JGR Atmospheres

RESEARCH ARTICLE

10.1029/2018JD029904

Key Points:

- Aging processes of submicron nonrefractory aerosols were investigated comparatively at two suburban sites in northern and southern China
- Both sites showed dominant mass increment from organics after aging, but aerosols in northern China had higher aging potential
- The distinct aging processes at the two sites reflected influence from ambient precursors

Supporting Information:

- Supporting Information S1

Correspondence to:

Y. Li, and J. Z. Yu,
yongjieli@um.edu.mo;
jian.yu@ust.hk

Citation:

Li, J., Liu, Q., Li, Y., Liu, T., Huang, D., Zheng, J., et al. (2019). Characterization of aerosol aging potentials at suburban sites in northern and southern China utilizing a potential aerosol mass (Go:PAM) reactor and an aerosol mass spectrometer. *Journal of Geophysical Research: Atmospheres*, 124, 5629–5649. <https://doi.org/10.1029/2018JD029904>

Received 29 OCT 2018

Accepted 9 APR 2019

Accepted article online 23 APR 2019

Published online 29 MAY 2019

Characterization of Aerosol Aging Potentials at Suburban Sites in Northern and Southern China Utilizing a Potential Aerosol Mass (Go:PAM) Reactor and an Aerosol Mass Spectrometer

Jinjian Li¹ , Qianyun Liu¹ , Yongjie Li² , Tengyu Liu³ , Dandan Huang⁴ , Jing Zheng⁵, Wenfei Zhu⁴, Min Hu⁵, Yusheng Wu⁵ , Shengrong Lou⁴ , Åsa M. Hallquist⁶, Mattias Hallquist⁷ , Chak K. Chan³ , Francesco Canonaco⁸ , André S. H. Prévôt⁸, Jimmy C. H. Fung¹ , Alexis K. H. Lau¹, and Jian Zhen Yu^{1,9}

¹Division of Environment and Sustainability, Hong Kong University of Science and Technology, Hong Kong, China,

²Department of Civil and Environmental Engineering, Faculty of Science and Technology, University of Macau, Macau, China,

³School of Energy and Environment, City University of Hong Kong, Hong Kong, China, ⁴Shanghai Academy of Environmental Sciences, Shanghai, China, ⁵State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China, ⁶IVL Swedish Environmental Research Institute, Gothenburg, Sweden, ⁷Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden, ⁸Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland, ⁹Department of Chemistry, Hong Kong University of Science and Technology, Hong Kong, China

Abstract Aerosol mass spectrometry was used to characterize submicron aerosols before and after aging in a Gothenburg Potential Aerosol Mass (Go:PAM) reactor at two suburban sites in China, one in northern China at Changping (CP), Beijing, and a second in southern China at Hong Kong (HK). Organic aerosol (OA) dominated in the ambient nonrefractory particulate matter <1 μm (NR-PM₁) for both CP (42–71%) and HK (43–61%), with a large contribution from secondary OA factors that were semivolatile oxygenated (SVOOA) and low-volatility oxygenated (LVOOA). Under constant OH exposure, OA enhancement (78–98%) dominated the NR-PM₁ mass increment at both sites, while nitrate was enhanced the most among the inorganic species (7–9%). Overall, the CP site exhibited higher OA oxidation potential and more enhancement of SVOOA than LVOOA (7.5 vs. 2.7 $\mu\text{g}/\text{m}^3$), but the reverse was observed in HK (0.8 vs. 2.6 $\mu\text{g}/\text{m}^3$). In CP, more enhancement of the less oxygenated SVOOA suggests that aerosol aging was more sensitive to the abundant locally emitted primary OA and volatile organic compound precursors. On the contrary, the more formation of the highly oxidized LVOOA in HK indicates that aerosol aging mainly escalated the degree of oxygenation of OA as ambient aerosol was already quite aged and there was a lack of volatile organic compound precursors. The comparative measurements using the same oxidation system reveal distinct key factors and mechanisms that influence secondary aerosol formation in two suburban locations in China, providing scientific insights to assist formulation of location-specific mitigation measures of secondary pollution.

Plain Language Summary Atmospheric submicron particles have significant impacts on the climate and human health. A large part of these particles are formed secondarily through successive aging of primary emissions. To study such aging processes, we used a reactor that can provide highly oxidizing conditions to simulate the oxidation of ambient aerosols at accelerated rates. An online mass spectrometer was connected after the reactor to measure changes in aerosol mass concentration and chemical composition between the ambient samples and the oxidized ones. We presented the first comparative measurements of the aging potentials of ambient aerosols in two suburban sites in northern and southern China (Changping District in Beijing, and Hong Kong). Results showed that generally aerosols at the Changping site had higher aging potentials after passing through the oxidation reactor, probably due to more local emissions of precursors, while air masses in Hong Kong were already in a higher oxidation state with lower aging potentials, mainly because of strong impacts from long-range transported pollution sources. Distinct aerosol aging pathways related to different ambient precursors were observed at the two sites. Understanding of the different characteristics of aerosol aging processes can lead to advances in air quality modeling and pollution management.

1. Introduction

Atmospheric submicron aerosols are closely related to various environmental effects, including climate change (Stocker et al., 2014), visibility degradation (Shen et al., 2014), and public health threat (Carmichael et al., 2009; Lim et al., 2012). Such issues have attracted increasing attention in China, especially in the most densely populated geographical areas with rapid economic growth, such as the North China Plain (NCP) in northern China and the Pearl River Delta (PRD) in southern China. Beijing and Hong Kong are two representative megacities located in NCP and PRD, respectively. In recent years, these two cities are being plagued by severe influence of atmospheric pollution caused by both locally emitted and regionally transported aerosols. However, the chemical and physical properties, as well as the dominating sources of aerosols at these two typical megacities in China, are quite different (Hu, Hu, Hu, Jimenez, et al., 2016; Hu et al., 2017; Lee et al., 2015; Li et al., 2015; Li et al., 2017; Sun, Wang, Fu, Yang, et al., 2013; Sun et al., 2015, 2018; Zhang et al., 2014). For example, secondary organic aerosols (SOA) contribute more to total organic aerosols (OA) in Hong Kong than in Beijing, while nitrate is more abundant in Beijing than in Hong Kong (Hu et al., 2017; Li et al., 2017). In addition, more complex primary sources such as coal combustion can be found in Beijing, especially during the winter heating season (Hu, Hu, Hu, Jimenez, et al., 2016; Hu et al., 2017; Sun, Wang, Fu, Yang, et al., 2013; Sun et al., 2014, 2016; Wang et al., 2015; Zhang et al., 2014, 2016), but are not observed in Hong Kong. Thus, it is highly desirable to perform comparative studies in such cities for a better understanding in the differences of submicron aerosols in the northern and southern Chinese megacities.

In the last decade, a series of online studies applying the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) have been conducted in Beijing and Hong Kong to characterize the mass concentration, chemical composition, and size distribution of nonrefractory submicron aerosols (NR-PM₁, defined as nonrefractory particulate matter with an aerodynamic diameter of less than 1 μm). Source apportionment through positive matrix factorization (PMF) analysis of OA components in NR-PM₁ can help identify contributions from the primary emission sources and secondary formation processes. However, our understanding of the formation pathways and fates of NR-PM₁ constituents remains spatiotemporally limited because of their heterogeneous distribution and short atmospheric lifetimes (Mohr et al., 2011).

Recently, the Oxidation Flow Reactors (OFRs) have been increasingly used to study the aging processes of aerosols in ambient air with various precursors (e.g., SO₂, NO_x = NO + NO₂, and volatile organic compounds, VOCs), especially the potential SOA formation. OFR is a small and portable reactor that employs relatively high oxidant (OH, O₃, or NO₃) concentrations with a short residence time (usually some minutes) to achieve equivalent atmospheric oxidation ranging from hours to days (Kang et al., 2007; Lambe et al., 2011; Palm et al., 2018). Slowik et al. (2012) presented the first study that applied an OFR and PMF analysis to characterize the controlled OH oxidation of ambient aerosol in a remote forest and observed evidence for OH reaction products through identification of secondary factors from PMF. Studies have also been conducted in a larger variety of environments, including the forested area with mainly biogenic emissions (Palm et al., 2016), the urban area with mainly anthropogenic emissions (Ortega et al., 2016), the near-road area affected by both traffic and biogenic emissions (Saha et al., 2018), and the Central Amazon forest under mixed biogenic, urban, and biomass burning sources (Palm et al., 2018). However, there are only a few studies applying OFRs to investigate ambient aerosol aging processes in China so far (Breton et al., 2018; Liu et al., 2018).

In this work, we deployed a new type of OFR named the Gothenburg Potential Aerosol Mass (Go:PAM; Watne et al., 2018) to comparatively study the aging characteristics of submicron aerosols at two representative suburban sites in Beijing (northern China in NCP) and Hong Kong (southern China in PRD). The sampling periods selected in this study are the prime time for photochemical smog with expected high ozone levels and similar high temperatures at both sites (CP: O₃ = 49.5 $\pm$ 37.5 ppb, T = 25.2 $\pm$ 5.1 $^{\circ}\text{C}$; HK: O₃ = 44.0 $\pm$ 19.5 ppb, T = 25.3 $\pm$ 3.1 $^{\circ}\text{C}$). Measurements of submicron aerosols (specifically NR-PM₁) were made with an Aerodyne HR-ToF-AMS (referred to as AMS in the following discussion for the sake of simplicity) before and after aging. After aging by OH in the Go:PAM, mass increments and composition changes of NR-PM₁ were investigated in detail to reveal the different oxidation potentials of ambient air at these two sites. Comparison of possible precursor(s) contributing to mass increments at these two representative sites

peripheral to megacities in northern and southern China will also be discussed, which has implications for control policies to mitigate particulate pollution in China (Hallquist et al., 2016).

2. Method

2.1. Site Description

Online measurements of the NR-PM₁ components were conducted at two suburban sites, namely, the Changping campus of Peking University (CP: 40°8'24"N; 116°6'36"E) in Beijing and the Hong Kong University of Science and Technology (HKUST) Supersite (HK: 22°20'16"N, 114°16'3"E) in Hong Kong (see Figure S1 in the supporting information) during the "Photochemical Smog in China" campaign (Hallquist et al., 2016). The CP site is set on the fourth floor of a building on the Changping campus outside the north-west section of the sixth Ring Road of Beijing and is approximately 40 km from the center of the city (Tang et al., 2018; Wang et al., 2010). The HK site is on the hillside of Clear Water Bay at the east coast of Hong Kong (Lee et al., 2013; Li et al., 2013). The sampling periods for the CP and HK sites were from 12 to 21 June 2016 (summer) and from 11 to 21 October 2016 (autumn), respectively.

2.2. Measurements

2.2.1. Go:PAM

In this work, we used the Go:PAM reactor for aerosol aging experiments. The 100-cm long, 9.6-cm i.d. flow reactor is made of quartz glass (Raesh GmbH RQ 200). Inside the Go:PAM, OH radicals were produced by photolysis of ozone with two 254-nm ultraviolet lamps, followed by reaction of excited oxygen atoms with water in competition with producing ground state atomic oxygen. The sample flow (6 L/min) was introduced to the center of the Go:PAM reactor, and the oxidant flow (4 L/min) with O₃ and humidified ambient air (constant flow) was distributed across the reactor by a perforated plate to ensure good mixing. A periodical variation of the OH production was achieved by changing the O₃ concentration, and the system was operated at ambient temperature (CP: 16.3–34.9 °C; HK: 20.5–33.4 °C) and relative humidity (RH, CP: 15.7–82.4%; HK: 32.3–95.6%). The OH exposures in the Go:PAM reactor were determined by the SO₂ calibration (Text S1.1), and the effect of RH on the OH exposure was calculated by the model (Figure S3). The OH exposure estimation can be biased by ambient pollutants that react with OH radicals. Results from the kinetic modeling indicated that the decrease of OH exposure due to the reactive species was minor in this study (Text S1.2). During the CP and HK campaigns, the OH exposures were equivalent to 3–4 days of atmospheric oxidation (Text S1), assuming that the average ambient OH concentration was 1.5×10^6 molecules/cm³ (24-hr average; Mao et al., 2009). Recent measurements showed a peak of OA enhancement in the range of 2–4 days of photochemical aging by OFRs in diverse settings (Saha et al., 2018; Slowik et al., 2012; Tkacik et al., 2014); thus, the OH exposure of the Go:PAM system in our study fell within the OH exposure range that can produce the maximum possible aerosol mass increases.

Details about the design of the Go:PAM, as well as the flow profile, residence time, particle loss, and flow mixing tests, are described by Watne (2018). In short, the Go:PAM used in this study has a median residence time of 36 s, enabling measurements of potential secondary products in high time resolutions. The mixing of the sample flow and the oxidant flow was tested by consecutively adding SO₂ to the two flow inlets. There was no impact of different inlets on the measured SO₂ concentration of the processed flow, indicating a good mixing of the sample flow and oxidant flow (see Text S2.1 for detailed information). The Go:PAM was connected before the AMS to provide periodic oxidation condition in situ to process sampled ambient air. Measurements at both CP and HK sites adopted the same setup of the Go:PAM-AMS system, which was operated with ultraviolet lamps turned on and off every 45 min. Accordingly, the submicron aerosols measured by AMS were in the cycle of the Go:PAM-oxidized period (referred to as the "aged" period) and the ambient air period (referred to as the "fresh" period). Since the flow in Go:PAM approached a laminar flow after initial mixing and only the central part of the Go:PAM was sampled by the AMS, the particle wall losses in Go:PAM were generally small (<10% when the particle size was above 25 nm; see Text S2.2 for detailed information; Watne et al., 2018). In particular, since the focus of this work is on the relative changes between the aged and the fresh periods, which were subject to the same wall loss, the influence of the particle loss can be neglected in our analysis. Organic gases oxidized in the Go:PAM reactor can form low-volatility organic compounds (LVOCs). Apart from condensation onto preexisting particles, which is the dominant fate of LVOCs in ambient atmosphere (Donahue et al., 2013; Knote et al., 2015), other fates can also play a role

for LVOCs in an OFR because of the shorter timescales and high OH concentrations. These fates include reaction with OH to produce condensable or noncondensable products, loss to the OFR walls, and exiting the OFR as gas phase LVOCs to condense on surfaces of the sampling line (Ortega et al., 2016; Palm et al., 2016; Saha et al., 2018). The LVOC fates in the Go:PAM during our measurements were modeled following the method of Palm et al. (2016). Detailed information is described in Text S2.3.

2.2.2. HR-ToF-AMS

NR-PM₁ components including organics, sulfate, nitrate, ammonium, and chloride were measured using an Aerodyne HR-ToF-AMS. A detailed description of the instrument principle can be found in DeCarlo et al. (2006). The AMS was operated under the “V-mode” and “W-mode” alternately for 2 min each. The former gives better sensitivity and is used for determination of mass concentration, whereas the latter provides higher mass spectral resolution with information of OA elemental composition (Aiken et al., 2008; DeCarlo et al., 2006). A diffusion dryer (BMI, San Francisco, CA) was placed before the inlet of the AMS to reduce RH of the sample air down to <30% in order to achieve a consistent collection efficiency (CE). At the CP and HK sites, the aerosol nitrate content characterized by the NH₄NO₃ mass fraction was lower than the threshold value (0.4) that significantly affects the CE, and the particle acidity level characterized by NH₄⁺_{measured}/NH₄⁺_{predicted} was much larger than the threshold 0.75. Thus, the default CE of 0.5 was applied for data sets from both campaigns (Middlebrook et al., 2012).

Ionization efficiency calibration using size-selected (300 nm) ammonium nitrate particles and the inlet flow rate calibration were conducted following standard protocols (Drewnick et al., 2005; Jayne et al., 2000; Jimenez et al., 2003). Filtered periods by adding a HEPA filter in front of the AMS inlet were used to measure the particle-free air, and 3 times of its standard deviation was calculated as the detection limits of each NR-PM₁ species.

2.3. Other Collocated Instruments

At the HK site, an online gas chromatograph analyzer GC 955 (Syntech Spectras, Groningen, Netherlands) was also deployed to measure VOCs including isoprene, benzene, and toluene. There were no VOC measurements at the CP site. Other additional data from various collocated instruments including meteorological data (temperature, RH, wind speed, wind direction, barometric pressure, and solar radiation), gaseous species (O₃, SO₂, CO, and NO_x), and the PM_{2.5} mass concentration were available at both CP and HK sites.

2.4. Data Analysis

2.4.1. AMS Data Analysis

The unit mass resolution data and the high-resolution data of the AMS were analyzed using the data analysis toolkit SQUIRREL 1.57I and PIKA 1.16I, respectively (<http://cires.colorado.edu/jimenez-group/ToFAMSResources>). A CE of 0.5, which has been widely used in field studies with a dryer installed in front of the AMS inlet, was applied for both CP and HK measurements. The relative ionization efficiency values were 1.4 for organics, 1.2 for sulfate, 1.1 for nitrate, 4.0 for ammonium, and 1.3 for chloride (Jimenez et al., 2003).

Elemental analysis with the “Improved-Ambient” method (Canagaratna et al., 2015) was performed for high-resolution ions to obtain the oxygen-to-carbon atomic ratio (O/C), the hydrogen-to-carbon atomic ratio (H/C), and the organic matter to organic carbon ratio (OM/OC). The degree of oxygenation of organics can be reflected by the O/C ratio (Aiken et al., 2007, 2008), as well as the average carbon oxidation state ($\overline{\text{OS}}_{\text{C}}$), which can be approximated by $2 \times \text{O/C} - \text{H/C}$ (Kroll et al., 2011).

2.4.2. PMF Analysis

PMF analyses (Paatero & Tapper, 1994) for the ambient (fresh) and the Go:PAM-aged (aged) OA were conducted using the high-resolution mass spectra of organics by an improved source apportionment bilinear model of the multilinear engine (ME-2; Paatero, 1999; Canonaco et al., 2013; Zhu et al., 2018). The ME-2 approach is a constrained PMF method that applies the Source Finder analysis software (SoFi, version 6.3; Canonaco et al., 2013) based on Igor Pro (Igor WaveMetrics, Inc., Portland, OR, USA). Ions with *m/z* values of 12–115 were used as input for PMF for the CP and HK measurements. Isotopes were removed because of the excess weight given by them to the parent ions (Setyan et al., 2012; Zhang et al., 2014). The “bad” ions with a signal-to-noise ratio < 0.2 were removed from the high-resolution mass spectra data and error matrices, and the “weak” ions with signal-to-noise ratio between 0.2 and 2 were downweighted by

Table 1*Summary (Average $\pm$ Standard Deviation) of Meteorological Parameters and Air Quality Data During Subperiods in the CP and HK Measurements*

Subperiod	CP_all	CP1	CP2	CP3	HK_all ^a	HK1	HK2
Date	12–21 Jun 2016	12–14 Jun 2016	15–19 Jun 2016	20–21 Jun 2016	11–21 Oct 2016	11–17 Oct 2016	20–21 Oct 2016
Dominant wind direction	—	Southeast	Northwest	South	—	Continental (northeast)	Continental (post-Typhoon)
RH (%)	51.5 $\pm$ 17.6	66.0 $\pm$ 16.4	44.6 $\pm$ 16.3	57.0 $\pm$ 11.2	69.8 $\pm$ 16.4	70.5 $\pm$ 17.1	64.6 $\pm$ 6.7
T (°C)	25.2 $\pm$ 5.1	21.3 $\pm$ 4.3	26.0 $\pm$ 5.2	26.4 $\pm$ 3.7	25.3 $\pm$ 3.1	25.1 $\pm$ 3.2	26.7 $\pm$ 1.3
WS (m/s)	1.8 $\pm$ 1.0	1.5 $\pm$ 0.7	2.0 $\pm$ 1.1	1.6 $\pm$ 0.8	3.5 $\pm$ 1.4	3.3 $\pm$ 1.1	5.1 $\pm$ 2.1
WD (°)	167 $\pm$ 65	151 $\pm$ 61	172 $\pm$ 68	168 $\pm$ 62	230 $\pm$ 118	218 $\pm$ 119	332 $\pm$ 15
O ₃ (ppb)	49.5 $\pm$ 37.5	54.3 $\pm$ 37.4	46.1 $\pm$ 33.5	54.7 $\pm$ 46.3	44.0 $\pm$ 19.5	44.2 $\pm$ 17.6	42.5 $\pm$ 32.2
SO ₂ (ppb)	0.7 $\pm$ 0.6	0.7 $\pm$ 0.8	0.7 $\pm$ 0.5	0.7 $\pm$ 0.5	3.3 $\pm$ 1.7	2.9 $\pm$ 1.1	7.2 $\pm$ 1.0
CO (ppb) ^b	384 $\pm$ 145	420 $\pm$ 150	308 $\pm$ 69	531 $\pm$ 150	669 $\pm$ 57	658 $\pm$ 35	765 $\pm$ 103
NO _x (ppb)	18.7 $\pm$ 14.6	16.7 $\pm$ 15.3	18.2 $\pm$ 13.7	22.0 $\pm$ 16.1	3.7 $\pm$ 2.4	3.1 $\pm$ 1.4	9.0 $\pm$ 3.1
PM _{2.5} ($\mu\text{g}/\text{m}^3$)	20.9 $\pm$ 16.0	19.4 $\pm$ 11.8	15.1 $\pm$ 9.7	37.9 $\pm$ 20.3	21.4 $\pm$ 8.3	21.4 $\pm$ 8.6	21.4 $\pm$ 6.0
NR-PM ₁ ($\mu\text{g}/\text{m}^3$)	14.2 $\pm$ 9.4	16.7 $\pm$ 7.3	10.2 $\pm$ 6.5	24.5 $\pm$ 9.7	16.2 $\pm$ 5.6	16.1 $\pm$ 5.6	16.5 $\pm$ 6.3

Note. To be consistent with the Go:PAM-AMS measurements, here the average and standard deviation of all parameters only refer to periods when the Go:PAM-AMS was working. CP = Changping; HK = Hong Kong; RH = relative humidity; NR-PM₁ = nonrefractory particulate matter <1 μm ; Go:PAM-AMS = Gothenburg Potential Aerosol Mass reactor coupled with Aerosol Mass Spectrometer.

^aThere was no Go:PAM-AMS data during the noon of 17 October to the noon of 20 October due to the failure of the Go:PAM reactor. A Typhoon oriented from East China Sea occurred during 15:00 LT on 17 October to 07:00 LT on 20 October. ^bThe CO data in HK were obtained from the Tseung Kwan O air quality monitoring station, which is 2.2 km away from the Hong Kong University of Science and Technology site.

increasing their errors by a factor of 2 (Ulbrich et al., 2009). Unconstrained PMF analyses were performed first for one to eight factors separately for ambient data (fresh samples) of the two measurements then the ME-2 approach was applied for both the fresh and aged data sets. For the source apportionment of the aged OA, we constrained the primary OA (POA) factors to be exactly the same (i.e., setting α value to be 0 in SoFi) as the factor profiles resolved from the ambient measurements (i.e., the fresh data set), so as to calculate age-dependent changes in their mass concentrations according to constant factor profiles (mass spectra). Therefore, there will be little interference from possible profile variations to confuse the interpretation of mass changes (Palm et al., 2018). The optimal solutions were determined by considering the mass spectral signatures such as marker ions and the correlation with the resolved OA factors from the high-resolution AMS spectral database, their correlation of time series with external tracers, and diurnal patterns (Lanz et al., 2007; Ulbrich et al., 2009; Zhang et al., 2005, 2014).

As shown in Figures 3, S24, and S25, source apportionment of OA in CP presented three POA factors, namely, cooking-related OA (COA), biomass burning OA (BBOA), and hydrocarbon-like OA (HOA) and two oxygenated OA factors, including semivolatile oxygenated OA (SVOOA) and low-volatility oxygenated (LVOOA). The two oxygenated OA factors are used as surrogates of SOA (Jimenez et al., 2009). While in the HK measurement, three OA factors were resolved, including a POA factor related to the mixed influence from traffic and cooking emissions (HOA+COA) and two SOA factors (SVOOA and LVOOA). Details of the factor determination are shown in the supporting information (Text S3).

3. Results and Discussion

3.1. Concentration and Chemical Composition of NR-PM₁

Since the mass concentrations and proportions of NR-PM₁ species have a strong dependence on the air mass origin, it is necessary to separate different subperiods at each site for detailed comparisons. In this study, 72-hr backward trajectories were calculated every 12 hr (1600 UTC which is 0000 LT and 0400 UTC which is 1200 LT) using the National Oceanic and Atmospheric Administration's Hybrid Single-Particle Lagrangian Integrated Trajectory model (<http://www.ready.noaa.gov>) for the sampling periods in CP and HK. Results of backward trajectories are shown in Figures S19 and S20. Meteorological conditions changed significantly within both sampling periods at the CP and HK sites. Considering both the meteorological conditions and the general characteristics of NR-PM₁ speciation, we identified three and two subperiods for the CP and HK measurements, respectively. Table 1 summarizes the division of the subperiods, together with meteorological parameters and air quality data during the two observations.

Figure 1. Overview of time series of meteorological conditions, ambient gases, the total NR-PM₁ and organics, and pie charts of the five NR-PM₁ species (organics, sulfate, nitrate, ammonium, and chloride) before (labeled as “fresh”) and after (labeled as “aged”) the Gothenburg Potential Aerosol Mass oxidation in CP. Three subperiods are marked. The yellow shade areas denote the daytime. Time series of the five NR-PM₁ species are shown in Figure S21. RH = relative humidity; CP = Changping; NR-PM₁ = nonrefractory particulate matter <1 μm.

Figures 1 and 2 show the time series of meteorological conditions, ambient gases, and the total NR-PM₁ and organics before (labeled as fresh) and after (labeled as aged) the Go: PAM oxidation at the two sites. During the CP campaign, the mass concentration and chemical composition of NR-PM₁ varied significantly between the three subperiods. Although the total NR-PM₁ concentration in CP1 ($16.7 \pm 7.3 \mu\text{g}/\text{m}^3$) was lower than in CP3 ($24.5 \pm 9.7 \mu\text{g}/\text{m}^3$), the two subperiods exhibited quite similar compositional characteristics. The total secondary inorganic aerosol (SIA = sulfate + nitrate + ammonium) dominated with proportions of 55% and 57% in NR-PM₁ during CP1 and CP3, respectively. The proportion of organics was 42–44%, with an approximate 1:3 of the POA-to-SOA ratio (Figure S24). CP2 stood out with a particularly high

Figure 2. Overview of time series of meteorological conditions, ambient gases, the total NR-PM₁ and organics, and pie charts of the five NR-PM₁ species (organics, sulfate, nitrate, ammonium, and chloride) before (labeled as “fresh”) and after (labeled as “aged”) the Gothenburg Potential Aerosol Mass oxidation in HK. Two subperiods are marked. The yellow shade areas denote the daytime. Time series of the five NR-PM₁ species are shown in Figure S22. RH = relative humidity; HK = Hong Kong; NR-PM₁ = nonrefractory particulate matter <1 µm.

proportion of organics (71%), although its average NR-PM₁ concentration was the lowest ($10.2 \pm 6.5 \mu\text{g}/\text{m}^3$). In CP2, primary emission played an important role as POA reached up to 42% of total OA (Figure S24).

For the HK campaign, the total mass loadings of NR-PM₁ were similar, but the chemical composition of NR-PM₁ was quite different between the two subperiods. During the HK1 period, meteorological conditions were relatively stable and repeated daily, except for the continuous high RH during daytime on 12 October. The average NR-PM₁ concentration in HK1 was $16.1 \pm 5.6 \mu\text{g}/\text{m}^3$. OA was the most abundant component (43%), with 17% and 83% of total OA coming from POA and SOA, respectively (Figure S25). The total

SIA took up a larger proportion (57%). Thus, secondary formation (SIA + SOA) with 93% contribution is the dominant source of NR-PM₁ during this subperiod. The HK2 period was right after a Typhoon event and before a rainfall. During this period, there was an apparent drop in the atmospheric pressure (Figure S23). Although the total NR-PM₁ mass loading remained similar ($16.5 \pm 6.3 \mu\text{g}/\text{m}^3$) to HK1, changes of the meteorological conditions led to a substantial higher contribution from OA (61%), with a raised proportion of primary components (38% of POA in total OA compared to 17% during HK1, as displayed in Figure S25).

A remarkable difference between the two suburban sites lies in the nitrate proportion. Nitrate could contribute to more than 10% of NR-PM₁ on average in CP but only to 4–6% in HK. Such results agree generally with previous studies from AMS- or ACSM-based measurements in Beijing and Hong Kong (Hu et al., 2017; Lee et al., 2013; Li et al., 2015; Sun, Wang, Fu, Jiang, et al., 2013). The ion balance between the total cation (NH_4^+) and the total anions (SO_4^{2-} , NO_3^- , and Cl^-) showed slopes of 0.91 ($R^2 = 1.00$) and 0.88 ($R^2 = 0.99$) in CP and HK, respectively, indicating that ammonium sulfate is the dominant form for sulfate at both sites. Both sites could be categorized in ammonium-rich regime (Griffith et al., 2015), under which nitrate is proportional to excess $[\text{NH}_4^+]$, which is defined as the amount of ammonium in excess of that required for satisfying $[\text{NH}_4^+]/[\text{SO}_4^{2-}] = 1.5$. The excess $[\text{NH}_4^+]$ at CP was 47% higher than at HK, explaining the higher nitrate at CP. The relatively low nitrate fraction in NR-PM₁ observed in HK is also consistent with the much lower NO_x levels (Table 1) in HK and previous PM_{2.5} nitrate measurements at this site (Griffith et al., 2015; Huang et al., 2014).

3.2. Source Apportionment of OA

The OA components of the fresh and aged air at the two measurement sites were resolved through the PMF analysis by ME-2. Contributions from different OA factors imply the relative impacts of emission sources or formation processes. Difference in the relative contribution of OA factors before and after the Go:PAM oxidation process can also indicate the oxidation potential and possible formation pathways of SOA. Figure 3 shows the mass spectra of OA factors resolved through PMF analysis. Figures S24 and S25 show the correlation of time series of OA factors with external tracers for the CP and HK measurements, respectively.

In CP, source apportionment of fresh OA samples resolved three POA factors (COA, BBOA, and HOA) and two oxygenated OA factors (SVOOA and LVOOA). The two oxygenated OA factors, SVOOA and LVOOA, are used as surrogates of SOA (Jimenez et al., 2009). COA, with prominent mass fragments in m/z 41 and m/z 55 (He et al., 2010) and a distinctly higher ratio of m/z 55 to m/z 57 compared with other noncooking OA (Mohr et al., 2012; Sun et al., 2011), showed good correlation with one of the marker ions, $\text{C}_6\text{H}_{10}\text{O}^+$ ($R_p = 0.92$). This agrees with the finding of Sun et al. (2011) that COA has the most significant correlation with a few $\text{C}_x\text{H}_y\text{O}_1^+$ ions (e.g., $\text{C}_5\text{H}_8\text{O}^+$, $\text{C}_6\text{H}_{10}\text{O}^+$, and $\text{C}_7\text{H}_{12}\text{O}^+$), which could serve as marker ions for cooking emission. BBOA correlated relatively well with its marker ion $\text{C}_2\text{H}_4\text{O}_2^+$ ($R_p = 0.60$), consistent with previously reported strong association between mass fragments at m/z 60 and 73 and biomass burning emissions (Alfarra et al., 2007). HOA tracked well with NO_x ($R_p = 0.61$), indicating the traffic influence. The similar trend between SVOOA and nitrate ($R_p = 0.60$) agreed with results from previous studies, which suggested that this tight correlation stemmed from similar volatility and partitioning behavior of these two species (Crippa et al., 2014; Qin et al., 2017; Zhang et al., 2011). The highly oxidized LVOOA exhibited good correlation with sulfate with the R_p value of 0.83 because they are secondary species and mostly driven by regional production (DeCarlo et al., 2010; He et al., 2011; Sun et al., 2011; Ulbrich et al., 2009).

For CP1 and CP3, POA accounted for 23% and 25% of total OA mass, respectively, with the highest contribution coming from COA, followed by HOA. BBOA was the primary source with the lowest mass loading. For CP2, however, the proportion of POA raised up to as high as 30% in total OA, mainly caused by the dramatically increased contribution from HOA. Some episodic events with high HOA concentrations occurred, during which NO_x and CO concentrations were also high (Figure 1), indicating an obvious influence from traffic emissions. In addition, relatively low wind speeds during the episodes could lead to more efficient accumulation of pollutants.

Three OA factors were resolved for the fresh samples of the HK measurement, including a mixture of POA related to traffic and cooking emissions (HOA+COA), SVOOA, and LVOOA. In our previous campaign conducted in September 2011 at the same site in HK, the HOA factor was in a quite high oxidation state, mainly caused by the high contribution of overwhelmingly dominating m/z 44 (Li et al., 2015). This might be a

Figure 3. Mass spectra of resolved OA factors in (a) CP and (b) HK. The elemental ratios in each resolved OA factors are also shown in each mass spectra plot. Mass spectra of the primary factors (COA, BBOA, and HOA for the CP measurement or HOA+COA for the HK measurement) were constrained to be exactly the same for the ambient (“fresh”) and Gothenburg Potential Aerosol Mass-oxidized (“aged”) samples. Detailed discussion about the differences in secondary organic aerosols mass spectra in fresh versus aged samples is in Text S4. CP = Changping; HK = Hong Kong; COA = cooking-related OA; BBOA = biomass burning OA; HOA = hydrocarbon-like OA; SVOOA = semivolatile oxygenated OA; LVOOA = low-volatility oxygenated OA.

reason that HOA and COA cannot be well separated in this data set. Zhang et al. (2013) also reported that the HOA component resolved by the principal component analysis showed peaks at noon in all seasons in Beijing, more obvious in spring and summer, which may result from cooking emissions. In the HK1 period, the mass concentration of HOA+COA, a surrogate of local emissions, contributed to 18% of the total organics, while SVOOA and LVOOA constituted 55% and 28% of the total organics, respectively. In the HK2 period, higher proportions of HOA+COA (38%) and SVOOA (55%) versus substantially lower LVOOA (7%) indicated more influence from local emissions and possibly in situ production of SOA.

PMF analysis of OA after aging in Go:PAM with OH radicals was performed applying SoFi software to constrain the primary factors (COA, BBOA, and HOA for the CP measurement; HOA+COA for the HK measurement). The profiles used for constraints were set to be exactly the same (α value = 0) as those of the resolved OA factors in the fresh state (before aging), since these factors were anticipated to be consumed,

Figure 4. (a) Variations of mass fractions of NR-PM₁ components as a function of NR-PM₁ mass loadings and (b) variations of mass fractions of organic aerosol (OA) factors as a function of OA mass loadings in CP. The probability density of NR-PM₁ or OA mass concentration in each subperiod is shown as the white lines (the right axes), which sums to 100% in each subpanel. CP = Changping; NR-PM₁ = nonrefractory particulate matter <1 μm; COA = cooking-related OA; BBOA = biomass burning OA; HOA = hydrocarbon-like OA; SVOOA = semivolatile oxygenated OA; LVOOA = low-volatility oxygenated OA.

if any, but not altered in the Go:PAM reactor (Palm et al., 2018). The secondary factors were left unconstrained. Details of the aging characteristics of OA factors in the two measurements will be discussed in section 3.4.

3.3. Chemically Resolved PM Pollution

Figures 4 and 5 show variations in the mass fractions of NR-PM₁ components or OA factors as a function of total NR-PM₁ or OA mass concentrations in each subperiod of the CP and HK measurements, respectively.

Figure 5. (a) Variations of mass fractions of NR-PM₁ components as a function of NR-PM₁ mass loadings; and (b) variations of mass fractions of organic aerosol (OA) factors as a function of OA mass loadings in HK. The probability density of NR-PM₁ or OA mass concentration in each subperiod are shown as the white lines (the right axes), which sums to 100% in each subpanel. HK = Hong Kong; NR-PM₁ = nonrefractory particulate matter <1 μm; HOA = hydrocarbon-like OA; COA = cooking-related OA; SVOOA = semivolatile oxygenated OA; LVOOA = low-volatility oxygenated OA.

In CP, the fraction of inorganic species played a more significant role with increasing NR-PM₁ concentration in the CP1 and CP3 subperiods, during which the prevailing wind direction was southeast and south, respectively (Table 1). In particular, the average contribution of nitrate increased from 6–8% at NR-PM₁ <10 µg/m³ to 33–36% at NR-PM₁ >30 µg/m³ during CP1, despite that there was a low-proportion period with few data points during NR-PM₁ concentrations of 25–30 µg/m³. The average contribution of nitrate increased from ~10% at the mass loadings <20 µg/m³ to 30–32% at the total mass >50 µg/m³ during CP3. Similarly, the fraction of chloride increased by a factor of 3–4 from 0.3% to 0.9% and from 0.3% to 1.3% during CP1 and CP3, respectively. Such results are probably due to the formation of ammonium nitrate and ammonium chloride under high RH conditions in these two periods (66.0 ± 16.4% in CP1 and 57.0 ± 11.2% in CP3, compared to 44.6 ± 16.3% in CP2), which favors the partitioning of gas phase species (e.g., HNO₃, NH₃, and HCl) into the particle phase. Similar significant increases of nitrate and chloride contributions with NR-PM₁ loadings were also observed at an urban site in Beijing in summer (Sun et al., 2012). SIA and SOA accounted for 89% of the total mass during both CP1 and CP3, suggesting that the high NR-PM₁ loadings during these two subperiods were mainly caused by secondary particles. Compared with the predominant wind direction from the city center of Beijing during CP1 and CP3, the sources during CP2 were in the less urbanized areas due to the prevailing wind from northwest. Thus, locally emitted pollutants played a more important role, and the increase of organics became the dominant force for ambient PM mass enhancement in CP2. When the NR-PM₁ concentration increased from 25 to 50 µg/m³, the OA fraction increased from 70% to 90%, while the SOA fraction decreased from 30% to 10%, pointing to contributions of primary emissions to high NR-PM₁ concentration during CP2. As depicted in Figure 4b, the dramatic increase of HOA contributed the most to the high PM mass loadings, with the overwhelming proportion of >97% in OA when NR-PM₁ >40 µg/m³. The episodic heavy pollution event occurred during 22:30 on 16 June to 00:30 on 17 June (Figure S24), with HOA as high as 31.5 µg/m³. This may reflect local traffic emissions from the heavy duty vehicles that were only permitted on roads inside the city during 22:00 to 06:00 (Zhang et al., 2014). The ban of highly polluting diesel trucks during daytime is also implemented in many other Chinese megacities and thus resulted in nighttime peaks of vehicular pollutants (Zhang & Cao, 2015). For example, Qin et al. (2017) also observed an increase of HOA at night in the downwind periphery of the megacity Guangzhou, China, due to heavy duty trucks on the roads to the city center during the unregulated period (22:00–07:00). However, this is still a speculative cause due to the limited data available. In future studies, it would be very helpful to include VOC measurements, which can be used to link SOA formation potential with the precursors responsible.

The mass loading-dependent aerosol composition is quite different in HK. The NR-PM₁ species maintained a relatively stable composition across different mass concentration levels during the HK1 period (Figure 5a). Organics, sulfate, nitrate, ammonium, and chloride accounted for 36–48%, 35–43%, 3–4%, 13–16%, and 0.1–0.3% of the total NR-PM₁ mass, respectively. In the HK2 period, however, organics showed an increasing trend with increased total mass (e.g., from ~50% at low mass levels to ~70% at high mass levels). In the low NR-PM₁ range, HOA+COA contributed to 41–55% of the total OA, while this fraction dropped to 20–27% at NR-PM₁ mass loadings higher than 13 µg/m³ (Figure 5b). Instead, the SVOOA fraction increased sharply, indicating that the high PM period in HK2 was dominated by less oxidized secondary organic components.

3.4. Enhancement of NR-PM₁ Species by Go:PAM-Oxidation

Oxidation processes in the Go:PAM reactor enable observations of the aerosol aging potential, which refers to the potential of the secondary aerosol formation from ambient aerosols due to oxidation. Figure 6a and Table S6 show the absolute mass concentration increments of five NR-PM₁ species (organics, sulfate, nitrate, ammonium, and chloride) after the oxidation and the aged/fresh mass ratios (except for the ratio of chloride which had very low mass concentrations). Aging in the Go:PAM reactor showed nearly no influence on sulfate concentration (aged/fresh ratio = 0.9–1.1). The maximum concentrations of SO₂, the precursor of secondary particulate sulfate, were less than 10 ppb for both CP (range = 0.05–2.6 ppb; mean = 0.7 ± 0.6 ppb) and HK (range = 1.0–9.0 ppb; mean = 3.3 ± 1.7 ppb) sites. Kinetic model results (Text S1.2) indicated that around 30–40% of the SO₂ introduced to the Go:PAM system was reacted, resulting in a theoretical maximum aged/fresh mass ratio of sulfate of 1.6 for both CP and HK. The discrepancy between this maximum ratios and those observed in the measurements might be due to combined effects of (a) possible competition

Figure 6. Mass changes after the Gothenburg Potential Aerosol Mass oxidation in CP and HK. (a) Mass concentration of the “fresh” and “aged” nonrefractory particulate matter $<1 \mu\text{m}$ species. The aged/fresh mass ratios of organics, sulfate, nitrate, and ammonium were also marked. (b) Mass increment of secondary organic aerosols components (SVOOA and LVOOA). CP = Changping; HK = Hong Kong; SVOOA = semivolatile oxygenated OA; LVOOA = low-volatility oxygenated OA.

from the external OH reactivity by other VOCs than those considered in the model, (b) possible loss of sulfuric acid to walls of the Go:PAM and/or tubing, or (c) measurement uncertainties. This suggests that formation of new sulfate from OH-exposure aging may not be properly characterized in the current Go:PAM setting. Caution should be exercised in using the Go:PAM to gauge aging potential associated with new sulfate formation. Substantial growths of nitrate concentration, however, were observed at both sites (aged/fresh ratio = 1.2–1.7 and 1.2–2.2 for CP and HK, respectively), especially for the HK2 period ($1.1 \mu\text{g}/\text{m}^3$ mass increase with an aged/fresh ratio of 2.2). Ammonium showed moderate increments with aged/fresh ratios of 1.3 and 1.1 for CP and HK, respectively, likely due to increased nitrate.

At both sites, organics contributed the most (78–98%) to the increase of total NR-PM₁ mass after OH oxidation in the Go:PAM, highlighting the importance of further studies of SOA formation. The occasional higher mass concentrations of some POA factors (COA and BBOA) after the Go:PAM than those in the ambient air at the CP site could be due to the effects of decreased concentrations during the time span in the ambient-Go:PAM cycle, which was the 45-min ambient interval (fresh) + 45-min Go:PAM oxidized interval (aged). An alternative explanation could be uncertainties in the source apportionment analysis, which include the measurement uncertainty and the model uncertainty. The details of uncertainty analysis are described in Text S3.3. Figure 6b and Table S7 show mass increments of the two secondary OA factors (SVOOA and LVOOA) at each site. In CP, aging in Go:PAM led to a mass increment of $2.7 \mu\text{g}/\text{m}^3$ (or 25% of total OA increment) for the more oxidized LVOOA, while the mass gain for the less oxidized SOA factor, SVOOA, was more than 3 times ($7.5 \mu\text{g}/\text{m}^3$ or 68%) that of LVOOA. When separated into subperiods, the oxidation brought much more increase of SVOOA ($9.7 \mu\text{g}/\text{m}^3$) compared to that of LVOOA ($2.1 \mu\text{g}/\text{m}^3$) during CP2. This observation could be explained by the fact that the ambient air in this subperiod was more affected by local primary emissions, especially HOA (see section 3.3 above). The Go:PAM aging in HK caused a mass decrease in its POA factor (-0.4 and $-1.9 \mu\text{g}/\text{m}^3$ for HK1 and HK2, respectively). Different from that in CP, the mass increase of SOA in HK was generally dominated by contribution from LVOOA ($2.6 \mu\text{g}/\text{m}^3$ or 93% of total OA increment), and SVOOA accounted for a relatively small part ($0.8 \mu\text{g}/\text{m}^3$ or 29%). But the two subperiods showed quite different features: HK1 had nearly no change in the SVOOA amount, while LVOOA increased substantially; on the contrary, in HK2, most of the POA loss was compensated by the gain of SVOOA, indicating a conversion from POA to SVOOA. Comparing the overall degree of oxygenation between the two suburban sites (Table 2), OA in CP was less aged, with higher aging potentials. Although the average ambient O₃ concentration level in CP (49.5 ppb) was slightly higher than that in HK (44.0 ppb), more local emissions under a relatively low wind speed condition might facilitate the formation of “fresher” SOA with larger mass enhancements after aging in the Go:PAM in CP. The enhanced CO (ΔCO), which is defined as the observed CO concentration minus its background concentration, can help

Table 2

Summary of Average Elemental Ratios and Slopes in the Van Krevelen Diagrams at the CP and HK Sites, As Well As Previous Field Observations at Urban and Suburban Sites in China

Site (type)	Sampling period (season)	O/C	H/C	$\overline{OS}_C$	Slope	Intercept	R^2	Reference
CP_fresh, Beijing (suburban, NCP)	Jun 2016 (summer)	0.52	1.64	−0.61	−0.73	2.02	0.84	This study
CP_aged, Beijing (suburban, NCP)		0.55	1.67	−0.57	−0.63	2.02	0.78	
HK_fresh, Hong Kong (suburban, PRD)	Oct 2016 (autumn)	0.68	1.57	−0.21	−0.59	1.98	0.84	
HK_aged, Hong Kong (suburban, PRD)		0.83	1.51	0.15	−0.60	2.00	0.92	
Beijing (urban, NCP)	Mar–May 2012 (spring)	0.49	1.63	−0.64	−0.57	1.91	0.74	Hu et al. (2017)
	Jul–Aug 2012 (summer)	0.53	1.61	−0.54	−0.62	1.94	0.79	
	Oct–Nov 2012 (autumn)	0.46	1.58	−0.66	−0.67	1.90	0.70	
	Jan–Mar 2013 (winter)	0.47	1.52	−0.58	−0.08	1.56	0.02	
Hong Kong ^a (suburban, PRD)	Apr–Jun 2011 (spring)	0.48	1.50	−0.54	−0.96	1.96	—	Li et al. (2015)
	Sep 2011 (summer)	0.66	1.51	−0.19	−0.74	2.00	—	
	Oct–Dec 2011 (autumn)	0.53	1.54	−0.48	−0.77	1.95	—	
	Jan–Mar 2012 (winter)	0.55	1.55	−0.45	−0.74	1.95	—	
Hong Kong (urban roadside, PRD)	Mar–Jul 2013	0.29	1.84	−1.26	−0.70	1.85	0.86	Lee et al. (2015)
	(spring and summer)							
Panyu (suburban, PRD)	Nov–Dec (winter)	0.53	1.64	−0.58	—	—	—	Qin et al. (2017)
Ziyang (suburban, southwestern China)	Dec 2012–Jan 2013 (winter)	0.65	1.56	−0.26	−0.44	1.84	0.70	Hu, Hu, Hu, Niu, et al. (2016)
Changdao ^a (receptor, central eastern China)	Mar–Apr 2011 (spring)	0.75	1.48	0.02	−0.55	1.89	0.76	Hu et al. (2013)

Note. The elemental ratios are obtained by the “Improved-Ambient” method (Canagaratna et al., 2015). CP = Changping; HK = Hong Kong; NCP = North China Plain; PRD = Pearl River Delta.

^aThe elemental ratios were obtained using the “Aiken-Ambient” method (Aiken et al., 2007). Improved-Ambient elemental ratios were estimated by scaling up Aiken-Ambient O/C, and H/C ratios by 27% and 11% (the empirical corrections for ambient OA; Canagaratna et al., 2015), respectively. The $\overline{OS}_C$, slope, and intercept were calculated after scaling the O/C and H/C ratios.

reduce the dilution effect (Hayes et al., 2013; Ortega et al., 2016; Saha et al., 2018). ΔCO was used to normalize the OA enhancement concentrations in the CP and HK measurements. Based on the time series of CO during the campaigns, the background CO concentration (using the lowest 5% concentration to avoid influence from extreme values) was on average ~ 224 and ~ 513 ppb in CP and HK, respectively. The campaign average ΔCO concentration was estimated to be 174 and 156 ppb in CP and HK, respectively. Consequently, the dilution-corrected SOA enhancement ($\Delta SOA/\Delta CO$) in CP ($0.059 \mu g/(m^3 \text{ ppb})$) were still significantly higher than that in HK ($0.022 \mu g/(m^3 \text{ ppb})$), consistent with the previous conclusion that more SOA was formed in CP than HK.

The van Krevelen (VK) diagram of H/C against O/C is often used to illustrate the dynamic evolution and functional group alteration of OA (Heald et al., 2010). As shown in Figure 7, H/C and O/C ratios of ambient OA in both CP and HK showed good anticorrelations, with slopes of -0.73 ($R^2 = 0.84$) and -0.59 ($R^2 = 0.84$) and intercepts of 2.02 and 1.98, respectively. The slopes in the VK diagram illustrate organic atmospheric functionalization reactions. For example, a slope of -1 implies the simultaneous addition of a carbonyl group ($-C(=O)-$) and an alcohol group ($-OH$), forming a carboxylic acid without fragmentation or alcohol and carbonyl on different carbons, while the slope of -0.5 indicates the formation of carboxylic acid together with fragmentation (Heald et al., 2010; Ng et al., 2011). The data from measurements in CP and HK exhibited influence from two processes, but the latter process appeared to be more dominant at the HK site. After the Go:PAM oxidation process, the slope in CP apparently shallowed to -0.63 ($R^2 = 0.78$) with an intercept of 2.02, reflecting a change in the aging mechanism, shifting toward greater impact of carboxylic group addition combined with fragmentation, while no obvious change was found in HK (slope = -0.60 , intercept = 2.00, $R^2 = 0.92$). Such difference reveals that aging processes at the CP site had more significant changes to the degree of oxygenation for OA. The gap of the slopes between the two studied sites narrowed, indicating that aging of ambient OA led to convergent oxygenation of organics at both sites, although oxidation mechanisms or dominating precursors might differ. Variations in relative positions of OA factors between the fresh and aged OA can further indicate the aging mechanisms. In CP, the Go:PAM oxidation led to a significant shift of SVOOA toward the upper right in the VK diagram, while LVOOA hardly moved. This signifies a major change in the freshly formed SOA components in CP. On the contrary, LVOOA exhibited a more prominent change compared to SVOOA in HK, indicative of a dominating role of oxidation of OA that was already quite aged or perhaps more heterogeneous oxidations of OA in HK due to the higher

Figure 7. The van Krevelen diagram of aerosols before (labeled as “fresh”) and after (labeled as “aged”) the Gothenburg Potential Aerosol Mass oxidation during CP and HK measurements. The PMF-resolved OA factors are marked as circles (CP) and triangles (HK) in the diagram. The moving directions of SOA factors (SVOOA and LVOOA) from fresh to aged samples are shown by the arrows. The blue and red dashed lines represent the left and right boundaries of the Sally Triangle (Ng et al., 2011). CP = Changping; HK = Hong Kong; HOA = hydrocarbon-like OA; COA = cooking-related OA; BBOA = biomass burning OA; SVOOA = semivolatile oxygenated OA; LVOOA = low-volatility oxygenated OA.

RH. Note that the position for POA factors did not change in the VK diagram because their mass spectral profiles were constrained during the ME-2 runs.

The average carbon oxidation states ($\overline{OS}_C$) in CP and HK are listed in Table 2 and shown in Figure 7. In CP, $\overline{OS}_C$ of the fresh and aged OA were -0.61 ± 0.34 and -0.57 ± 0.19 , respectively. $\overline{OS}_C$ of ambient OA in CP, Beijing, is comparable to previous observations at another site in Beijing, where the values were in the range of -0.66 to -0.54 (Hu et al., 2017). $\overline{OS}_C$ estimated in HK were much higher, with an average of -0.21 ± 0.24 and 0.15 ± 0.30 for the fresh and aged OA, respectively. The high O/C ratio (0.68) and $\overline{OS}_C$ of ambient OA resembled those observed by Li et al. (2015) at the same site in September 2011 (O/C = 0.66; $\overline{OS}_C = -0.19$). A comparable high oxidation state of ambient OA was also found in a suburban site in the southwestern China, Ziyang, with a value of -0.26 (Hu, Hu, Hu, Niu, et al., 2016). However, the oxidation state of OA in HK was lower than that observed in the Changdao island (O/C = 0.75; $\overline{OS}_C = -0.02$), an offshore receptor site which is located downwind of major pollution sources from central eastern China (Hu et al., 2013). Besides elemental analysis of bulk OA, the higher oxidation state of aerosols in HK is also reflected by the higher O/C ratios in the PMF-resolved OA factors (Figure 7). In HK, the O/C ratio of the POA factor (HOA+COA) was 0.21, which is much higher than that of the HOA factor (0.05) in CP and very close to O/C of its COA factor (0.22). The O/C ratios of the SVOOA (0.75) and LVOOA (1.04) factors in HK were substantially higher than those observed in CP (SVOOA = 0.48, LVOOA = 0.79) and higher than those in another urban peripheral site, Panyu, in the PRD region (SVOOA = 0.69, LVOOA = 0.92; Qin et al., 2017). Differences in both representations of the degree of oxidation ($\overline{OS}_C$ and O/C) at the two suburban sites reflect that the air masses in CP had comparatively higher oxidation potential, while aerosols at the coastal

Figure 8. Time series of meteorological conditions, gases, NR-PM₁ species, and mass fraction of OA factors during the two case periods in the HK campaign: HK_a (left) and HK_b (right). RH = relative humidity; OA = organic aerosol; NR-PM₁ = nonrefractory particulate matter <1 μm; HOA = hydrocarbon-like OA; COA = cooking-related OA; SVOOA = semivolatile oxygenated OA; LVOOA = low-volatility oxygenated OA; HK = Hong Kong.

HK site were already more aged, possibly due to the strong impacts from long-range transportation. Such results are consistent with previous studies conducted at the same HK site in that the diurnal pattern of the degree of oxygenation varied little in autumn when the air masses originated from the continent with long-range transport (Li et al., 2015).

3.5. Case Study of SOA Formation by Go:PAM-Oxidation

To further investigate the difference in oxidation mechanisms of NR-PM₁ components, especially OA factors, two pairs of typical periods in HK and CP were chosen for case studies (Figures 8 and S27). In HK, the periods from the late afternoon to the early morning (17:00–04:00) on 13–14 October (HK_a) and 20–21 October (HK_b) had comparable NR-PM₁ mass concentrations with an average of 16.4 μg/m³, while HK_a differed from HK_b by a much higher proportion of secondary species (SOA+SIA, 94.9% compared with 76.4%). After Go:PAM aging, HK_a gained a mass increment of 4.3 μg/m³, with 1.6 and 2.7 μg/m³ from the inorganic and organic components, respectively. Although the increment from inorganics in HK_a was the same as that in HK_b, a much higher total mass gain was observed in the latter case because of the prominent mass increase from organics (7.9 μg/m³). Among different OA factors, increment from the more oxidized LVOOA (5.3 μg/m³) dominated in HK_a, while the less oxidized SVOOA (6.1 μg/m³) contributed to the largest mass increment in HK_b. Such differences can be explained by the distinct precursor gases and oxidants in ambient air in the two cases. During the first case (HK_a), the wind mainly came from the east, bringing relatively clean coastal air masses. Thus, gas phase pollutants such as CO, SO₂, NO_x, and VOCs all showed relatively low concentrations (Table S8). LVOOA showed an increase of correlation with the oxidants (here represented by odd oxygen, O_x = O₃ + NO₂) from the fresh to aged samples with

R_p values of 0.50 and 0.71, respectively (Table S9). The second case (HK_b) experienced predominantly north-northwesterly winds from inland areas with more anthropogenic emissions, bringing about higher levels of gaseous pollutants (Table S8) and POA (HOA+COA), as well as SVOOA after Go:PAM aging. For example, CO (770 ppb) correlated well with both HOA+COA and SVOOA ($R_p = 0.68$ and 0.81 , respectively) in the fresh sample, and such correlations became stronger in the aged sample ($R_p = 0.72$ and 0.96 , respectively). In the fresh sample, high correlations were observed between NO_x (9.7 ppb) and HOA+COA ($R_p = 0.90$), but NO_x showed nearly no correlation with SVOOA factor ($R_p = 0.07$), while SVOOA enhancement in the Go:PAM oxidation condition (aged SVOOA – fresh SVOOA) was strongly associated with NO_x ($R_p = 0.87$). The same was true for VOC precursors such as toluene and benzene ($R_p = 0.88$ and 0.60 , respectively). Liu et al. (2018) also observed positive correlations between OA enhancement and gaseous pollutants, such as CO, NO_x , and toluene ($R^2 = 0.66$, 0.41 , and 0.57 , respectively) in the field experiment on the SOA formation in Beijing urban ambient air. On the contrary, the O_x level in HK_b was much lower (46.7 ppb) than that in HK_a (70.1 ppb). Although O_x showed a good correlation with the fresh SVOOA ($R_p = 0.98$, Table S10), its insufficient amount limited further formation of the more oxygenated LVOOA. The above analysis reveals that the relative abundance of both precursor gases and oxidants can strongly affect the aging potential of OA, both for mass increment and chemical composition.

Similarly, we identified two cases during the CP campaign, namely, CP_a (21:00–07:00 on 18–19 June) and CP_b (21:00–07:00 on 20–21 June), respectively, with comparable fresh NR-PM₁ mass loadings (CP_a = $18.8 \mu\text{g}/\text{m}^3$ and CP_b = $20.1 \mu\text{g}/\text{m}^3$) but very different mass increments (CP_a = $13.9 \mu\text{g}/\text{m}^3$ and CP_b = $6.3 \mu\text{g}/\text{m}^3$) after Go:PAM aging (Figure S27 and Tables S11–S13). Although both case periods experienced winds mainly from the southeast, their chemical composition was different as CP_a showed a lower proportion of secondary species (83.4%) compared to CP_b (88.5%). The mass increment after the Go:PAM processing reached up to $13.9 \mu\text{g}/\text{m}^3$ in CP_a, with organics and inorganics contributing to 13.2 and $0.7 \mu\text{g}/\text{m}^3$, respectively. However, with a slightly higher initial total mass, CP_b showed much lower mass gain ($6.3 \mu\text{g}/\text{m}^3$), mainly due to a much less mass increment for OA ($5.1 \mu\text{g}/\text{m}^3$) compared to CP_a. This observation is in line with that in HK, suggesting that aerosols with larger proportions of primary components would show higher aging potential under the same oxidation process in the Go:PAM. Such phenomenon can be explained partly by the level of gaseous pollutants: more NO_x and SO_2 in CP_a may indicate a strong influence from primary anthropogenic emissions. Without direct VOC data during the Go:PAM-AMS experiment in CP, we could not investigate the correlations between OA changes in NR-PM₁ and VOC precursors. Yet the good correlation between the POA or SVOOA and VOCs in HK hint there is a linkage between OA aging and VOC precursors. Comparing the pairs of cases in CP and HK, there is a worth-noting difference: SVOOA contributed to the largest fraction of the OA mass increment in both CP cases (Table S11) and generally in the whole sampling period (Figure 6), while in HK, the formation of LVOOA played a more significant role. This difference suggests that although both suburban sites can be considered as receptor sites, OA arriving at the HK site was already more aged and further aging in the Go:PAM led to highly oxidized LVOOA, as opposed to the fresher OA at the CP site that mainly led to less oxidized SVOOA even after aging. Wang et al. (2018) reported the average concentrations of 0.30 and 0.44 ppbv for isoprene and benzene, respectively, in CP in the same period of time as our measurements (summer 2016) but not on the days of our measurements. These VOC concentrations were much higher than those in our HK measurements (isoprene = 0.16 ppbv, benzene = 0.28 ppbv), which further supports the suggestion that the higher aerosol aging potential in CP was due to more local precursor emissions.

4. Conclusions

Besides the primary emission control, effective intervention on mitigating the secondary particulate matter pollution formed from oxidation is also an important issue in suburban regions. Comparative characterization of the aging potential of submicron nonrefractory aerosols (NR-PM₁) was carried out for the first time in two suburban environments in northern and southern China (Changping District in Beijing, and Hong Kong), using a Potential Aerosol Mass reactor (Go:PAM) and HR-ToF-AMS. The ambient NR-PM₁ mass concentrations in the three subperiods in CP varied from 10.2 to $24.5 \mu\text{g}/\text{m}^3$, with an average of $14.2 \pm 9.4 \mu\text{g}/\text{m}^3$, while the NR-PM₁ level in the two subperiods in HK was similar (16.1 – $16.5 \mu\text{g}/\text{m}^3$), with an average of $16.2 \pm 5.6 \mu\text{g}/\text{m}^3$. Organics dominated at both sites, accounting for 42–71% and 43–61% of NR-

PM₁ mass in CP and HK, respectively. Source apportionment of OA with ME-2 resolved three primary factors (COA, BBOA, and HOA), and two secondary factors (SVOOA and LVOOA) during the CP measurement, while for HK, there was one primary factor that represented the mixed influence from traffic and cooking emissions (HOA+COA) and two secondary factors (SVOOA and LVOOA). Secondary OA (SOA) factors were found to dominate at the two suburban sites, representing 58–77% of the total OA in CP and 62–83% in HK. The Go:PAM reactor, connected before the HR-ToF-AMS, provided cyclic periods of high concentration of OH radicals to generate controlled oxidation environments, which enabled the investigation of changes in mass concentration and chemical composition between the ambient (fresh) and Go:PAM-oxidized (aged) aerosols at the two sites. The Go:PAM oxidation processes led to a total mass increment of 7.8–13.1 $\mu\text{g}/\text{m}^3$ with an average of 12.6 $\mu\text{g}/\text{m}^3$ in the three subperiods in CP and 2.5–9.9 $\mu\text{g}/\text{m}^3$ with an average of 3.3 $\mu\text{g}/\text{m}^3$ in the two subperiods in HK. OA increase dominated the total NR-PM₁ mass increment (78–98%) at both sites, while nitrate contributed the most (7–9%) among the inorganic components. Generally, higher increase of SVOOA (7.5 $\mu\text{g}/\text{m}^3$) than LVOOA (2.7 $\mu\text{g}/\text{m}^3$) was observed in CP after Go:PAM aging, while the reverse was true in HK (0.8 $\mu\text{g}/\text{m}^3$ for SVOOA and 2.6 $\mu\text{g}/\text{m}^3$ for LVOOA). Variations in relative positions of the bulk OA and PMF-resolved OA factors in the VK diagram between the fresh and aged samples indicated different oxidation mechanisms of organics between the two sites. An obvious shift of SVOOA toward the upper right in the VK plot occurred for CP data, signifying a major change in the freshly formed SOA, while in HK, LVOOA exhibited a more prominent change compared to SVOOA, indicative of a dominating role of oxidation of the more aged OA. Elemental analysis further reflected that air masses in HK were in a comparatively high oxidation state, possibly because the HK site is a receptor site with most pollutants being transported from other regions. Two pairs of case studies at the two sites demonstrated the important roles of ambient precursor gases and oxidant levels for the aerosol aging potentials.

The comparative measurements reveal different potentials of secondary aerosol formation via OH oxidation and clarify the distinct aging characteristics of OA in suburban environments in northern and southern China. Under the relatively constant OH exposure, ambient aerosols in the suburb of Beijing (CP) showed higher oxidation potentials and the SOA enhancement was largely contributed by the oxidation of POA and the relatively high concentration of VOC precursors. On the contrary, the SOA formation in Hong Kong showed higher sensitivity to POA or less oxygenated SOA (SVOOA). Accordingly, secondary OA in suburban Beijing may be moderated by reducing the more controllable local emissions including VOCs and cooking- and traffic-related POA, while secondary pollution abatement of suburbs in Hong Kong should be achieved through joint pollution prevention and control in larger surrounding areas.

This study methodologically demonstrates how the combination of an OFR with AMS can be used to provide information on key factors and mechanisms that influence secondary aerosol formation. In this study, we focused on the oxidation range of the maximum secondary mass enhancement under ambient temperature and RH conditions. As a result, certain temporal information of the oxidation process could not be obtained, such as the changes of the aerosol aging potential and influence from the gas phase and heterogeneous oxidations with various oxidation levels. In the future, it is important to vary the OH exposure over a wider range and control the temperature and/or RH to investigate how the aerosol mass changes as a function of equivalent days of atmospheric oxidation and under different ambient conditions.

Acknowledgments

The work was carried out under the bilateral Sweden-China framework research program on “Photochemical Smog in China: formation, transformation, impact, and abatement strategies” financed by the Swedish Research Council (639-2013-6917). We thank Hong Kong University Grant Council Special Equipment Grant (SEG HKUST07) and the Environment and Conservation Fund/Woo Wheelock Green Fund (ECWW09EG04) for providing much of the instrumentation at the HKUST Air Quality Supersite facility. Y. J. Li acknowledges funding support from the National Natural Science Foundation of China (41675120) and Macau Science and Technology Development Fund (016/2017/A1). M. Hu acknowledges funding support from the National Key Research and Development Program of China (2016YFC0202000: Task 3). Chemical composition data are provided as a.csv file in the supporting information section.

References

- Aiken, A. C., DeCarlo, P. F., & Jimenez, J. L. (2007). Elemental analysis of organic species with electron ionization high-resolution mass spectrometry. *Analytical Chemistry*, 79(21), 8350–8358. <https://doi.org/10.1021/ac071150w>
- Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., et al. (2008). O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environmental Science & Technology*, 42(12), 4478–4485. <https://doi.org/10.1021/es703009q>
- Alfarra, M. R., Prevot, A. S., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V. A., et al. (2007). Identification of the mass spectral signature of organic aerosols from wood burning emissions. *Environmental Science & Technology*, 41(16), 5770–5777. <https://doi.org/10.1021/es062289b>
- Breton, M. L., Wang, Y., Hallquist, Å. M., Pathak, R. K., Zheng, J., Yang, Y., et al. (2018). Online gas-and particle-phase measurements of organosulfates, organosulfonates and nitrooxy organosulfates in Beijing utilizing a FIGAERO ToF-CIMS. *Atmospheric Chemistry and Physics*, 18(14), 10,355–10,371. <https://doi.org/10.5194/acp-18-10355-2018>
- Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., et al. (2015). Elemental ratio measurements of organic compounds using aerosol mass spectrometry: Characterization, improved calibration, and implications. *Atmospheric Chemistry and Physics*, 15(1), 253–272. <https://doi.org/10.5194/acp-15-253-2015>

- Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., & Prévôt, A. S. H. (2013). SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data. *Atmospheric Measurement Techniques*, 6(12), 3649–3661. <https://doi.org/10.5194/amt-6-3649-2013>
- Carmichael, G. R., Adhikary, B., Kulkarni, S., D'Allura, A., Tang, Y., Streets, D., et al. (2009). Asian aerosols: Current and year 2030 distributions and implications to human health and regional climate change. *Environmental Science & Technology*, 43(15), 5811–5817. <https://doi.org/10.1021/es8036803>
- Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J. D., Carbone, S., et al. (2014). Organic aerosol components derived from 25 AMS data sets across Europe using a consistent ME-2 based source apportionment approach. *Atmospheric Chemistry and Physics*, 14(12), 6159–6176. <https://doi.org/10.5194/acp-14-6159-2014>
- DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., et al. (2006). Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Analytical Chemistry*, 78(24), 8281–8289. <https://doi.org/10.1021/ac061249n>
- DeCarlo, P. F., Ulbrich, I. M., Crounse, J., Foy, B. D., Dunlea, E. J., Aiken, A. C., et al. (2010). Investigation of the sources and processing of organic aerosol over the Central Mexican Plateau from aircraft measurements during MILAGRO. *Atmospheric Chemistry and Physics*, 10(12), 5257–5280. <https://doi.org/10.5194/acp-10-5257-2010>
- Donahue, N. M., Chuang, W., Epstein, S. A., Kroll, J. H., Worsnop, D. R., Robinson, A. L., et al. (2013). Why do organic aerosols exist? Understanding aerosol lifetimes using the two-dimensional volatility basis set. *Environmental Chemistry*, 10(3), 151–157. <https://doi.org/doi:10.1071/En13022>
- Drewnick, F., Hings, S. S., DeCarlo, P., Jayne, J. T., Gonin, M., Fuhrer, K., et al. (2005). A new time-of-flight aerosol mass spectrometer (TOF-AMS)—Instrument description and first field deployment. *Aerosol Science and Technology*, 39(7), 637–658. <https://doi.org/10.1080/02786820500182040>
- Griffith, S. M., Huang, X. H., Louie, P. K. K., & Yu, J. Z. (2015). Characterizing the thermodynamic and chemical composition factors controlling PM_{2.5} nitrate: Insights gained from two years of online measurements in Hong Kong. *Atmospheric Environment*, 122, 864–875. <https://doi.org/10.1016/j.atmosenv.2015.02.009>
- Hallquist, M., Munthe, J., Hu, M., Wang, T., Chan, C. K., Gao, J., et al. (2016). Photochemical smog in China: Scientific challenges and implications for air-quality policies. *National Science Review*, 3(4), 401–403. <https://doi.org/10.1093/nsr/nww080>
- Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., et al. (2013). Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign. *Journal of Geophysical Research: Atmospheres*, 118, 9233–9257. <https://doi.org/10.1002/jgrd.50530>
- He, L. Y., Huang, X. F., Xue, L., Hu, M., Lin, Y., Zheng, J., et al. (2011). Submicron aerosol analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China using high-resolution aerosol mass spectrometry. *Journal of Geophysical Research*, 116, D12304. <https://doi.org/10.1029/2010JD014566>
- He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., et al. (2010). Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning. *Atmospheric Chemistry and Physics*, 10(23), 11,535–11,543. <https://doi.org/10.5194/acp-10-11535-2010>
- Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., et al. (2010). A simplified description of the evolution of organic aerosol composition in the atmosphere. *Geophysical Research Letters*, 37, L08803. <https://doi.org/10.1029/2010GL042737>
- Hu, W., Hu, M., Hu, W., Jimenez, J. L., Yuan, B., Chen, W., et al. (2016). Chemical composition, sources, and aging process of submicron aerosols in Beijing: Contrast between summer and winter. *Journal of Geophysical Research: Atmospheres*, 121, 1955–1977. <https://doi.org/10.1002/2015JD024020>
- Hu, W., Hu, M., Hu, W. W., Niu, H., Zheng, J., Wu, Y., et al. (2016). Characterization of submicron aerosols influenced by biomass burning at a site in the Sichuan Basin, southwestern China. *Atmospheric Chemistry and Physics*, 16(20), 13,213–13,230. <https://doi.org/10.5194/acp-16-13213-2016>
- Hu, W., Hu, M., Hu, W. W., Zheng, J., Chen, C., Wu, Y., & Guo, S. (2017). Seasonal variations in high time-resolved chemical compositions, sources, and evolution of atmospheric submicron aerosols in the megacity Beijing. *Atmospheric Chemistry and Physics*, 17(16), 9979–10,000. <https://doi.org/10.5194/acp-17-9979-2017>
- Hu, W. W., Hu, M., Yuan, B., Jimenez, J. L., Tang, Q., Peng, J. F., et al. (2013). Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of central eastern China. *Atmospheric Chemistry and Physics Discussions*, 13(19), 10,095–10,112. <https://doi.org/10.5194/acp-13-10095-2013>
- Huang, X. H., Bian, Q. J., Ng, W. M., Louie, P. K., & Yu, J. Z. (2014). Characterization of PM_{2.5} major components and source investigation in suburban Hong Kong: A one year monitoring study. *Aerosol and Air Quality Research*, 14(1), 237–250. <https://doi.org/10.4209/aaqr.2013.01.0020>
- Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., & Worsnop, D. R. (2000). Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Science & Technology*, 33(1-2), 49–70. <https://doi.org/10.1080/027868200410840>
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prévôt, A. S. H., Zhang, Q., Kroll, J. H., et al. (2009). Evolution of organic aerosols in the atmosphere. *Science*, 326(5959), 1525–1529. <https://doi.org/10.1126/science.1180353>
- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., et al. (2003). Ambient aerosol sampling using the aerodyne aerosol mass spectrometer. *Journal of Geophysical Research*, 108(D7), 8425. <https://doi.org/10.1029/2001JD001213>
- Kang, E., Root, M. J., Toohey, D. W., & Brune, W. H. (2007). Introducing the concept of potential aerosol mass (PAM). *Atmospheric Chemistry and Physics*, 7(22), 5727–5744. <https://doi.org/10.5194/acp-7-5727-2007>
- Knote, C., Hodzic, A., & Jimenez, J. L. (2015). The effect of dry and wet deposition of condensable vapors on secondary organic aerosol concentrations over the continental US. *Atmospheric Chemistry and Physics*, 15(1), 1–18. <https://doi.org/10.5194/acp-15-1-2015>
- Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., et al. (2011). Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nature Chemistry*, 3(2), 133–139. <https://doi.org/10.1038/NCHEM.948>
- Lambe, A. T., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., et al. (2011). Characterization of aerosol photo-oxidation flow reactors: Heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements. *Atmospheric Measurement Techniques*, 4(3), 445–461. <https://doi.org/10.5194/amt-4-445-2011>
- Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., & Prévôt, A. S. H. (2007). Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra. *Atmospheric Chemistry and Physics*, 7(6), 1503–1522. <https://doi.org/10.5194/acp-7-1503-2007>

- Lee, B. P., Li, Y. J., Yu, J. Z., Louie, P. K., & Chan, C. K. (2013). Physical and chemical characterization of ambient aerosol by HR-ToF-AMS at a suburban site in Hong Kong during springtime 2011. *Journal of Geophysical Research: Atmospheres*, 118, 8625–8639. <https://doi.org/10.1002/jgrd.50658>
- Lee, B. P., Li, Y. J., Yu, J. Z., Louie, P. K., & Chan, C. K. (2015). Characteristics of submicron particulate matter at the urban roadside in downtown Hong Kong—Overview of 4 months of continuous high-resolution aerosol mass spectrometer measurements. *Journal of Geophysical Research: Atmospheres*, 120, 7040–7058. <https://doi.org/10.1002/2015JD023311>
- Li, Y. J., Lee, B. P., Su, L., Fung, J. C. H., & Chan, C. K. (2015). Seasonal characteristics of fine particulate matter (PM) based on high-resolution time-of-flight aerosol mass spectrometric (HR-ToF-AMS) measurements at the HKUST Supersite in Hong Kong. *Atmospheric Chemistry and Physics*, 15(1), 37–53. <https://doi.org/10.5194/acp-15-37-2015>
- Li, Y. J., Lee, B. Y. L., Yu, J. Z., Ng, N. L., & Chan, C. K. (2013). Evaluating the degree of oxygenation of organic aerosol during foggy and hazy days in Hong Kong using high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS). *Atmospheric Chemistry and Physics*, 13(17), 8739–8753. <https://doi.org/10.5194/acp-13-8739-2013>
- Li, Y. J., Sun, Y., Zhang, Q., Li, X., Li, M., Zhou, Z., & Chan, C. K. (2017). Real-time chemical characterization of atmospheric particulate matter in China: A review. *Atmospheric Environment*, 158, 270–304. <https://doi.org/10.1016/j.atmosenv.2017.02.027>
- Lim, S. S., Vos, T., Flaxman, A. D., Danaei, G., Shibuya, K., Adair-Rohani, H., et al. (2012). A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: A systematic analysis for the Global Burden of Disease Study 2010. *The Lancet*, 380(9859), 2224–2260. [https://doi.org/10.1016/S0140-6736\(12\)61766-8](https://doi.org/10.1016/S0140-6736(12)61766-8)
- Liu, J., Chu, B., Chen, T., Liu, C., Wang, L., Bao, X., & He, H. (2018). Secondary organic aerosol formation from ambient air at an urban site in Beijing: Effects of OH exposure and precursor concentrations. *Environmental Science & Technology*, 52(12), 6834–6841. <https://doi.org/10.1021/acs.est.7b05701>
- Mao, J., Ren, X., Brune, W. H., Olson, J. R., Crawford, J. H., Fried, A., et al. (2009). Airborne measurement of OH reactivity during INTEX-B. *Atmospheric Chemistry and Physics*, 9(1), 163–173. <https://doi.org/10.5194/acp-9-163-2009>
- Middlebrook, A. M., Bahreini, R., Jimenez, J. L., & Canagaratna, M. R. (2012). Evaluation of composition-dependent collection efficiencies for the aerodyne aerosol mass spectrometer using field data. *Aerosol Science and Technology*, 46(3), 258–271. <https://doi.org/10.1080/02786826.2011.620041>
- Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., et al. (2012). Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. *Atmospheric Chemistry and Physics*, 12(4), 1649–1665. <https://doi.org/10.5194/acp-12-1649-2012>
- Mohr, C., Richter, R., DeCarlo, P. F., Prévôt, A. S. H., & Baltensperger, U. (2011). Spatial variation of chemical composition and sources of submicron aerosol in Zurich during wintertime using mobile aerosol mass spectrometer data. *Atmospheric Chemistry and Physics*, 11(15), 7465–7482. <https://doi.org/10.5194/acp-11-7465-2011>
- Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., & Worsnop, D. R. (2011). Changes in organic aerosol composition with aging inferred from aerosol mass spectra. *Atmospheric Chemistry and Physics*, 11(13), 6465–6474. <https://doi.org/10.5194/acp-11-6465-2011>
- Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., et al. (2016). Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area. *Atmospheric Chemistry and Physics*, 16(11), 7411–7433. <https://doi.org/10.5194/acp-16-7411-2016>
- Paatero, P. (1999). The multilinear engine—A table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model. *Journal of Computational and Graphical Statistics*, 8(4), 854–888. <https://doi.org/10.1080/10618600.1999.10474853>
- Paatero, P., & Tapper, U. (1994). Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics*, 5(2), 111–126. <https://doi.org/10.1002/env.3170050203>
- Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., et al. (2016). In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor. *Atmospheric Chemistry and Physics*, 16(5), 2943–2970. <https://doi.org/10.5194/acp-16-2943-2016>
- Palm, B. B., Sá, S. S. D., Day, D. A., Campuzano-Jost, P., Hu, W., Seco, R., et al. (2018). Secondary organic aerosol formation from ambient air in an oxidation flow reactor in central Amazonia. *Atmospheric Chemistry and Physics*, 18(1), 467–493. <https://doi.org/10.5194/acp-18-467-2018>
- Qin, Y. M., Tan, H. B., Li, Y. J., Schurman, M. I., Li, F., Canonaco, F., et al. (2017). Impacts of traffic emissions on atmospheric particulate nitrate and organics at a downwind site on the periphery of Guangzhou, China. *Atmospheric Chemistry and Physics*, 17(17), 10245–10258. <https://doi.org/10.5194/acp-17-10245-2017>
- Saha, P. K., Reece, S. M., & Grieshop, A. P. (2018). Seasonally varying secondary organic aerosol formation from in-situ oxidation of near-highway air. *Environmental Science & Technology*, 52(13), 7192–7202. <https://doi.org/10.1021/acs.est.8b01134>
- Setyan, A., Zhang, Q., Merkel, M., Knighton, W. B., Sun, Y., Song, C., et al. (2012). Characterization of submicron particles influenced by mixed biogenic and anthropogenic emissions using high-resolution aerosol mass spectrometry: Results from CARES. *Atmospheric Chemistry and Physics*, 12(17), 8131–8156. <https://doi.org/10.5194/acp-12-8131-2012>
- Shen, G., Xue, M., Yuan, S., Zhang, J., Zhao, Q., Li, B., et al. (2014). Chemical compositions and reconstructed light extinction coefficients of particulate matter in a mega-city in the western Yangtze River Delta, China. *Atmospheric Environment*, 83, 14–20. <https://doi.org/10.1016/j.atmosenv.2013.10.055>
- Slowik, J. G., Wong, J. P. S., & Abbatt, J. P. D. (2012). Real-time, controlled OH-initiated oxidation of biogenic secondary organic aerosol. *Atmospheric Chemistry and Physics*, 12(20), 9775–9790. <https://doi.org/10.5194/acp-12-9775-2012>
- Stocker, T. (2014). *Climate change 2013: the physical science basis: Working Group I contribution to the Fifth assessment report of the Intergovernmental Panel on Climate Change*. Cambridge, UK: Cambridge University Press.
- Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., et al. (2016). Primary and secondary aerosols in Beijing in winter: sources, variations and processes. *Atmospheric Chemistry and Physics*, 16(13), 8309–8329. <https://doi.org/10.5194/acp-16-8309-2016>
- Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., & Yin, Y. (2014). Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013. *Journal of Geophysical Research: Atmospheres*, 119, 4380–4398. <https://doi.org/10.1002/2014JD021641>
- Sun, Y., Wang, Z., Dong, H., Yang, T., Li, J., Pan, X., et al. (2012). Characterization of summer organic and inorganic aerosols in Beijing, China with an aerosol chemical speciation monitor. *Atmospheric Environment*, 51, 250–259. <https://doi.org/10.1016/j.atmosenv.2012.01.013>
- Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., & Ge, X. (2013). The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China. *Atmospheric Environment*, 77, 927–934. <https://doi.org/10.1016/j.atmosenv.2013.06.019>

- Sun, Y., Xu, W., Zhang, Q., Jiang, Q., Canonaco, F., Prévôt, A. S., et al. (2018). Source apportionment of organic aerosol from 2-year highly time-resolved measurements by an aerosol chemical speciation monitor in Beijing, China. *Atmospheric Chemistry & Physics*, 18(12), 8469–8489. <https://doi.org/10.5194/acp-18-8469-2018>
- Sun, Y. L., Wang, Z. F., Du, W., Zhang, Q., Wang, Q. Q., Fu, P. Q., et al. (2015). Long-term real-time measurements of aerosol particle composition in Beijing, China: Seasonal variations, meteorological effects, and source analysis. *Atmospheric Chemistry and Physics*, 15(17), 10,149–10,165. <https://doi.org/10.5194/acp-15-10149-2015>
- Sun, Y. L., Wang, Z. F., Fu, P. Q., Yang, T., Jiang, Q., Dong, H. B., et al. (2013). Aerosol composition, sources and processes during wintertime in Beijing, China. *Atmospheric Chemistry and Physics*, 13(9), 4577–4592. <https://doi.org/10.5194/acp-13-4577-2013>
- Sun, Y. L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W. N., Bae, M. S., et al. (2011). Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass spectrometer. *Atmospheric Chemistry and Physics*, 11(4), 1581–1602. <https://doi.org/10.5194/acp-11-1581-2011>
- Tang, R., Wu, Z., Li, X., Wang, Y., Shang, D., Xiao, Y., et al. (2018). Primary and secondary organic aerosols in summer 2016 in Beijing. *Atmospheric Chemistry and Physics*, 18(6), 4055–4068. <https://doi.org/10.5194/acp-18-4055-2018>
- Tkacik, D. S., Lambe, A. T., Jathar, S., Li, X., Presto, A. A., Zhao, Y., et al. (2014). Secondary organic aerosol formation from in-use motor vehicle emissions using a potential aerosol mass reactor. *Environmental Science & Technology*, 48(19), 11,235–11,242. <https://doi.org/10.1021/es502239v>
- Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., & Jimenez, J. L. (2009). Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data. *Atmospheric Chemistry and Physics*, 9(9), 2891–2918. <https://doi.org/10.5194/acp-9-2891-2009>
- Wang, B., Shao, M., Lu, S. H., Yuan, B., Zhao, Y., Wang, M., et al. (2010). Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008. *Atmospheric Chemistry & Physics*, 10(13), 5911–5923. <https://doi.org/10.5194/acp-10-5911-2010>
- Wang, Q., Sun, Y., Jiang, Q., Du, W., Sun, C., Fu, P., & Wang, Z. (2015). Chemical composition of aerosol particles and light extinction apportionment before and during the heating season in Beijing, China. *Journal of Geophysical Research: Atmospheres*, 120, 12,708–12,722. <https://doi.org/10.1002/2015JD023871>
- Wang, Y., Hu, M., Guo, S., Wang, Y., Zheng, J., Yang, Y., et al. (2018). The secondary formation of organosulfates under interactions between biogenic emissions and anthropogenic pollutants in summer in Beijing. *Atmospheric Chemistry and Physics*, 18(14), 10,693–10,713. <https://doi.org/10.5194/acp-18-10693-2018>
- Watne, Å. K. (2018). *Atmospheric oxidation: Formation and aging of biogenic and traffic-related secondary aerosols*, (Doctoral dissertation). Gothenburg, Sweden: University of Gothenburg.
- Watne, Å. K., Psichoudaki, M., Ljungstrom, E., Le Breton, M., Hallquist, M., Jerksjö, M., et al. (2018). Fresh and oxidized emissions from in-use transit buses running on diesel, biodiesel and CNG. *Environmental Science & Technology*, 52(14), 7720–7728. <https://doi.org/10.1021/acs.est.8b01394>
- Zhang, J. K., Cheng, M. T., Ji, D. S., Liu, Z. R., Hu, B., Sun, Y., & Wang, Y. S. (2016). Characterization of submicron particles during biomass burning and coal combustion periods in Beijing, China. *Science of the Total Environment*, 562, 812–821. <https://doi.org/10.1016/j.scitotenv.2016.04.015>
- Zhang, J. K., Sun, Y., Liu, Z. R., Ji, D. S., Hu, B., Liu, Q., & Wang, Y. S. (2014). Characterization of submicron aerosols during a month of serious pollution in Beijing, 2013. *Atmospheric Chemistry and Physics*, 14(6), 2887–2903. <https://doi.org/10.5194/acp-14-2887-2014>
- Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., & Sun, Y. (2011). Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: A review. *Analytical and Bioanalytical Chemistry*, 401(10), 3045–3067. <https://doi.org/10.1007/s00216-011-5355-y>
- Zhang, Q., Worsnop, D. R., Canagaratna, M. R., & Jimenez, J. L. (2005). Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: Insights into sources and processes of organic aerosols. *Atmospheric Chemistry and Physics*, 5(12), 3289–3311. <https://doi.org/10.5194/acp-5-3289-2005>
- Zhang, Y., Sun, J., Zhang, X., Shen, X., Wang, T., & Qin, M. (2013). Seasonal characterization of components and size distributions for submicron aerosols in Beijing. *Science China Earth Sciences*, 56(5), 890–900. <https://doi.org/10.1007/s11430-012-4515-z>
- Zhang, Y. L., & Cao, F. (2015). Fine particulate matter (PM_{2.5}) in China at a city level. *Scientific Reports*, 5, 14884(1). <https://doi.org/10.1038/srep14884>
- Zhu, Q., Huang, X. F., Cao, L. M., Wei, L. T., Zhang, B., He, L. Y., et al. (2018). Improved source apportionment of organic aerosols in complex urban air pollution using the multilinear engine (ME-2). *Atmospheric Measurement Techniques*, 11(2), 1049–1060. <https://doi.org/10.5194/amt-11-1049-2018>