed and introduced into the CIMS with 2 L/min N_2 carrier gas. The N_2 flow was ramped from ambient temperature to 175℃ in 12 minutes and held for another 20 minutes. Schematic diagram of working modes and temperature profile of FIGAERO heating in a single cycle is shown in Fig. S4. Particle background was determined every 6^{th} 1-hour running cycles in which ambient air passed over a filter (Parker Balston, model 9922-11-CQ) in front of the FIGAERO filter.

2.2.2 Calibration experiments

Using various techniques, we calibrated dozens of chemical compounds in the laboratory. Table S1 summarizes the calibrated species and corresponding calibration methods. (1) Gas cylinders are commercially available for a few species (e.g. chlorine, hydrogen cyanide). The gaseous standards were diluted down to different concentrations and then introduced to the CIMS. (2) For those VOCs of which standards are liquid or solid, solutions with known concentrations are made and then vaporized using the liquid calibration unit (LCU, Ionicon Analytic GmbH) to provide gaseous standards. (3) Commercial permeation tubes are available for some species (e.g. nitric acid). (4) Some gaseous chemicals were generated in the laboratory. For example, isocyanic acid was generated from thermal decomposition of cyanuric acid in a diffusion cell (Li et al., 2021; Wang et al., 2020d), and dinitrogen pentoxide was generated via the reaction of ozone with excess nitrogen dioxide in a flow reactor (Bertram et al., 2009). (5) Compounds of low vapor pressure were calibrated through the FIGAERO (Lopez-Hilfiker et al., 2014). Briefly, certain amounts of target species dissolved in organic solvents (e.g. isopropanol or acetone) were deposited onto the PTFE filter of the FIGAERO using a syringe, and the droplet was then subjected to a temperature-programmed thermal desorption by N_2 gas. The sensitivity ~~for particle phase~~ was determined as the integrated signals under thermogram profiles versus the ~~amount~~amounts of deposited calibrant.

~~In addition to sensitivity calibration, the effects of humidity on the sensitivity for various species were investigated in the laboratory, some of which are shown in Fig. S5.~~ In addition to sensitivity calibration, the effect of humidity on the sensitivity for various species was investigated in the laboratory, some of which are shown in Fig. S5. ~~Considering water vapor pressure in the IMR, our humidity-dependent curves are generally consistent with those reported in Lee et al. (2014) (see detailed discussions in Section S3 in the supplement).~~ Low-molecular-weight acids, e.g., formic acid and nitric acid, tend to be more sensitive to the humidity changes than multi-functional compounds. Similar tendency of multi-functional compounds associated with less humidity dependence was also reported in previous work (Lee et al., 2014). Considering water vapor pressure in the IMR, our humidity-dependent curves are generally consistent with those reported in Lee et al. (2014) (see detailed discussions in Section S3 in the Supplement).

In the later part of the campaign (after Oct. 22), an isotopically labeled formic acid (DCOOH, Cambridge Isotope Laboratories, Inc.) permeation tube held at constant temperature (65 ℃), was mixed with 10 mL/min N_2 and continuously delivered into the entrance of sampling inlet in order to derive a humidity dependence function from the field measurements. DCOOH signals during the campaign exhibited a humidity-dependent curve consistent with formic acid obtained in the laboratory (Fig. S5). We applied humidity correction to the species with the humidity-dependent ~~curve~~curves determined in the laboratory (underlined species in Table S1). For other compounds, humidity correction was not applied, as there is no universal pattern of humidity dependence for all detected species and multi-functional compounds that comprise the majority of the species measured by FIGAERO-I-CIMS are usually less influenced by humidity.

The measured concentration of DCOOH was steady after ~~being applied to~~ humidity correction was applied (Fig. S6g), indicating the stability of our instrument. In addition, we also performed field calibrations throughout the campaign to check the instrument status by spotting a solution mixture of levoglucosan, heptaethylene glycol and octaethylene glycol ~~on~~onto the FIGAERO filter every 2-3 days (Fig. S6). Multiple-

point calibrations for these organic species were performed in the beginning and the end of the campaign. The concentration of the solution used in the first two calibration experiments was too high, so we prepared a new solution for calibrations ~~after~~in November. The relative changes of the determined calibration factors in November were within 50% for the calibrated species.

2.2.3 Data processing

The TofWare software (version 3.0.3; Tofwerk AG, Switzerland) was used to conduct the high-resolution peak fitting for the mass spectra data of ToF-CIMS, including mass calibration, instrumental parameters optimization (peak shape and peak width) and bunch fitting of high-resolution peaks (Stark et al., 2015). In this study, the signals of ions were normalized to the sum signals of I^- and H_2OI^- at 10^6 cps. Hourly particle-phase data were obtained by integrating the signals of various ions during each FIGAERO desorption period. Background corrected signals were obtained by subtracting linearly interpolated background signals from ambient signals (and integrated signals) for ions in the gas (and particle) phase.

In order to determine the sensitivities of uncalibrated species, voltage scanning procedure was performed from time to time throughout the campaign covering different times of the day (Iyer et al., 2016; Lopez-Hilfiker et al., 2016). Here, we selected four representative periods including morning, afternoon, evening and night on polluted days. By performing sigmoidal fitting on the remaining signals as a function of voltages, a dV_{50} value of each ion from each period was determined at which voltage half of one kind of ion dissociated (Lopez-Hilfiker et al., 2016). We observed a positive correlation between the sensitivities of the ions relative to maximum sensitivity and their average dV_{50} values (Fig. S7), consistent with previous studies (Isaacman-VanWertz et al., 2018; Lopez-Hilfiker et al., 2016). This relationship was used to calculate response factors for uncalibrated species, after taking into account the relative transmission efficiency for the ions (see Section S1 in the Supplement for detailed analysis).

3 Results and discussion

3.1 Overview of detected species in the mass spectra

We identify 1334 ions adducted with iodide from the mass spectra, among which 427 are charged closed-shell organic compounds containing only C, H, O elements ($C_xH_yO_zI^-$) and 388 are charged closed-shell organic compounds containing C, H, O and N elements ($C_xH_yN_{1,2}O_zI^-$). For species with the formula of $C_xH_yO_z$, x ranges from 1 to 20; y is an even number and no more than 2x+2; z is greater than or equal to 2. The range of carbon number x for the ions with $C_xH_yN_{1,2}O_z$ is the same as the ions with $C_xH_yO_z$. For species containing one nitrogen ($C_xH_yNO_z$), y is an odd number and less than 2x+2; z is larger than or equal to 2. For species containing two nitrogen atoms ($C_xH_yN_2O_z$), y is an even number and less than 2x+1; z is larger than or equal to 4. Table 1 summarizes species discussed in the main text. Although ~~Iodide~~iodide clusters with two nitrogen atoms and zero nitrogen atoms both lie on odd masses, they can be separated for certain ions with the current resolving power, as demonstrated by the peak fitting results of mass spectrum at m/z 311 (Fig. S8).

The campaign-averaged mass spectra of detected ions in the both gas and particle phases are shown in Fig. 1. In general, molecules in particle-phase have larger molecular weights compared to those in gas-phase ~~compounds~~. Signals in the mass range of 150~~—~~-300 Th comprise a large fraction of gas-phase compounds, and concentrations in the gas phase decrease quickly with m/z higher than 250 Th. In contrast, the detected signals in the particle phase are mainly distributed within the range of 200-320 Th.

~~We compare the concentration for various ions between the~~ Average nighttime (10 pm - 6 am) and daytime (10 am - 6 pm) ~~and nighttime (10 pm - 6 am), by determining concentration~~mixing ratios ~~between at night and during the daytime (~~for various species were shown in Fig. 2~~).~~. Most species have higher concentrations during the daytime, especially for relatively volatile compounds in gas-phase, despite the fact that lower boundary layer height at night should increase nighttime ~~mixing ratios~~concentration, as ~~behaved for~~ many primary gases behaved, e.g. CO (Fig. S1) (Wu et al., 2020). The higher concentrations during the daytime for most species detected by FIGAERO-I-CIMS suggest the dominant role of photochemical induced oxidation in forming these oxidized compounds. In addition to typical nocturnal species including

nitryl chloride ($ClNO_2I^-$), chlorine nitrate ($ClONO_2I^-$) and dinitrogen pentoxide ($N_2O_5I^-$), higher concentrations for the ions of $C_6H_{10}O_5I^-$ and $C_6H_{12}O_5I^-$ were also observed, which will be discussed in the next section. A large number of particulate N-containing organic compounds increase ~~during the~~at night as well, as shown by mass defect diagrams of $C_xH_yO_z$ and $C_xH_yN_{1,2}O_z$ color coded by the night to day ratios (Fig. S9).

Based on the mass spectra shown in Fig. 1, we identify a number of ions associated with high concentrations in both gas and particle phases. In the following Section 3.2-3.7, we will perform interpretation of the mass spectra by analyzing variability and correlation of these important ions, including monosaccharide-derived compounds (with brown tags in Fig. 1), oxygenated aromatics (with purple tags), organic acids (with pink tags), oxidation products of biogenic volatile organic compounds (BVOCs, with green tags), sulfur-containing compounds, and inorganics (with blue tags). After going through detailed analysis ~~in~~at the species level, Section 3.8 will provide an overall picture about bulk chemical characteristics of detected organic compounds in terms of the distributions of average carbon oxidation states, carbon number and oxygen number. Lastly, Section 3.9 will compare our measurement of organic aerosol (OA) with AMS data.

3.2 Monosaccharide-derived compounds

$C_6H_{10}O_5$ and $C_6H_{12}O_5$ are highly correlated with each other in aerosol (r=0.92), and they are two of ~~a~~the few $C_xH_yO_z$ compounds with higher concentrations at night. Previous work assigned them as monosaccharide derived compounds emitted from biomass burning (Bhattarai et al., 2019; Qi et al., 2019; Reyes-Villegas et al., 2018; Simoneit et al., 1999).

In this campaign, $C_6H_{10}O_5$ was detected mostly in the particle phase (the fraction in the particle phase F_p=0.81±0.09) with an average concentration of 0.073±0.076 μg/m^3. Its diurnal profile started increasing ~~during~~at dusk, reaching a peak at about midnight and then fell off, as shown in Fig. 3. The mass fraction of $C_6H_{10}O_5$ in OA had a similar diurnal profile, and the ratios of $C_6H_{10}O_5$ to CO increased at night (from

0.17±0.02 to 0.5±0.03 μg·m^{-3}/ppm, Fig. 3c), both suggesting enhanced emissions of this compound were related with combustion activities ~~during~~in the evening, e.g., residential biofuel burning for cooking as reported by some previous measurements in China (Wang et al., 2020c; Zhang et al., 2015). Furthermore, the time variations of particle-phase $C_6H_{10}O_5I^-$ were very similar to ~~that~~those of the m/z 60 fragment in AMS mass spectra (Fig. 3a), which is an identified tracer of biomass burning OA produced from the thermal decomposition of levoglucosan and similar compounds ~~during detection by~~on the vaporizer of AMS (Brege et al., 2018; Cubison et al., 2011; Schneider et al., 2006). Therefore, $C_6H_{10}O_5$ was probably levoglucosan and its isomers (mannosan and galactosan), and $C_6H_{12}O_5$ was probably also a ~~similar~~ monosaccharide compound ~~emitted from biomass burning~~that had similar sources to $C_6H_{10}O_5$.

3.3 Oxygenated aromatic compounds

Combustion activities emit a great deal of compounds besides saccharides that the I-CIMS instrument can detect including nitro-aromatics and guaiacol derivatives (Gaston et al., 2016; Kong et al., 2021). Nitro-benzenediols ($C_6H_5NO_4I^-$) as well as the highly correlated homologue methyl nitro-benzenediols ($C_7H_7NO_4I^-$) (r=0.88 in the particle phase), exhibited double peaks in their diurnal profiles (Fig. 4). ~~Concentrations of $C_6H_5NO_4$ and $C_7H_7NO_4$ were enhanced~~One was in the evening, similar to levoglucosan ($C_6H_{10}O_5$). ~~Another concentration~~The other peak was at noon ~~was also observed for $C_6H_5NO_4$ and $C_7H_7NO_4$~~. The scatterplot of $C_6H_5NO_4$ as the function of $C_6H_{10}O_5$ exhibits two different slopes (Fig. 5): the lower slope at night (0.088±0.005) indicates the contribution of biomass burning, while the higher slope during the daytime (0.26±0.02) suggests there were other important sources for nitro-aromatics, potentially secondary formation from photooxidation of aromatics (Jenkin et al., 2003). Guaiacol derivatives may have similar sources with nitro-aromatics, as implied by the resemblance of the scatterplots of these two chemical classes versus levoglucosan (cf., Fig. S10 and Fig. 5).

Nitrophenols ($C_6H_5NO_3I^-$), methyl nitrophenols ($C_7H_7NO_3I^-$) and dinitrophenols ($C_6H_4N_2O_5I^-$) were the most significant components of nitro-aromatics

in the gas phase. Despite the fact that nitrated phenols could be formed by photochemical oxidation ~~from~~of their aromatic hydrocarbon precursors (Wang et al., 2020a; Yuan et al., 2016), none of them peaked in the daytime, consistent with a previous proposal on photolysis as ~~a~~the dominant ~~chemical~~ loss pathway for these compounds (Chen et al., 2011; Yuan et al., 2016). ~~Nitrophenols~~$C_6H_5NO_3$ and ~~methyl nitrophenols~~$C_7H_7NO_3$ peaked in the evening, suggesting ~~either~~important contributions of NO_3 ~~oxidation~~ -induced reactions and/or primary emissions ~~was important sources. It is interesting to observe that the~~. The peak ~~concentration for~~time of $C_6H_4N_2O_5$ was later than ~~the nitrophenols~~that of $C_6H_5NO_3$, in agreement with dinitrophenols as the oxidation products from nitrophenols (Harrison et al., 2005).

~~Several ions~~We also detected non-N-containing compounds that were identified as oxidation products of aromatics in the literature, including $C_7H_6O_4I^-$, $C_7H_8O_4I^-$ and $C_7H_8O_5I^-$ (Mehra et al., 2020; Schwantes et al., 2017)~~, were detected during the campaign.~~. $C_7H_6O_4$ and $C_7H_8O_4$ correlated well with each other (r=0.72 in gas-phase and 0.91 in particle-phase). High concentrations of $C_7H_6O_4$ and $C_7H_8O_4$ were mainly observed during the periods with lower NOx concentration, which was a contrast to the variations of nitrophenols (Fig. S10). ~~We observed~~In addition, the concentration ratios of $C_7H_8O_4I^-$ and $C_7H_7NO_3I^-$ ~~were~~are lower for higher NOx ~~concentrations~~concentration (Fig. 5), consistent with the literature that the formation of $C_7H_6O_4$ and $C_7H_8O_4$ is suppressed at high NOx ~~concentrations~~concentration (Schwantes et al., 2017). $C_7H_8O_5$ ~~was~~is reported as the ring-retaining oxidation product of $C_7H_8O_4$ which is a typical oxidation product of toluene and cresol (Schwantes et al., 2017; Wang et al., 2020b), as well as the ring-scission products of aromatic hydrocarbons with more carbon atoms, e.g. trimethyl benzenes (Mehra et al., 2020). Given that $C_7H_8O_5$ closely followed with $C_7H_8O_4$ (r=0.93 in particles), toluene oxidation was probably the main contributor to this ~~ion~~compound.

3.4 Organic acids and related compounds

Organic acids were one of the most abundant species classes detected by I-CIMS (Fig. 1). Low-molecular-weight organic acids (e.g., formic, acetic, glycolic and pyruvic

acid) constituted a significant fraction of signals in the mass spectra ~~detected from~~of the gas phase. As shown in Fig. 6 (and also Fig. S11), they had very similar temporal trends with diurnal maxima in the afternoon, indicating photochemical oxidation played a dominant role in their formation (de Gouw et al., 2018; Yuan et al., 2015).

In contrast to monocarboxylic acids, dicarboxylic acids partitioned mostly to particle-phase. As the dominant dicarboxylic acids in aerosol (Kawamura and Bikkina, 2016; Mellouki et al., 2015), 94±5% and 74±13% (mean ± one standard deviation of F_p) of $C_2H_2O_4$ and $C_3H_4O_4$, assigned as oxalic and malonic acid, were found in particle-phase, respectively. The concentrations of $C_4H_6O_4$ were significantly lower compared to ~~that of~~ C2 and C3 homologous series, but $C_5H_8O_4$ and $C_6H_{10}O_4$ had unexpected ~~higher~~high abundance (Fig. 7). Additionally, $C_5H_8O_4$ and $C_6H_{10}O_4$ had considerable fractions in the gas phase (45±13% and 43±11%), significantly higher than their C2-C3 homologous series. These two compounds were correlated well with each other in temporal variations (r=0.97 and 0.91 in the gas and particle phases, respectively), and their diurnal variations were different from those of oxalic and malonic acid (Fig. 6). Therefore, dicarboxylic acids may not be the dominant contributing species for the two ~~ions~~compounds. $C_5H_8O_4$ and $C_6H_{10}O_4$ have been observed from previous ~~study~~studies on isoprene oxidation (Berndt et al., 2018, 2019), attributing them as epoxy hydroperoxyl carbonyl and accretion product, respectively. However, the relative contributions from these possibilities remain unclear.

In addition to the series of $C_nH_{2n-2}O_4$ (i.e. $C_2H_2O_4$, $C_3H_4O_4$), we also observed comparable concentrations of $C_nH_{2n-4}O_4$ ~~ions~~series, especially for carbon number of 4 and 5 ($C_4H_4O_4$ and $C_5H_6O_4$). Considering the double bonds in the molecules, $C_nH_{2n-4}O_4$ should be more reactive than $C_nH_{2n-2}O_4$, suggesting there were large sources for these compounds. Previous studies have reported photo-oxidation of aromatics can generate $C_nH_{2n-4}O_4$, including $C_4H_4O_4$ and $C_5H_6O_4$ (Brege et al., 2018; Kawamura et al., 1996; Kawamura and Bikkina, 2016). Our measurements showed that temporal trends of $C_4H_4O_4$ and $C_5H_6O_4$ followed well with those of aromatic hydrocarbons (Fig. S11b), and thus oxidation of aromatics could be an important contributor to $C_nH_{2n-4}O_4$ in the urban air.

3.5 Oxidation products of Biogenic VOCs ~~(BVOCs)~~

In addition to high anthropogenic emissions of aromatics, terrestrial vegetations nearby also released significant amounts of biogenic VOCs (BVOCs) (Wu et al., 2020). During the campaign, the concentrations of isoprene at noon were between 0.1 and 1.5 ppb, whereas the range of daily maxima of monoterpenes was 0.05-2.5 ppb. Hence, a number of oxidation products of BVOCs were detected (Fig. 8 and Fig. S12).

The ion $C_4H_7NO_5I^-$ was the most abundant N-containing C4 organic compounds that were detected in the gas phase. Its daily maxima occurred in the afternoon and correlated moderately with methyl vinyl ketone (MVK) + methacrolein (MACR) measured by PTR-ToF-MS (Fig. ~~8~~8b, r=0.58). We consequently assigned $C_4H_7NO_5$ as MVK nitrates and MACR nitrates, which ~~was~~were reported as the second generation of organic nitrates formed from the oxidation of isoprene hydroxynitrates by OH in the presence of NOx (Fisher et al., 2016; Paulot et al., 2009). Strong correlations were observed between $C_5H_9NO_4I^-$, $C_5H_9NO_5I^-$ and $C_4H_7NO_5I^-$ (r=0.93 and 0.80, respectively), which was in accordance with their similar formation pathways (Jacobs et al., 2014; Wennberg et al., 2018; Xiong et al., 2015). Hence, we ~~expect~~expected these three compounds ~~are~~were common oxidation products of isoprene in the polluted atmosphere. While in aerosol, 2-methylglyceric acid ($C_4H_8O_4$) is a commonly reported oxidation product of isoprene formed in high-NOx conditions (Surratt et al., 2010). We observed the corresponding ion $C_4H_8O_4I^-$ contributing to OA especially in dry conditions with strong sunlight (Fig. S13). This evidence indicates that isoprene oxidation may contribute to $C_4H_8O_4$, but potential contribution from other sources cannot be ruled out in urban areas.

In terms of monoterpenes, a reasonable correlation (Fig. S14a, r=0.63) was found between the ions $C_{10}H_{16}O_3I^-$ and $C_{10}H_{16}O_2H^+$ measured by PTR-ToF-MS. $C_{10}H_{16}O_2H^+$ was attributed to pinonaldehyde formed from the oxidation of monoterpenes (Glasius et al., 2000; Larsen et al., 2001; Mutzel et al., 2016). Therefore, we tentatively assign ~~$C_{10}H_{16}O_3$~~$C_{10}H_{16}O_3I^-$ as pinonic acid and its oxocarboxylic acid isomers, which are formed via the oxidation of pinonaldehyde (Fang et al., 2017).

$C_8H_{13}NO_6$ also exhibited enhanced gas-phase formation during the day as pinonic acid did. The correlation coefficient of the two compounds ~~(r)~~ was 0.71. In contrast to other monoterpene nitrates, particle-phase $C_8H_{11}NO_7$ and $C_{10}H_{15}NO_6$ peaked at night and decreased during the daytime (Fig. S12), indicative of the role of NO_3 in producing organic nitrates as reported in the literature (Faxon et al., 2018). However, ~~$C_{10}H_{15}NO_6I^-$~~ $C_{10}H_{15}NO_6$ in the gas phase showed a distinct diurnal profile with peak before the noon. Two possible types of compounds were proposed for $C_{10}H_{15}NO_6$ in previous studies: peroxyacetyl nitrate from pinonaldehyde (Faxon et al., 2018; Nah et al., 2016; Schwantes et al., 2020), or organic nitrates (Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2015). Given the distinct diurnal profiles of $C_{10}H_{15}NO_6I^-$ in the gas and particle phases and the fact that peroxyacetyl nitrate is supposed to dissociate during the FIGAERO heating (Slusher et al., 2004), we speculate that both compounds contributed to this ion. As shown in Fig. S15, $C_8H_{12}O_4$ and $C_9H_{14}O_4$ existed mostly in particle-phase (F_p=0.63±0.11 and 0.67±0.10, respectively). We ~~interpreted~~interpret them as products of monoterpenes via photochemical processes, consistent with the interpretations presented in previous work (Mohr et al., 2013; Mutzel et al., 2015).

3.6 S-containing compounds

Organosulfates are concerned as important components of SOA (Hallquist et al., 2009; Surratt et al., 2007), and they can be detected by iodide anion via proton abstraction (Le Breton et al., 2018b; Lee et al., 2014). We detected the ion $C_2H_3SO_6^-$ with a diurnal peak ~~concentration~~ in the afternoon (Fig. 9). ~~We~~This ion was attributed ~~$C_2H_3SO_6^-$~~ to glycolic acid sulfate, as suggested by previous work (Galloway et al., 2009; Liao et al., 2015).

Abundant SO_3I^- was detected in particles, and it correlated well with the ion $C_2H_3SO_6^-$ (Fig. 9b) and sulfates measured by AMS (Fig. S16). Previous work observed the sulfite ion radical ($\cdot SO_3^-$) during the ionization of organosulfates in a liquid chromatography-electrospray ionization-tandem mass spectrometer (Huang et al., 2018). As a result, the ion SO_3I^- ~~ion~~ from FIGAERO-I-CIMS might be a potential

indicator for the total organosulfates. However, more future work is needed for evaluating this possibility.

Other sulfate-related ions during gas-phase modes were also detected including HSO_4^- (sulfuric acid), $CH_3SO_3^-$ (methanesulfonic acid) which were enhanced in the gas phase during the daytime, in agreement with the notions of ~~photochemically~~ photochemistry-induced gas-phase oxidation (Brandt and van Eldik, 1995). However, these data were not available for quantification given that these low-volatile species would condense on our long gas sampling inlet. It should be noted that measuring sulfuric acid in the gas-phase is difficult and generally requires a "wall-less" source design (Eisele and Tanner, 1993).

3.7 Inorganic compounds

There is a growing interest in N_2O_5 and its product nitryl chloride ($ClNO_2$) because $ClNO_2$ is found to serve as a nocturnal reservoir of Cl radical and reactive nitrogen, and hence enhance the ozone formation the next day (Osthoff et al., 2008; Wang et al., 2016). Time series of N_2O_5 and $ClNO_2$ exhibited two patterns. During most of the nights, N_2O_5 started to increase quickly at sunset and lasted for only 2-3 hours, and $ClNO_2$ increased in the meantime and ultimately reached its maximum at night, indicative of local formation of $ClNO_2$. However, sometimes a high level of N_2O_5 did not lead to an increase in $ClNO_2$ (tinted background in Fig. 10a), probably due to the lack of chloride salts on the aerosol. Other nocturnal species including $ClONO_2$ and Cl_2 were highly correlated with $ClNO_2$ as ~~we~~ expected (r=0.92 and 0.83, respectively), suggesting they had common formation mechanisms (Liu et al., 2017).

HNO_3I^- was observed as one of the most abundant species in the mass spectra of FIGAERO-I-CIMS ~~in~~ both in the gas and particle ~~phase~~phases. In the gas phase, the ion HNO_3I^- from I-CIMS has been used to quantify nitric acid (Lee et al., 2018a). The concentrations of gas-phase nitric acid peaked in the afternoon, suggesting photochemistry in the daytime as the dominant source for gas-phase nitric acid.

Previous study suggested that HNO_3I^- from particle-phase measurement by FIGAERO-I-CIMS can be indicative of nitrate in the particle phase (Lee et al., 2016).

Here, the concentrations of HNO_3I^- in the particle phase were compared with particulate nitrate measured by AMS (Fig. 11c). Strong correlation was observed (r=0.93), but the concentrations measured by FIGAERO-I-CIMS were higher (slope=1.6), especially for higher concentrations of organic nitrates. Using a threshold of 1 μg/m^3 for organic nitrates, the slopes and correlations were higher for the data points with particulate organic nitrates larger than 1 μg/m^3 (slope=1.8, r=0.94) than those ~~with~~ less than 1 μg/m^3 ~~of organic nitrates~~ (slope=1.1, r=0.90). In short, our measurements suggest that HNO_3I^- in the particle phase from FIGAERO-I-CIMS are formed from thermal-decomposition of both inorganic ~~nitrates~~nitrate (e.g. NH_4NO_3) and organic nitrates.

3.8 Bulk chemical properties of detected organic compounds

The above discussions on individual chemical groups provide insights into the identification of the mass spectra from FIGAERO-I-CIMS, along with sources and chemistry of oxygenated organic compounds in the urban atmosphere. In this section and the following one, we will provide a bulk analysis of the detected organic compounds.

~~The composition of organic~~Organic compounds detected by FIGAERO-I-CIMS ~~was~~were comprehensively characterized with detailed elementary composition in $\overline{OS_C} - n_C$ space (Fig. 12) which depicts the average oxidation states of carbon for closed-shell $C_xH_yO_z$ and $C_xH_yN_{1,2}O_z$ compounds ~~clustered with iodide~~ as a function of carbon number. The details in calculation of $\overline{OS_C}$ can be found in Section S2 in SI. S-containing compounds were omitted given their negligible variety and concentration compared to ~~the former two chemical classes (C_x~~$C_xH_yO_z$ and $C_xH_yN_{1,2}O_z$~~).~~. The average $\overline{OS_C}$ in the particle phase was higher than that in the gas phase at the same carbon number, especially for carbon number between 2 and 10. This agrees with our expectation that more oxidized compounds would partition more strongly in aerosol, as indicated by larger fractions in particles (Fp) for higher $\overline{OS_C}$. In addition, the average $\overline{OS_C}$ generally increased for lower carbon number, as a result of functionalization and fragmentation during VOCs aging. However, there was a notable exception in C5 which

had a significantly reduced $\overline{OS_C}$, probably as the result of emissions of isoprene. The analysis of the $\overline{OS_C} - n_C$ space indicates that the large number of organic compounds measured by FIGAERO-I-CIMS are useful to characterize the evolution of organic compounds in the atmosphere.

The distributions of carbon ~~number~~ and oxygen ~~number in the~~numbers of organic compounds~~ measured by FIGAERO-I-CIMS~~ were also investigated, as shown in Fig. 13. Most abundant organic compounds measured by FIGAERO-I-CIMS were C2-C3 compounds, which accounted for about 66% ~~of organic compounds~~ in the gas~~-~~ phase and 56% in the particle~~-~~ phase. It is unexpected that C2-C3 compounds made up such a significant portion ~~of~~in the particle phase, indicating a non-negligible role of thermal decomposition from low volatility compounds such as accretion products or extremely low volatile organic compounds which were reported from FIGAERO measurements on SOA (D'Ambro et al., 2018; Lopez-Hilfiker et al., 2014; Stark et al., 2017). Organic compounds with carbon numbers over 5 constituted only 3% in the gas phase, while they accounted for 30% in the particle phase. The oxygen numbers of the majority of gaseous organic compounds were ~~associated with~~ no more than 3~~ oxygen atoms.~~. Organic compounds containing ~~23~~2-3 oxygen atoms had the largest contribution in both gas-phase (96%) and particle-phase (56%). $C_xH_yN_{1,2}O_z$ accounted for less than 10% of the total oxygenated organic compounds. In the gas phase, compounds with 5-6 oxygen atoms accounted for 51% of $C_xH_yN_{1,2}O_z$, indicative of the high levels of organic nitrates in the urban atmosphere. Nitrophenols also contributed significantly to $C_xH_yN_{1,2}O_z$ compounds, as they accounted for 74% of $C_xH_yN_{1,2}O_z$ containing 3 oxygen atoms, which in turn contributed to 22% of $C_xH_yN_{1,2}O_z$. In contrast, in the particle phase, the oxygen ~~number~~numbers of $C_xH_yN_{1,2}O_z$ distributed relatively evenly, as the fractions of compounds with 3-8 oxygen atoms were similar (between 12% and 19%). Compared to measurements in a forest in the southeastern United States (cf., Table S1 from Lee et al., 2016), the fractions of N-containing organic compounds with less than 5 oxygen atoms were significantly larger in our measurements as a result of higher concentrations of nitro-aromatics.

We further ~~determine~~determined the fractions of N-containing organic compounds as a function of m/z. It is clear that the observed fractions of N-containing organic compounds ~~are~~were higher for elevated m/z (Fig. 14) and N-containing ions commonly ~~dominated~~dominated at even nominal masses (Fig. S17). The gas-phase CHON ions within the m/z range ~~from~~of 250~~ to -~~350 Th accounted for about half of the organic compounds in this range. The fractions of CHON ions in particle-phase ~~are~~were somewhat smaller than those in the gas phase ~~for~~within the above m/z ~~of 250-350 Th~~range, but ~~are~~were comparable for higher m/z. A possible explanation for this is that functional groups of nitrate and nitro reduce less in vapor pressure for organic compounds than functional groups of carboxylic ~~acid~~ or oxygen-equivalent hydroxyl ~~that without nitrogen atom~~do (Capouet and Müller, 2006; Nannoolal et al., 2008; Pankow and Asher, 2008). Consequently, CHON compounds are generally more volatile than CHO compounds with similar molecular weights.

In the end, we determined the total concentration of N-containing organic compounds in the particle~~-~~ phase measured by FIGAERO-I-CIMS and compared it with the particulate organic nitrates derived from AMS (Fig. 15). Good agreement was achieved when the ~~concentrations~~concentration of inorganic nitrate ~~were~~was relatively ~~lower~~low, e.g. below 8 μg/m^3. However, the discrepancies increased when inorganic nitrate ~~were higher~~concentration increased, which can affect the determination of organic nitrate from AMS. This encouraging result indicates that FIGAERO-I-CIMS is able to capture the variability of organic nitrates in the urban atmosphere, which can be helpful in understanding the sources and formation mechanism of these ~~organic nitrates~~compounds.

3.9 Organic aerosol measurements

The total ~~concentrations~~concentration of organic compounds in the particle phase measured by FIGAERO-I-CIMS ~~were~~was determined and compared with measurements of OA by AMS. The total organic compounds measured by FIGAERO-I-CIMS explained 24±0.8% (fitted slope ± one standard deviation) of the total OA in average (Fig. 16a), which is lower than the average fractions (~50%) reported

previously in boreal and temperate forests (Lopez-Hilfiker et al., 2016; Stark et al., 2017). The lower fractions determined here might be ~~as~~ the result of larger contributions to OA from primary emissions in the urban air, which are composed of a large number of compounds with little ~~signal~~signals in I-CIMS (Zhao et al., 2016). As shown in Fig. 16a, organic compounds measured by FIGAERO-I-CIMS ~~account~~accounted for higher fractions in OA concentrations by AMS for more aged OA, ~~which is~~ consistent with the fact that I-CIMS are more sensitive to oxygenated organic compounds with multiple functional groups (Lee et al., 2014; Lopez-Hilfiker et al., 2016). Furthermore, we expect this fraction to change with the relative contributions of primary emissions and secondary formation for organic compounds in the atmosphere. Similar trends were found in Le Breton et al. (2019), in which an acetate source was used. Acetate ions have been reported to selectively ionize highly oxygenated organic compounds as an iodide source does (Aljawhary et al., 2013).

Comparison of the Van Krevelen ~~diagram~~diagrams between FIGAERO-I-CIMS and AMS also provides useful insights on the measurement of organic compounds in OA. The Van Krevelen diagram has been used as a tool for analyzing functional groups and OA aging by plotting H/C ratios versus O/C ratios (Heald et al., 2010; Lambe et al., 2012). As shown in Fig. ~~16a~~16b, the data points ~~for~~of the bulk OA from FIGAERO-I-CIMS ~~follow~~followed the same trend as the data points from AMS. However, the bulk OA measured by FIGAERO-I-CIMS only occupied a much smaller region with ~~the~~ O/C ~~ratio~~ratios between 0.7 and 1.0. We further ~~plot~~plotted all of the organic compounds in the H/C versus O/C space color-coded with their campaign-average concentrations (Fig. S18a). We ~~observe~~observed that most ~~particle-phase concentrations measured by~~data points from FIGAERO-I-CIMS distributed across the zone between the slope of 0 and -1.0. These observations provide additional evidence that FIGAERO-I-CIMS may only measure the more oxidized organic compounds in OA.

The correlation coefficients between the particle~~-~~ phase concentrations at unit masses by FIGAERO-I-CIMS and OA mass concentration by AMS ~~are~~were calculated (Fig. S18b). The correlation coefficients ~~are~~were small for ions below m/z 200, as these ions ~~contribute~~contributed little to organic aerosol. Moderate and strong correlations

(r>0.7) were observed for the ions of m/z between ~~m/z~~ 200 and ~~m/z~~ 400 Th, implying that organic compounds with molecular ~~weight~~weights of 100-300 g/mol may account for significant fractions in organic aerosol. The possible reason for the lower correlations ~~of~~for heavier compounds (m/z >400 Th) with OA mass loadings is that these compounds might be related to specific sources or certain chemical processes, which might not contribute at large fractions to the total OA concentration.

4 Summary

We deployed a FIGAERO-I-CIMS instrument to measure oxygenated organic compounds in both gas phase and particle phase at a representative urban site in China. ~~The mass spectra measured by FIGAERO-I-CIMS was systematically interpreted. We detected high concentrations of several monosaccharide species (e.g., levoglucosan) potentially emitted from biomass burning, which also contributed to the enhancement of multiple nitro-aromatic species. Photochemistry was also identified as~~The experimental design and instrumentation setup were described in detail, which goes above and beyond typical studies, including (1) performing sensitivity calibrations in the laboratory using multiple methods for multiple species; (2) performing voltage scanning for unknown compounds detected in the ambient air; (3) performing humidity calibrations for multiple types of species, which we have not seen anyone do after Lee et al. (2014).

From the mass spectra, a number of important compounds in the urban atmosphere were identified. We detected high concentrations of several monosaccharide species (e.g., levoglucosan). They were potentially emitted from biomass burning which also contributed to the enhancement of many nitro-aromatic species. Photochemistry was also found to be a strong source of nitro-aromatics. Low-molecular-weight organic acids were mainly observed in the gas phase, and observations ~~support~~supported daytime photochemistry as the dominant source. Different diurnal profiles for various BVOC-derived organic nitrates were observed, reflecting their different formation pathways related to NO_X chemistry (i.e. daytime photo-oxidation, nocturnal NO_3 reactions). Local formation of nitryl chloride was

observed, highlighting the potential importance of nighttime chemistry in the urban region.

Our measurements show that oxygenated organic compounds dominated the majority of detected species by FIGAERO-I-CIMS, in which CHO and CHON compounds both accounted for significant fractions. Nitrogen-containing organic compounds occupied a significant fraction of the total signals in both the gas and particle phases, with elevated fractions at higher molecular weights. The most abundant organic compounds were formic acid and multifunctional organic compounds containing 3-5 oxygen atoms. Organic compounds containing 2 ~~or~~ 3 carbon atoms accounted for over half of the total organic compounds in both gas- and particle-phase measured by FIGAERO-I-CIMS. During the campaign, the FIGAERO-I-CIMS measurements explained 24±0.8% of OA mass measured by AMS, but the fractions ~~are~~were higher for ~~measurements of~~ more aged organic aerosol ~~in the urban atmosphere.~~. This evidence, along with the analysis of the Van Krevelen plot, ~~indicate~~indicates that FIGAERO-I-CIMS ~~were~~is measuring the more oxidized fraction of OA in the urban air.

Our observations suggest that oxygenated organic compounds in urban environments are complicated in both sources and chemistry. Oxygenated organic compounds can be both emitted from various emission sources (e.g. vehicular emissions and biomass burning) and also secondary produced in the atmosphere. The chemistry in forming and removing these oxygenated organic compounds can be associated with daytime and nocturnal reactions initiated from both anthropogenic and biogenic precursors with strong influences from NO_x chemistry. This work demonstrates that the rich information in both gas and particle phases provided by FIGAERO-I-CIMS can greatly promote the understanding of emission and chemistry of organic carbon in the atmosphere of urban regions.

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Data availability

The more detailed data can be provided by contacting the corresponding authors.

Author contributions

BY and MS designed the research. CSY, YL, ZLW, TGL, WWH, WC, CHW, CMW, SH, JPQ, BLW, CW, WS, XMW, ZYZ, XMW contributed to data collection. CSY performed the data analysis with contributions from WWH and WC. CSY and BY prepared the manuscript with contributions from JEK and other authors. All the authors reviewed the manuscript.

Competing interest

The authors declare that they have no conflicts of interest.

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1336 **Table 1.** The detected ions discussed in the text.

Ion formula	m/z	Assigned compounds	Possible formation pathways	References
$C_6H_{10}O_5I^-$	288.96	Levoglucosan, mannosan and galactosan	Biomass burning or cooking emissions	(Gaston et al., 2016; Reyes-Villegas et al., 2018)
$C_6H_{12}O_5I^-$	290.97	Fucose	Biomass burning emissions	(Qi et al., 2019)
$C_6H_5NO_3I^-$	265.93	Nitro-phenols	Direct emissions, oxidation of aromatics in the presence of NOx	(Gaston et al., 2016; Yuan et al., 2016)
$C_6H_5NO_4I^-$	281.93	Nitro-benzenediols	Direct emissions, oxidation of aromatics in the presence of NOx	(Gaston et al., 2016; Yuan et al., 2016)
$C_6H_4N_2O_5I^-$	310.92	Dinitro-phenols	Direct emissions, oxidation of aromatics in the presence of NOx	(Gaston et al., 2016; Yuan et al., 2016)
$C_7H_7NO_3I^-$	279.95	Methyl nitro-phenols	Direct emissions, oxidation of aromatics in the presence of NOx	(Gaston et al., 2016; Yuan et al., 2016)
$C_7H_7NO_4I^-$	295.94	Methyl nitro-benzenediols	Direct emissions, oxidation of aromatics in the presence of NOx	(Gaston et al., 2016; Yuan et al., 2016)
$C_7H_6O_4I^-$	280.93	Dihydroxy methyl benzoquinone	Aromatics + OH	(Schwantes et al., 2017; Wang et al., 2020b)
$C_7H_8O_4I^-$	282.95	Tetrahydroxy toluene	Aromatics + OH	(Schwantes et al., 2017; Wang et al., 2020b)
$C_7H_8O_5I^-$	298.94	Pentahydroxy toluene, fragments of C9 aromatics	Aromatics + OH	(Mehra et al., 2020; Schwantes et al., 2017)

$CH_2O_2I^-$	172.91	Formic acid	Oxidation of VOCs	(Lee et al., 2014; Yuan et al., 2015)
$C_2H_4O_2I^-$	186.93	Acetic acid	Oxidation of VOCs	(Lee et al., 2014; Mattila et al., 2018)
$C_5H_{10}O_2I^-$	228.97	Pentanoic acid	Traffic emissions, secondary formation	(Mattila et al., 2018)
$C_2H_4O_3I^-$	202.92	Glycolic acid	Oxidation of VOCs	(Lee et al., 2014; Lim et al., 2005)
$C_3H_4O_3I^-$	214.92	Pyruvic acid	Photolysis of methylglyoxal, BVOCs+OH, photo-oxidation of aromatics in the presence of NO_X	(Eger et al., 2020; Mattila et al., 2018)
$C_2H_2O_4I^-$	216.90	Oxalic acid	Aqueous-phase photooxidation of glyoxal, photo-oxidation of VOCs	(Carlton et al., 2007; Lee et al., 2014; Zhou et al., 2015)
$C_3H_4O_4I^-$	230.92	Malonic acid, hydroxypyruvic acid	Oxidation of VOCs	(Kawamura and Bikkina, 2016; Lee et al., 2014)
$C_4H_4O_4I^-$	242.92	Maleic acid, fumaric acid	Oxidation of aromatics	(Brege et al., 2018; Kawamura et al., 1996)
$C_5H_6O_4I^-$	256.93	Unsaturated dicarboxylic acid	Oxidation of aromatics	(Brege et al., 2018; Kawamura et al., 1996)
$C_5H_8O_4I^-$	258.95		Photo-oxidation of VOCs	(Berndt et al., 2019; Kawamura and Bikkina, 2016)
$C_6H_{10}O_4I^-$	272.96		Photo-oxidation of VOCs	(Berndt et al., 2019; Kawamura and Bikkina, 2016)

$C_4H_8O_4I^-$	246.95	2-methylglyceric acid	Isoprene SOA component under high NO_X conditions	(Surratt et al., 2006, 2010)
$C_5H_9NO_4I^-$	273.96	IHN (isoprene hydroxy nitrates)	1st-genetration organic nitrates from reaction: isoprene+OH+NO_X, isoprene+NO_3	(Jacobs et al., 2014; Xiong et al., 2015)
$C_4H_7NO_5I^-$	275.94	MVKN/ MACRN	2nd-genetration organic nitrates from oxidation of IHN in the presence of NO_X	(Fisher et al., 2016; Paulot et al., 2009)
$C_5H_9NO_5I^-$	289.95	C5 nitrooxy hydroperoxide, C5 nitrooxy hydroxyepoxide, C5 dihydroxy nitrate	isoprene+NO_3, isoprene+OH+NO_X	(Ng et al., 2017; Schwantes et al., 2015; Wennberg et al., 2018)
$C_8H_{12}O_4I^-$	298.98	Dicarboxylic and oxocarboxylic acids like norpinic acid, terpenylic acid	Monoterpenes+OH, monoterpenes O_3	(Fang et al., 2017; Mutzel et al., 2016; Yasmeen et al., 2011)
$C_9H_{14}O_4I^-$	312.99	Dicarboxylic and oxocarboxylic acids like pinic acid, homoterpenylic acid, caric acid	Monoterpenes+OH, monoterpenes O_3	(Fang et al., 2017; Mutzel et al., 2016; Yasmeen et al., 2011)
$C_{10}H_{16}O_3I^-$	311.02	Oxocarboxylic acids like	Monoterpenes+OH, monoterpenes O_3	(Fang et al., 2017; Glasius et al.,

		pinonic acid, caronic acid		2000; Yasmeen et al., 2011)
$C_8H_{13}NO_6I^-$	345.98	Organic nitrates from monoterpenes	Monoterpenes+OH+NO_X, monoterpenes +NO_3	(Lee et al., 2016; Nah et al., 2016)
$C_8H_{11}NO_7I^-$	359.96	Organic nitrates from monoterpenes	Monoterpenes+OH+NO_X, monoterpenes O_3+NO_3	(Carslaw, 2013; Lee et al., 2016)
$C_{10}H_{15}NO_6I^-$	372.00	Organic nitrates from monoterpenes, peroxyacetyl nitrate from pinonaldehyde	Monoterpenes+OH+NO_X, monoterpenes O_3+NO_3	(Boyd et al., 2015; Massoli et al., 2018; Schwantes et al., 2020)
HSO_4^-	96.96	Sulfuric acid	Oxidation of SO_2 etc.	(Le Breton et al., 2018b)
SO_3I^-	206.86	Sulfur trioxide, Fragment of organosulfates	Oxidation of SO_2, decomposition of organosulfates	(Surratt et al., 2007)
$C_2H_3SO_6^-$	154.96	Glycolic acid sulfate	Aqueous reaction of glycolic acid and sulfuric acid	(Galloway et al., 2009; Huang et al., 2018)
$CH_3SO_3^-$	94.98	Methanesulfonic acid	Oxidation of dimethyl sulfide	(Chen and Finlayson-Pitts, 2017; Gondwe et al., 2003)
$N_2O_5I^-$	234.89	Dinitrogen pentoxide	NO_3 + NO_2 + M	(Le Breton et al., 2018a; Wang et al., 2016)
$ClNO_2I^-$	207.87	Nitryl chloride	N_2O_5 (g) + Cl^- (aq)	(Le Breton et al., 2018a; Wang et al., 2016)

$ClNO_3I^-$	223.86	Chlorine nitrate	ClO + NO_2 + M	(Liu et al., 2017; Sander and Crutzen, 1996)
Cl_2I^-	196.84	Chlorine	Heterogeneous reactions of Cl^- and reactive chlorine like HOCl, $ClNO_2$ etc.	(Le Breton et al., 2018a; Liu et al., 2017; Wang et al., 2019)
HNO_3I^-	189.90	Nitric acid	NO_X + OH, hydrolysis of organic nitrates and N_2O_5	(Fisher et al., 2016; Wang et al., 2016)

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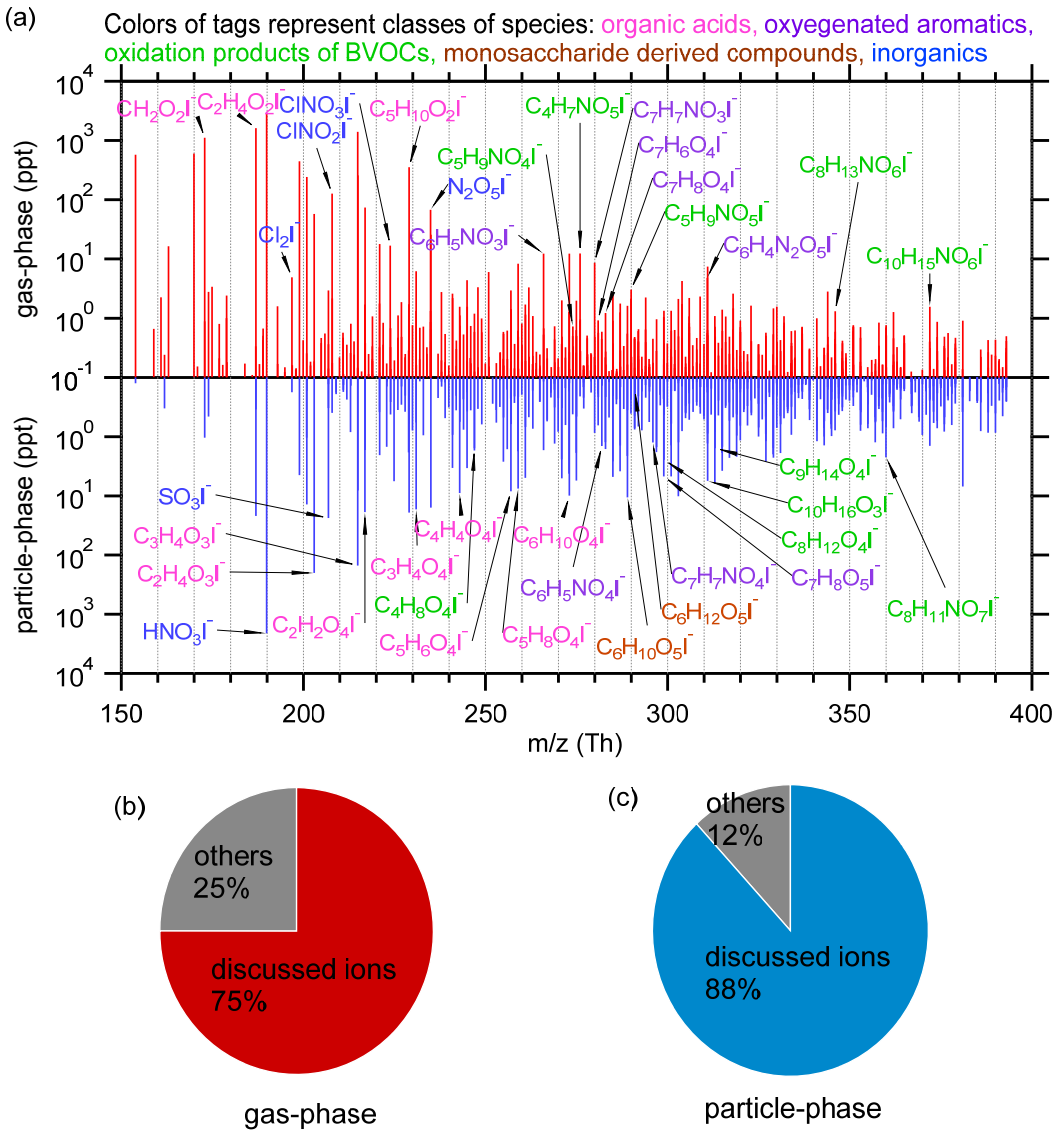


Figure 1. (a) Mass spectra of iodide charged ion within m/z 150-400 Th in gas-phase (red) and particle-phase (blue), respectively. (b and c) The fractions of I-adduct ions discussed in the main text (Table 1) in the total ion signals for I-adduct ions measured in gas-phase (b) and particle-phase (c), respectively.

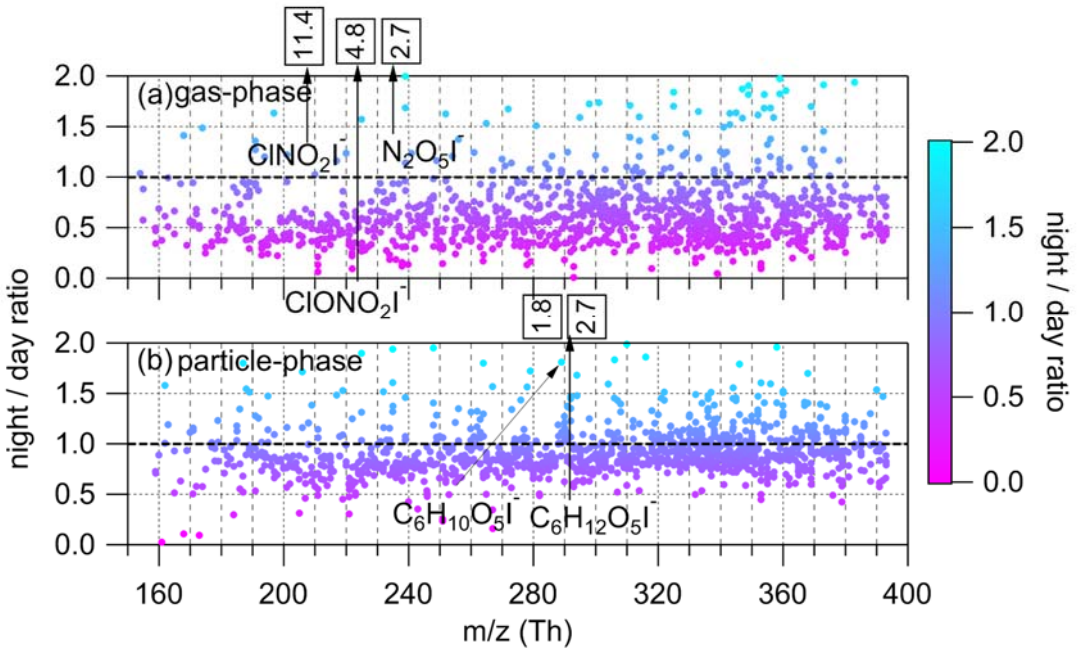


Figure 2. The ratios of concentrations at night (10 pm - 6 am) to concentrations during the day (10 am - 6 pm) for ions ranging from 150 to 400 Th in gas-phase (a) and particle-phase (b). The range of y-axis is set between 0 and 2 for clarity, although the ratios of some compounds are larger than 2. The numbers in boxes indicate the night/day ratios of tagged ions that exceed the y-axis ranges.

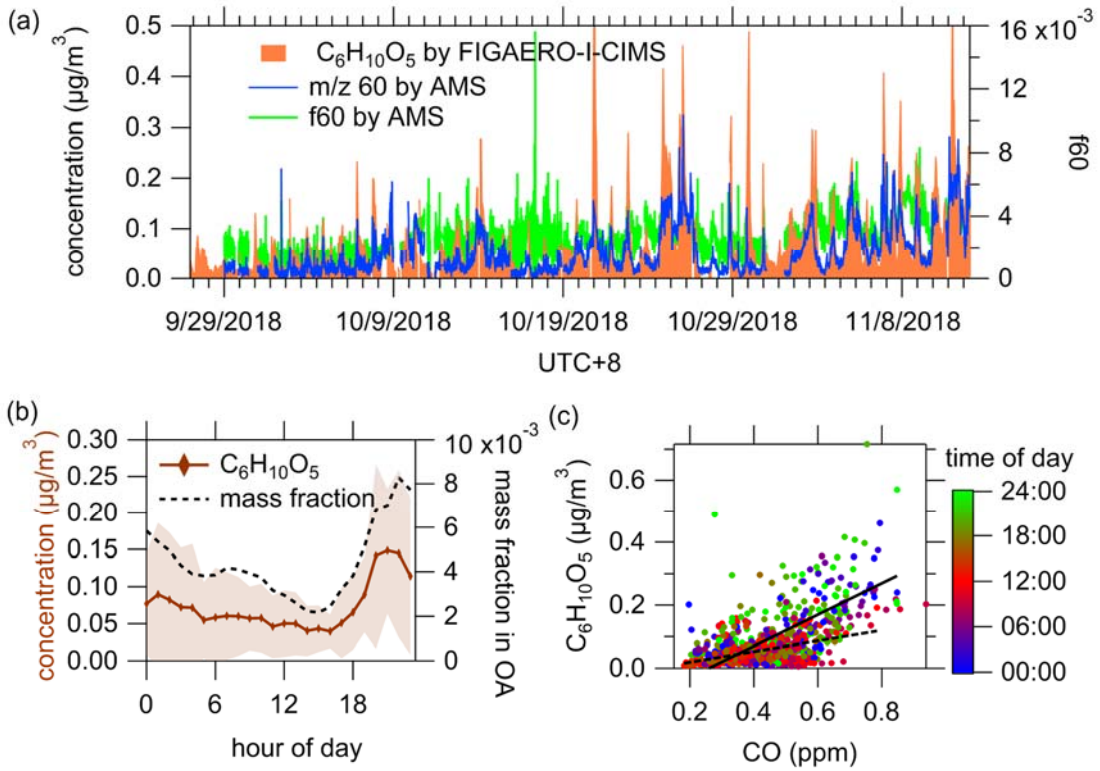


Figure 3. (a) Time series of particulate $C_6H_{10}O_5$ measured by FIGAERO-I-CIMS, m/z 60 fragment and f60 measured by AMS. Background f60=0.3% and background m/z 60=0.3%×OA were subtracted from f60 and m/z 60 (Cubison et al., 2011; Hu et al., 2016). (b) Diurnal variations of particulate $C_6H_{10}O_5$ and its mass fraction in OA. (c) Correlation between CO and particulate $C_6H_{10}O_5$. The dash and solid lines indicate the ratios during daytime (10 am - 6 pm, 0.17±0.02 μg·m^{-3}/ppm) and nighttime (10 pm - 6 am, 0.50±0.03 μg·m^{-3}/ppm), respectively.

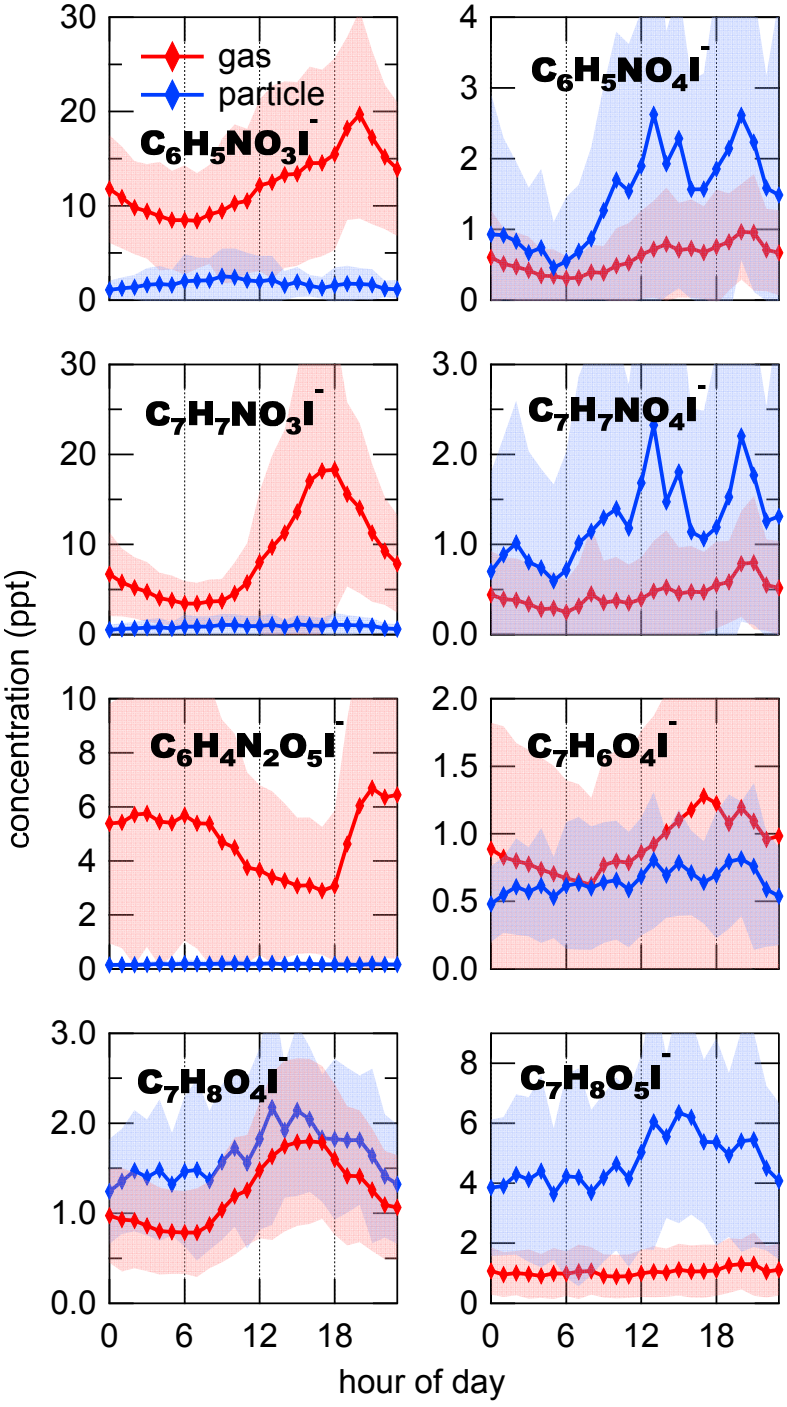
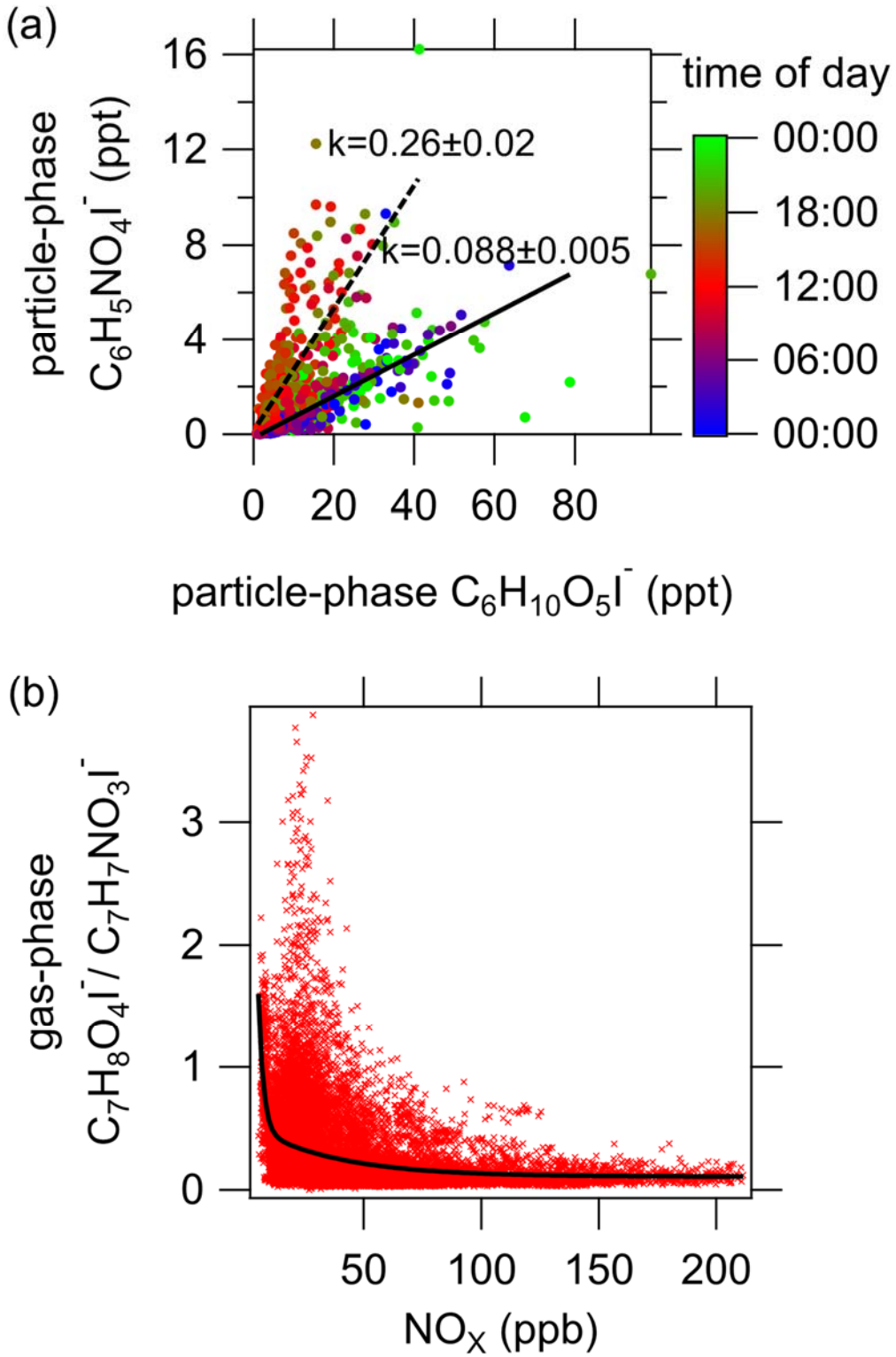


Figure 4. Diurnal variations of oxidized aromatics including nitro-phenols ($C_6H_5NO_3I^-$), nitro-benzenediols ($C_6H_5NO_4I^-$), methyl nitro-phenols ($C_7H_7NO_3I^-$), methyl nitro-benzenediols ($C_7H_7NO_4I^-$), dinitro-phenols ($C_6H_4N_2O_5I^-$), dihydroxy methyl benzoquinone ($C_7H_6O_4I^-$), tetrahydroxy toluene ($C_7H_8O_4I^-$), pentahydroxy toluene and fragments of C9 aromatics ($C_7H_8O_5I^-$). The shaded areas indicate one standard deviation.



1366

1367 **Figure 5.** (a) Correlation between particle-phase $C_6H_5NO_4I^-$ and $C_6H_{10}O_5I^-$. The

1368 data points are color-coded using the time of the day. Solid and dash lines represent the

1369 slopes during the nighttime and daytime, respectively. (b) Relative concentration of

1370 $C_7H_8O_4I^-$ and $C_7H_7NO_3I^-$ in the gas phase as a function of NOx concentration. The
1371 black line is the fitted curve using a double exponential function.

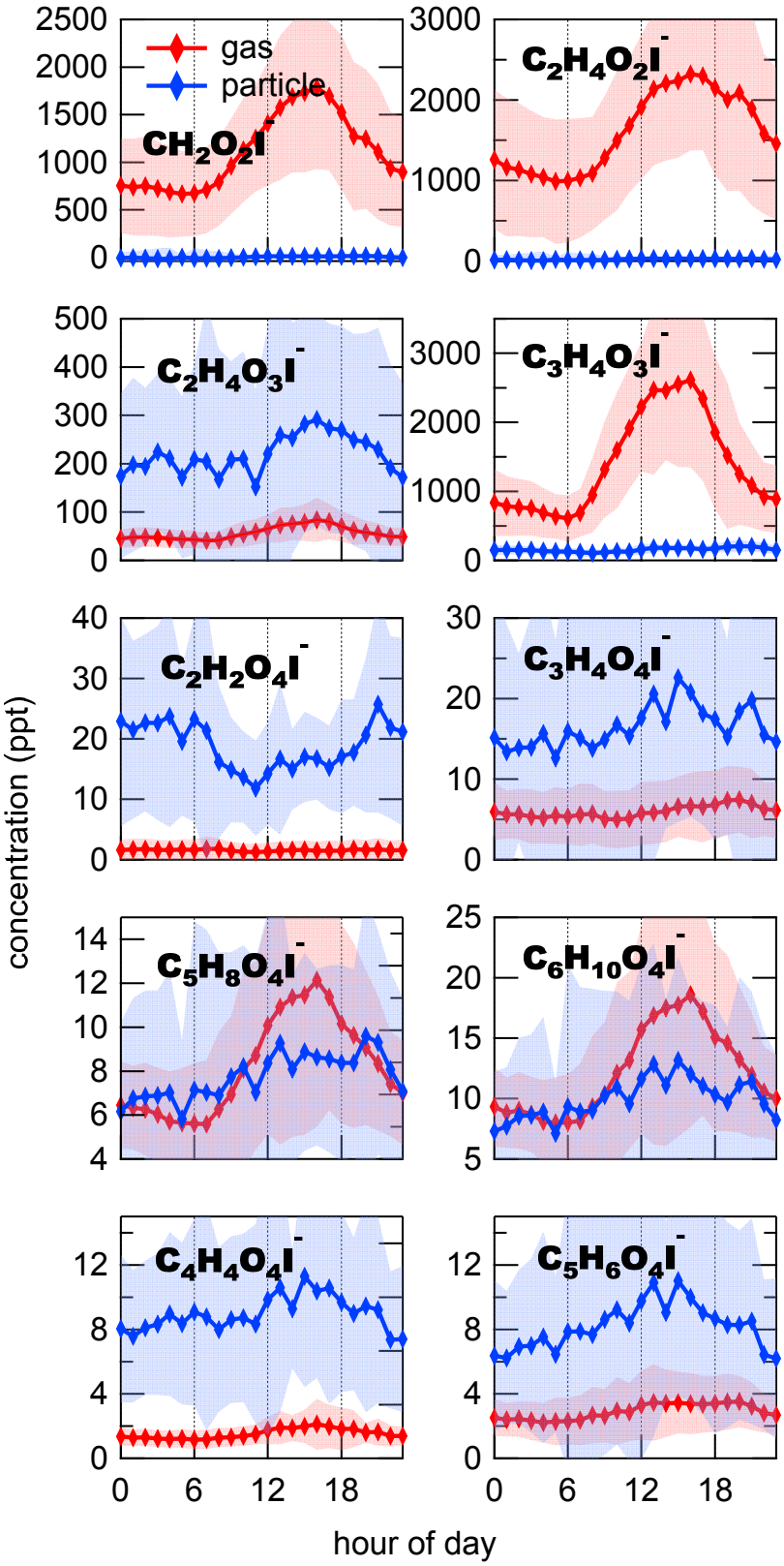
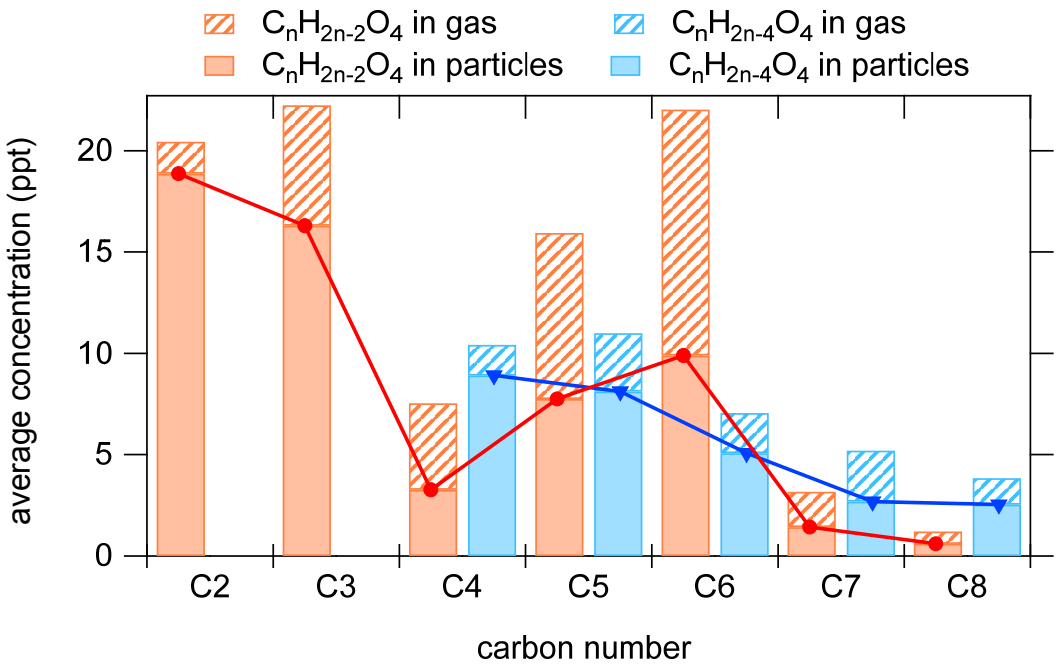


Figure 6. Diurnal variations of organic acids in the gas phase (red) and particle phase (blue). The shaded area indicates one standard deviation.



1375

1376 **Figure 7.** Average concentrations of compounds with the formulas of $C_nH_{2n-2}O_4$

1377 and $C_nH_{2n-4}O_4$.

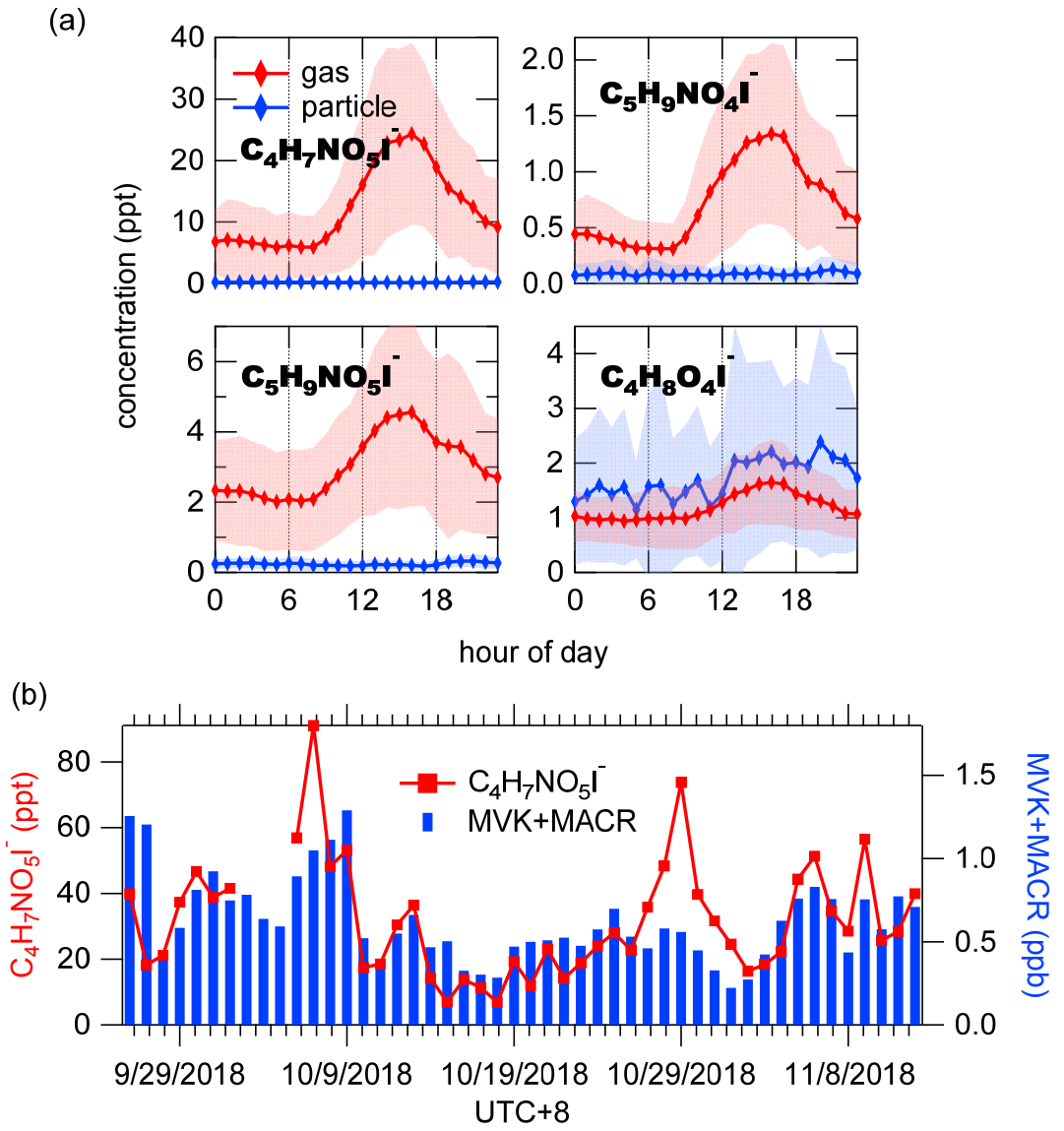
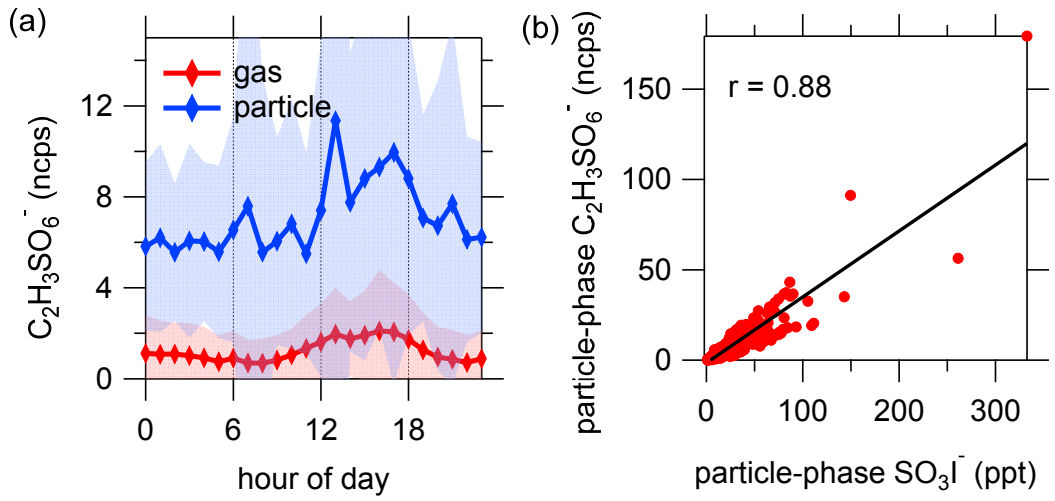


Figure 8. (a) Diurnal variations of isoprene oxidation products in the gas phase (red) and particle phase (blue). The shaded area indicates one standard deviation. (b) Time series of daily maximum concentrations of gaseous $C_4H_7NO_5I^-$ and MVK+MACR ($C_4H_6OH^+$, m/z 71.05) measured by PTR-ToF-MS.



1383

1384 **Figure 9.** (a) Diurnal variation of $C_2H_3SO_6^-$. The shaded areas indicate one standard

1385 deviation. (b) Correlation between particle-phase $C_2H_3SO_6^-$ and SO_3I^-.

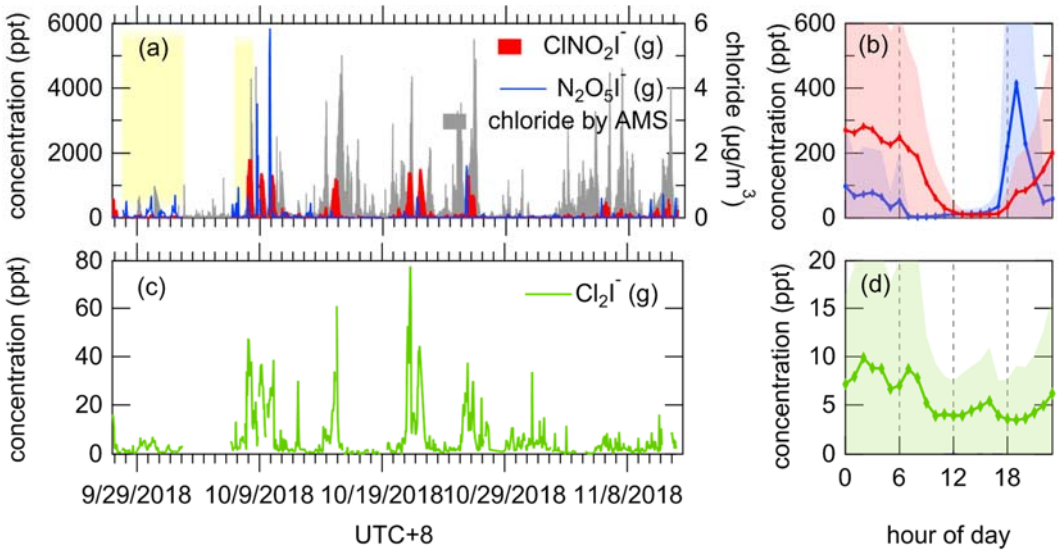


Figure 10. Time series and diurnal variations of humidity-corrected concentrations of N_2O_5 and $ClNO_2$ (a, b) and Cl_2 (c, d). The tinted background indicates the days with high concentrations of N_2O_5 but low concentrations of $ClNO_2$. The shaded areas indicate one standard deviation.

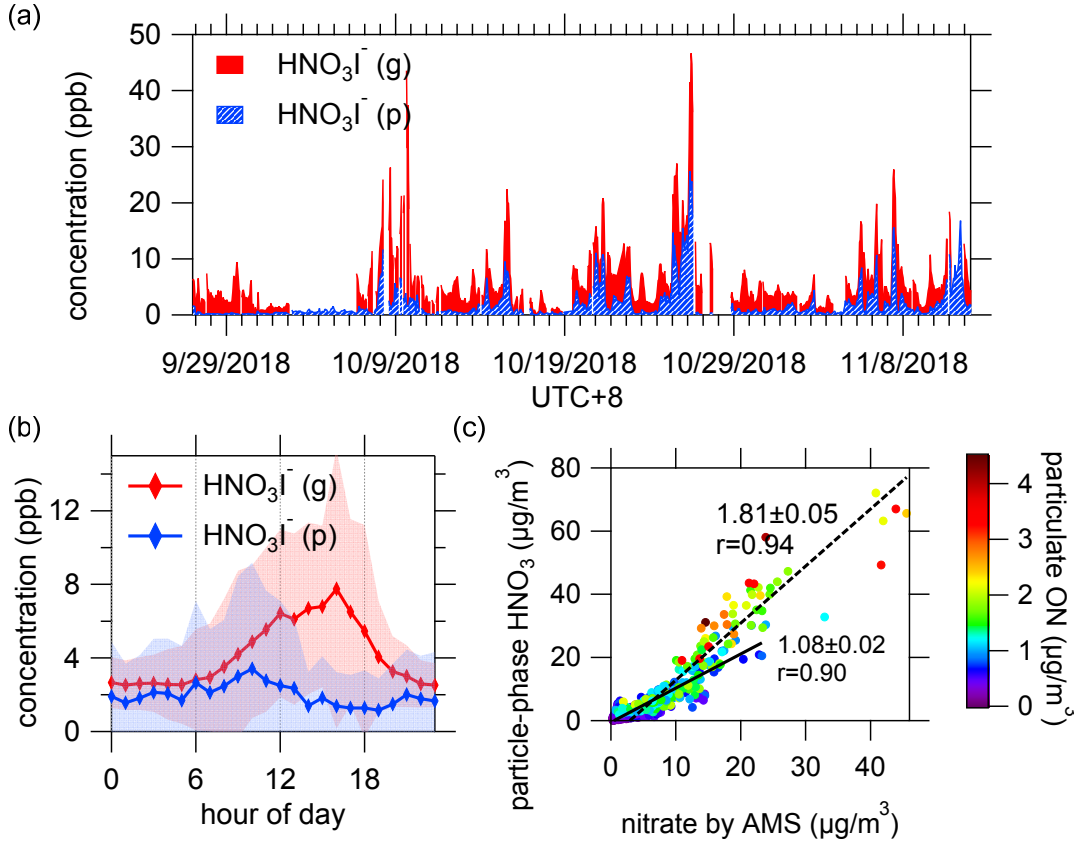


Figure 11. (a) Time series of humidity-corrected HNO_3I^- in both phases. (b) Diurnal variation of humidity-corrected HNO_3I^-. The shaded areas indicate one standard deviation. (c) Comparison of particle-phase HNO_3I^- and nitrate measured by AMS. The color scale denotes particulate N-containing organic compounds measured by FIGAERO-I-CIMS (pON). The solid and dash lines show the fitted results for the dataset of pON less than 1 μg/m^3 and more than 1 μg/m^3, respectively. The concentration of gaseous HNO_3I^- shown here only included the last 5-minute of every gas-phase working mode, as high level of HNO_3 came out of aerosol which then passed through the CIMS in a short time during particle analysis and a substantial amount would subsequently accumulate on the inner surfaces, leading to a persistent carried over signal that was long enough to disturb the next gas measurement cycle (Palm et al., 2019).

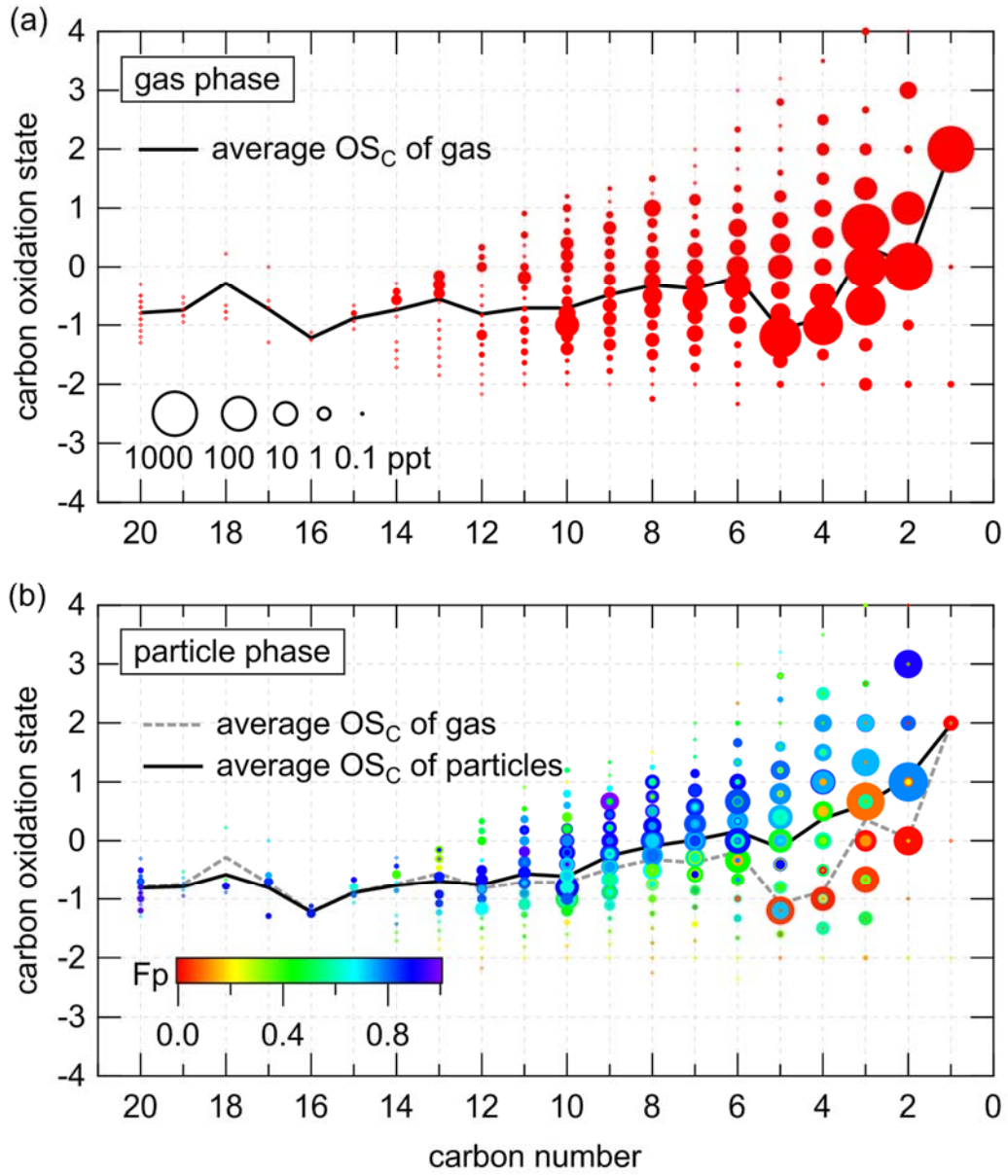
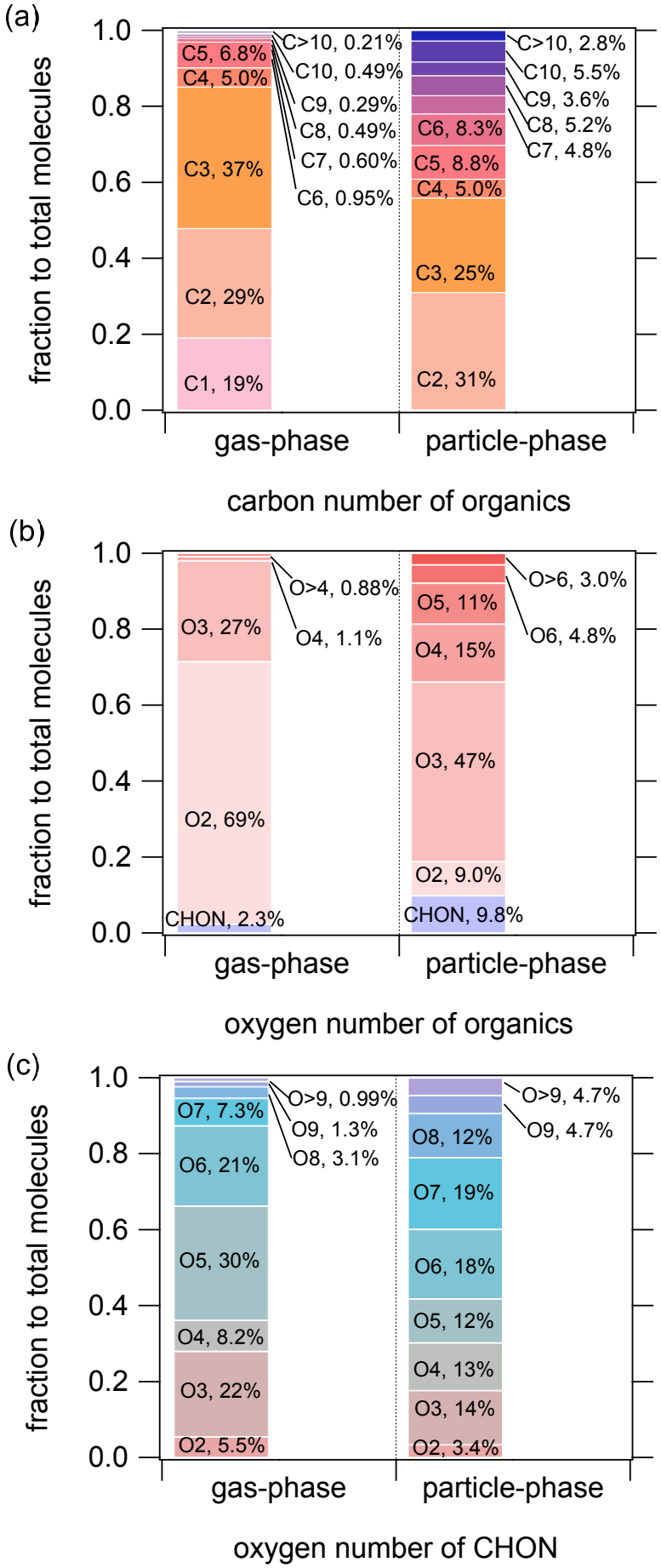


Figure 12. $\overline{OS_C} - n_C$ spaces for $C_xH_yO_z$ and $C_xH_yN_{1,2}O_z$ compounds in gas-phase (a) and particle-phase (b). The diameters of circles are proportional to the logarithmic average concentrations. The black lines are the average $\overline{OS_C}$ of each carbon number for compounds in gas-phase and particle-phase, respectively. The compounds in Fig. (b) are color-coded by their fractions in particles.


(a)
fraction to total molecules
1.0
0.8
0.6
0.4
0.2
0.0
C5, 6.8%
C4, 5.0%
C3, 37%
C2, 29%
C1, 19%
C>10, 0.21%
C10, 0.49%
C9, 0.29%
C8, 0.49%
C7, 0.60%
C6, 0.95%
C6, 8.3%
C5, 8.8%
C4, 5.0%
C3, 25%
C2, 31%
C>10, 2.8%
C10, 5.5%
C9, 3.6%
C8, 5.2%
C7, 4.8%
gas-phase
particle-phase
carbon number of organics
(b)
fraction to total molecules
1.0
0.8
0.6
0.4
0.2
0.0
O3, 27%
O2, 69%
CHON, 2.3%
O>4, 0.88%
O4, 1.1%
O5, 11%
O4, 15%
O3, 47%
O2, 9.0%
CHON, 9.8%
O>6, 3.0%
O6, 4.8%
gas-phase
particle-phase
oxygen number of organics
(c)
fraction to total molecules
1.0
0.8
0.6
0.4
0.2
0.0
O7, 7.3%
O6, 21%
O5, 30%
O4, 8.2%
O3, 22%
O2, 5.5%
O>9, 0.99%
O9, 1.3%
O8, 3.1%
O8, 12%
O7, 19%
O6, 18%
O5, 12%
O4, 13%
O3, 14%
O2, 3.4%
O>9, 4.7%
O9, 4.7%
gas-phase
particle-phase
oxygen number of CHON

1411

Figure 13. Carbon number distribution (a) and oxygen number distribution of total $C_xH_yO_z$ and $C_xH_yN_{1,2}O_z$ compounds (b), and oxygen number distribution of $C_xH_yN_{1,2}O_z$ compounds (c).

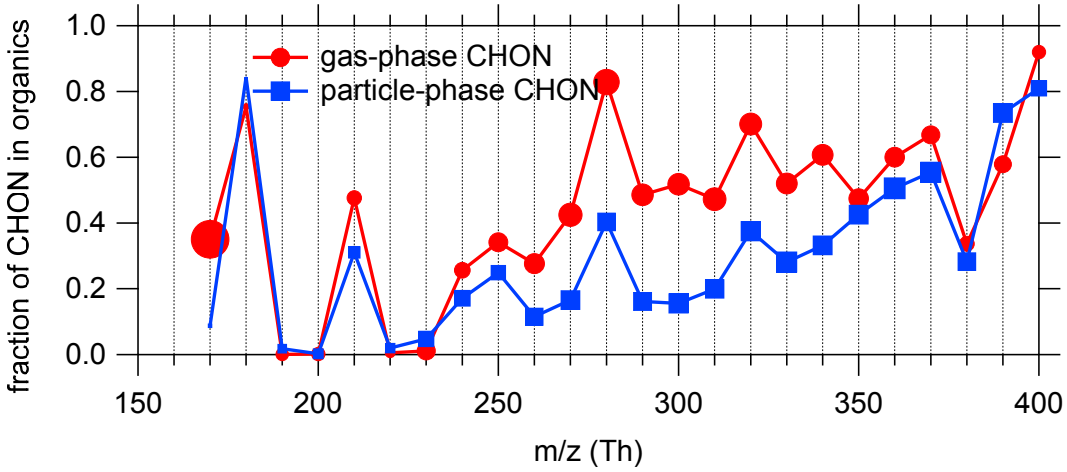


Figure 14. The average fractions of CHON to total organic compounds (CHO + CHON + CHOS + CHONS) of every 10 Th in both phases. See Fig. S16 for the overall distribution of the contributions of species classes to the total concentrations. Marker sizes indicate the total concentration level in each m/z bin. High ambient concentration of HNCO resulted in the large marker around m/z 170 in the gas phase (Wang et al., 2020d).

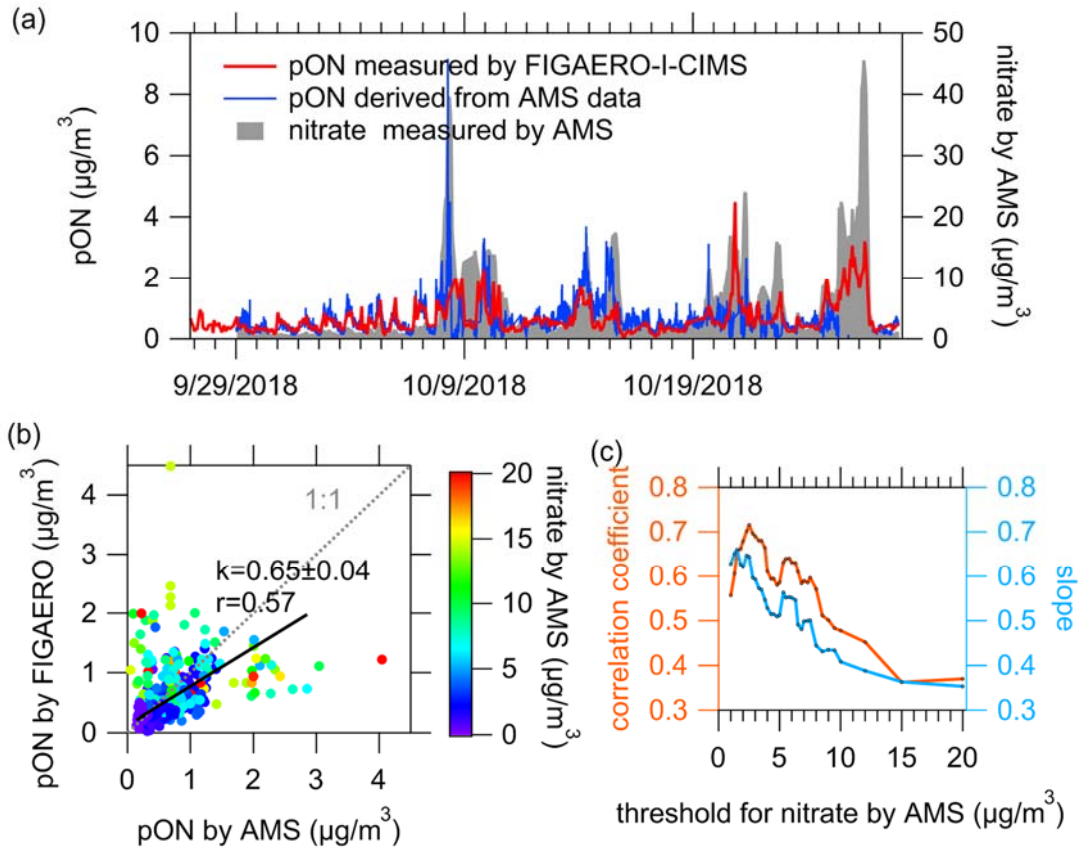


Figure 15. (a) Time series of particulate N-containing organic compounds measured by FIGAERO-I-CIMS (pON by FIGAERO), particulate organic nitrates derived from AMS data (pON by AMS) as well as particulate inorganic nitrate. (b) Comparison of pON by FIGAERO and pON by AMS, color-coded by the concentrations of particulate inorganic nitrate measured by AMS. The black line presents the linear fit for nitrate by AMS below 8 μg/m^3. (c) The determined slopes and correlation coefficients between pON by FIGAERO versus pON by AMS by filtering the data below different thresholds of particulate inorganic nitrate measured by AMS.

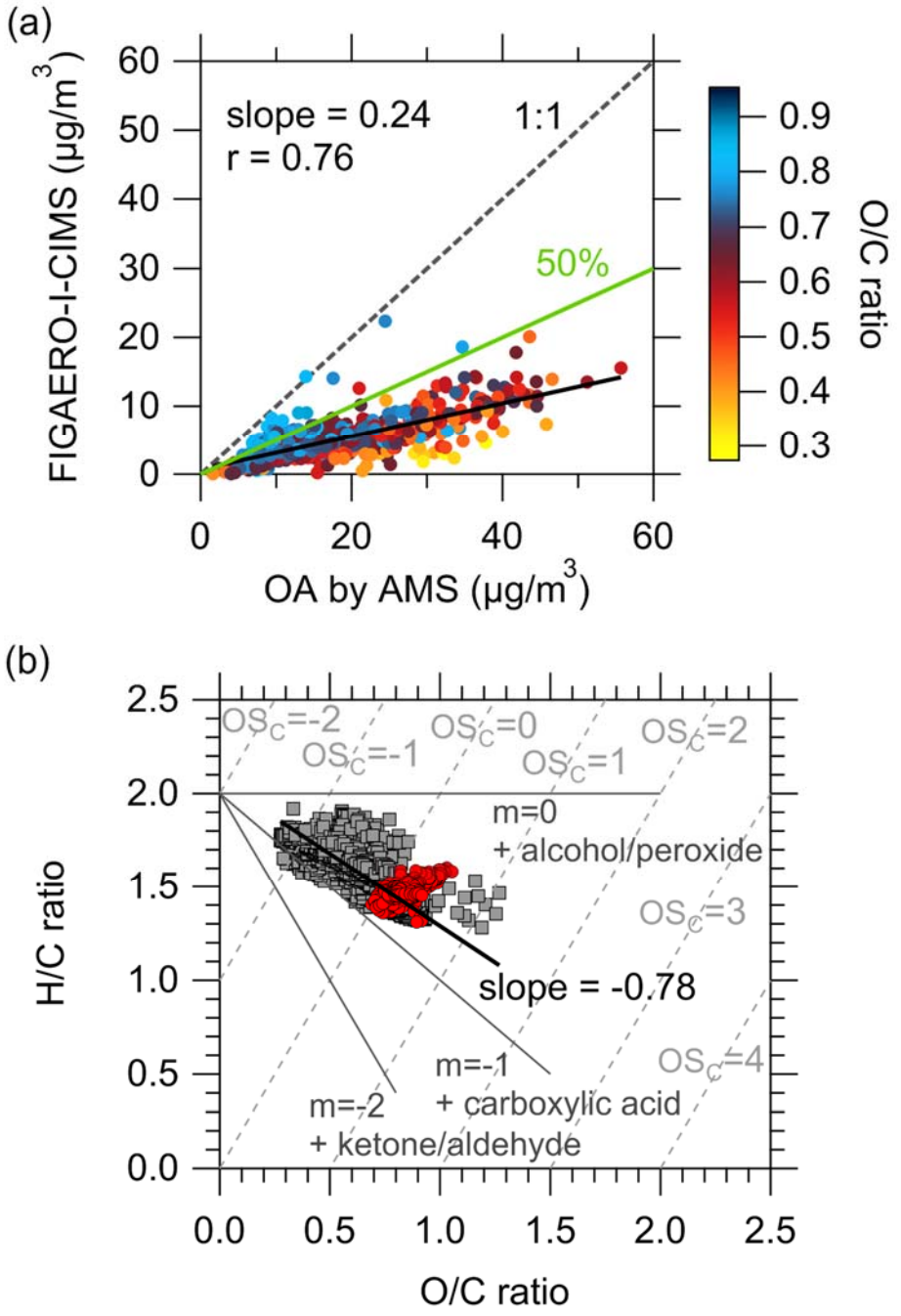


Figure 16. (a) Comparison of particulate organic compounds measured by the FIGAERO-I-CIMS and AMS, color-coded by O/C ratios measured by AMS. The black line is the slope which represents the fraction of OA explained by the measurements of FIGAERO-I-CIMS. The green line shows the results from previous work which were ~50% (Lopez-Hilfiker et al., 2016; Stark et al., 2017). (b) Van Krevelen diagrams for organic aerosol derived from AMS data (gray squares) and FIGAERO-I-CIMS data (red circles). Black line is the slope of AMS data. Gray dotted lines are estimated carbon oxidation state.