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- Real-time molecular characterization of air pollutants in a Hong Kong residence: implication of
- 2 indoor source emissions and heterogeneous chemistry
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 **Abstract:** Due to the high health risks associated with indoor air pollutants and long-term exposure, indoor air quality has received increasing attention. In this study, we put emphasis on the molecular composition, source emissions and chemical aging of air pollutants in a residence with designed activities mimicking ordinary Hong Kong homes. More than 150 air pollutants were detected at molecular level, 87 of which were quantified at a time resolution of not less than 1 hour. The indoor to outdoor ratios were higher than 1 for most of the primary air pollutants, due to emissions of indoor activities and indoor backgrounds (especially for aldehydes). In contrast, many secondary air pollutants exhibited higher concentrations in outdoor air. Painting ranked first in aldehyde emissions, which also caused great enhancement of aromatics. Incense burning had the highest emissions of particle-phase organics, with vanillic acid and syringic acid as markers. The other noteworthy fingerprints enabled by online measurements included linoleic acid, cholesterol and oleic acid for cooking, 2,5-dimethylfuran, stigmasterol, iso-/anteiso- alkanes and fructose isomers for smoking, C28–C34 even *n*-alkanes for candle burning, and monoterpenes for the use of air freshener, cleaning agents and camphor oil. We showed clear evidence of chemical aging of cooking emissions, giving a hint of indoor heterogeneous chemistry. This study highlights the value of organic molecules measured at high time resolutions in enhancing our knowledge on indoor air quality.

# **Practical Implications**

- 27 Online mass spectrometry technology enabled definite and fast-response detection of a large number of air pollutants in a residence with implications on source emissions and indoor chemistry.
- Incense burning caused intensive emissions of organic matters in both gas and particulate phases.
- Distinct tracers identified for nine individual activities facilitated the understanding of emission characteristics of indoor sources.
- Chemical aging of cooking emissions was clearly shown, indicating the importance of indoor heterogeneous chemistry.

 **Keywords:** Indoor air quality, volatile organic compounds, particulate matters, organic aerosol, indoor chemistry

### **1. Introduction**

 People spend up to 90% of their time indoors (Spengler and Sexton, 1983). Indoor air pollution causes heart disease, pneumonia, stroke, diabetes and lung cancer, resulting in 1.6 million 42 premature deaths globally in year 2017 (IHME, 2018). Some indoor sources, such as cooking emissions, also play significant roles in influencing ambient air quality (Lee et al., 2015; Wang et al., 2020a).

 Though no consensus has been reached on which air pollutants are most responsible for the health effects of indoor air pollution, many air pollutants have been confirmed to be harmful to human 47 health (Salthammer et al., 2010; Chi et al., 2019), such as the gaseous pollutant formaldehyde and fine particulate matters (PM2.5). Therefore, great efforts have been made to understand the 49 chemical compositions of indoor air pollution as comprehensively as possible (Lee et al., 2002; Weisel et al., 2008; Krugly et al., 2014; Zhao et al., 2019), plus the other characteristics of these air pollutants (e.g. size distributions of ultrafine particles) (Morawska et al., 2003). Indoor air pollutants are generated from a wide range of human activities (cooking, cigarette smoking, cleaning, human breath, etc.), furnishings, and building & decoration materials (Samet et al., 1987; Habre et al., 2014; Liu et al., 2016). It is well documented that combustion of solid fuels for cooking and heating is the leading source of indoor air pollution with most serious health consequence in developing countries (Ezzati, 2005). Additionally, outdoor air pollution presents to be a universal source of air pollutants indoors due to air exchange (Blondeau et al., 2005; Chen et al., 2012). The chemical evolutions of indoor air pollutants have not been studied as extensively as those in ambient air (Weschler and Carslaw, 2018; Gligorovski and Abbatt, 2018). However, recent studies discovered the higher-than-expected concentrations of hydroxyl radical (OH) in special indoor settings, due primarily to the photolysis of combustion-related nitrous acid (HONO) (Alvarez et al., 2013) and/or terpene-ozone reactions during cleaning (Carslaw et al., 2017). Besides, the high surface-to-volume ratios indoors enhance the possibility and significance of surface reactions (Ault et al., 2020; Wang et al., 2020b), accelerating heterogeneous formation of HONO for example (Gandolfo et al., 2017; Liu et al., 2020). Recently, by applying novel tools for studying atmospheric chemistry to indoor chemistry, researchers have made compelling breakthroughs in revealing indoor dynamic source emissions and ozone chemistry (Kristensen et al., 2019; Liu et al., 2019, 2021). Last but not the least, the occurrence and transformation of indoor air pollutants are not independent from the ventilation conditions (Godish and Spengler, 1996).

70 Hong Kong, a home of 7.5 million people with a land area of  $1,100 \text{ km}^2$ , is one of the cities with 71 world's smallest living space per capita  $(< 16 \text{ m}^2$  per capita for all housing and  $< 5$  for subdivided apartments) (NYT, 2019). The city is also known for its high densities of population, buildings and vehicles. Catering is well developed in Hong Kong, forming unique mix of Chinese and western foods. At a roadside site in vicinity of residential areas in this city, cooking emissions were found to be responsible for 38.6% (by mass) of the ambient organic aerosols (Lee et al., 2015). Besides, people in South China including Hong Kong succeed the custom of burning candles and/or incenses when worshiping ancestors, ghosts and gods in house at daily to monthly frequency depending on individuals. Other activities, such as smoking, cleaning and laundry, are also common in Hong Kong homes. The outdoor air pollution is mainly manifested as regional

 photochemical smog and street-level air pollution resulted from vehicle emissions (Wang et al., 81 2017; Zhu et al., 2018). Lastly, warm and humid climate prevails in Hong Kong for more than half of a year, making it unlikely to stay indoors without air conditioning, which is another factor influencing indoor air quality in Hong Kong.

 The concentrations, compositions and sources of regular air pollutants, e.g. volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and criteria air pollutants, were studied in Hong Kong (Lee et al., 2001, 2002; Guo et al., 2003, 2009; Ai et al., 2015). The health 87 implications of indoor air pollution or environmental factors were also investigated (Yu et al., 2004). In particular, Yu et al. (2004) and Li et al. (2007) indicated the airborne transmission of SARS virus in residential building and hospital, and its relationship with ventilation. However, the previous studies outline the gaps in understanding indoor air pollution in Hong Kong. Firstly, the molecular compositions of condensed organics, a dominant constituent of indoor particular matters (Polidori A et al., 2006), were seldom analyzed except for PAHs (Tong et al., 2019). The measurements lacked either high time resolution or chemical completeness. Secondly, it was difficult to recognize the emission characteristics of individual indoor sources due to the cumulative sampling methods. Lastly, we have little knowledge on indoor chemical evolutions in Hong Kong.

 In this context, we performed a real-time molecular characterization of indoor air pollutants in a residence with designed activities mimicking ordinary Hong Kong homes, using a set of online instruments. This study provides an overview of the sampling campaign, focusing on the concentrations and origins of air pollutants measured in the residence, emission characteristics of indoor activities, and the chemical evolution of cooking emissions. The real-time measurements of indoor air pollutants at the molecular level, especially organics, allowed an unprecedented insight on indoor air quality in Hong Kong homes.

## **2. Methodology**

 As shown in Figure 1, an apartment, consisting of a living room, 2 bedrooms, a kitchen and a 106 bathroom, was rented for the study. The apartment was located on the  $7<sup>th</sup>$  floor of a 22-year-old building with 17 floors in a residential area of Kowloon, Hong Kong. In addition to common sources of air pollutants in cities, *e.g.* vehicles, restaurants and gas station, two funeral parlors 109 were located  $\sim$ 220 m south. The floor area of the apartment was 25.4 m<sup>2</sup>, a typical space for an ordinary Hong Kong family with 3–4 members. The ventilation system comprised 5 windows, 3 air conditioners (ACs), an exhaust fan in the bathroom, and a range hood in the kitchen. The air exchange rate (AER) of the apartment was measured in a few scenarios, based on the decay of carbon dioxide (CO2) when there was no occupant in the apartment. To maintain comfort and ensure normal operation of the instruments, at least 1 AC was on all the time. Irrespective of which AC(s) was (were) on and which door(s) within the suite was (were) open, the AER remained 116 stable  $(1.1 - 1.2 h<sup>-1</sup>)$ . It did not change much, unless the range hood was on and the kitchen door 117 was open, which brought the AER to  $2.9 \text{ h}^{-1}$ .

 Common activities in Hong Kong homes were designed and carried out following the schedules shown in Figure 2. To mimic the real situations, the activities were conducted at time and frequencies close to actual since the normal operation of all instruments on 18 November 2019, while the activity frequencies were lower in the earlier phase of the sampling campaign. The intensity of the same activity was not necessarily consistent, e.g. simple breakfast *vs.* big dinner, usually 1 cigarette *vs.* occasionally 2 cigarettes for smoking, and the burning of scented candle *vs.* ritual candle. The consequent differences in indoor air quality are discussed where necessary. Natural gas was the main fuel for cooking, with electricity as an alternative when induction cooker was occasionally used. The types of cigarettes, incenses, and air fresheners were consistent throughout the study. In most of the daytime, there were 2 occupants in the apartment. The 129 recorded temperature and relative humidity in the apartment were in the range of 20.0–30.2 °C and  $22.1\% - 57.4\%$ , with an average of 25.5 °C and 33.7%, respectively.

 As shown in Figure 1, all the instruments were deployed in the living room. The indoor and outdoor 132 air was sampled through a  $\sim$ 2 m and  $\sim$ 3 m pre-cleaned copper tubing (Restek Cat.# 22629, ID: 133 0.19") at the flow rate of 16.7 L m<sup>-1</sup>, respectively. Due to the short residence time (<1 s), low wall loss of charged particles, and relatively low delay on transfer of organic vapors (Deming et al., 2019), the copper tubing was suitable for simultaneous gas and particle sampling. However, the partitioning and wall loss could not be completely ruled out. A High Resolution–Time of Flight– Aerosol Mass Spectrometer (HR-ToF-AMS, hereinafter referred to as AMS) was used to measure the non-refractory compositions of submicron particulate matters (PM1), including organic matters (PM1-OM), sulfate, nitrate, ammonium and chloride. The concentrations were recorded every 2 minutes. Speciated organic aerosol (OA) markers in PM2.5 were analyzed by a Thermal desorption Aerosol Gas chromatograph–Time of Flight–Mass Spectrometer (TAG-ToF-MS, hereinafter referred to as TAG). We identified 92 OA markers according to their retention time and mass spectra, and quantified the concentrations of 64 species at the time resolution of 1 hour. The operation principles, measurement configurations, calibrations and data quality control of AMS 145 and TAG were elaborated in Lyu et al. (2020). The accuracy and precision for the measurements were within the range of 1.5%–21.2% and 4.1%–33.9%, respectively.

 The VOCs were detected utilizing a quadruple Proton Transfer Reaction–Mass Spectrometer (PTR-MS, hereinafter referred to as PTR). The procedures for PTR calibration are described in Text S1 and Figure S1. 50 VOC species were identified, 12 of which were quantifiable with the accuracy of 3.0%–19.9% and precision of 1.6%–10.0%. The time resolution of PTR measurement 151 was 1 minute. Besides, 6 inorganic trace gases, including sulfur dioxide  $(SO<sub>2</sub>)$ , carbon monoxide  $(CO)$ , nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>), were monitored by a set of trace gas analyzers at the resolution of 1 minute (Table S1). All the online instruments measured the indoor and outdoor air in turn every other hour, which was achieved through automatic switching of 2 solenoid valves installed on the sampling lines (Figure 1). Exhausts of all the instruments were pumped out of the apartment. Due to malfunctions of some instruments (especially TAG), the periods with valid data for the species measured online were 158 not exactly the same (Table S1).

 In total, we obtained the mixing ratios (or concentrations) for 87 out of 153 air pollutants detected at the time resolution of 1 minute to 1 hour. While we mainly focus on the quantifiable air pollutants, the signal intensities of some air pollutants which were not quantified are also adopted for discussions. The sensitivity of PTR was relatively stable, based on the small changes in K values between every two calibrations (<7%). For TAG data, the signal intensities were the peak areas of target compounds scaled by those of corresponding internal standards (ISs), i.e. IS-scaled peak areas. The ISs, comprising 41 deuterated compounds, were used to track and correct the changes in instrument sensitivity (Lyu et al., 2020). Therefore, it is reasonable to use the signal intensities for ratio analyses.

- To facilitate discussions, the 64 quantifiable OA markers are classified as even *n*-alkanes, odd *n*- alkanes, PAHs, phenolic acids, phthalic acids, saccharides, sugar alcohols, fatty acids, oleic acid, dicarboxylic acids (DCA), hydroxyl dicarboxylic acids (OHDCA), Secondary Organic Aerosol (SOA) tracers of isoprene (Isop-SOA-T), monoterpenes SOA tracers (MT-SOA-T), and 2,3-
- 172 dihydroxy-4-oxopentanoic acid (DHOPA). The species in every group are listed in Table S2.

## **3. Results and Discussion**

## **3.1. Indoor versus outdoor concentrations**

 Figures S2–S5 show the time series of gas-phase and particle-phase air pollutants that were quantified in this study. The average mixing ratios (or concentrations) in 3 scenarios, i.e. with 177 indoor activities, without indoor activity and outdoors, are compared in Table 1.

 Most of the air pollutants with predominantly primary sources exhibited higher levels indoors, resulting in the indoor-to-outdoor (I/O) ratios of higher than 1. This did not necessarily mean the more intensive emissions of interior sources but demonstrated the great impacts of interior sources on indoor air quality, due to proximity to emissions and worse dispersion conditions indoors than outdoors. Exceptions were NO, NO2, SO2, chloride, PAHs, phenolic acids and phthalic acids, whose I/O ratios were close to or even lower than 1. Because of intensive emissions indoors, the low I/O ratios indicated significant outside emissions, such as NO, NO2 and PAHs in vehicle exhausts (Guo et al., 2003), and phenolic acids emitted from burning of worship supplies (mainly biomass) in nearby funeral parlors (Simoneit et al., 1999). The indoor mixing ratios (or concentrations) of all the primary air pollutants were considerably elevated in presence of activities, which partially accounted for the I/O ratios of higher than 1. In absence of activity, the concentrations of the primary particle compositions were lower than those in ambient air. However, it was interesting that the mixing ratios of CO2 and aldehydes indoors without activity still 191 overwhelmed those outdoors. While the higher  $CO<sub>2</sub>$  levels were explained by the breath of occupants, the more abundant aldehydes in the apartment even in absence of activity were likely caused by emissions from furnishings and building & decoration materials (Baumann et al., 2000, Uhde and Salthammer, 2007).

In contrast, the I/O ratios were lower than 1 for a majority of secondary air pollutants, excluding

- those having primary emissions as alternative sources (e.g. formaldehyde) and oxidation products
- of indoor emissions (e.g. 9-oxononanoic acid produced by ozonolysis of oleic acid, see section
- 198  $3.3$ ). O<sub>3</sub> is a typical photochemical air pollutant in ambient air (Lin et al., 1988), which presented

 indoors mainly due to air exchange. Sulfate, nitrate and ammonium are well-documented compositions of secondary inorganic aerosols (Huang et al., 2014). Oxidations of anthropogenic and biogenic VOCs lead to the formations of DCA, OHDCA, Isop-SOA-T, MT-SOA-T and DHOPA (Blando and Turpin, 2000, Hu et al., 2008), while DCA is also derived from primary emissions. According to the PTR data that were not quantified, the signal intensities of some VOC precursors of these SOA markers indoors were higher than those outdoors, such as isoprene (Isop- SOA-T precursor), monoterpenes (MT-SOA-T precursors), and toluene (one of DHOPA precursors). Therefore, the lower mixing ratios (or concentrations) of the secondary air pollutants indoors most likely indicated weaker oxidative capacity of the indoor air than ambient air.

### **3.2. Emission characteristics of indoor activities**

 As discussed, indoor activities caused obvious enhancements of primary air pollutants. Figure 3 shows the variations of some selected air pollutants on one day with intensive activities as an example. Increases of NO, NO2 and PM1-OM were observed during cooking noodles in the morning with range hood off. While all of them could be emitted from natural gas combustion 213 (Singer et al., 2017), the increase of PM<sub>1</sub>-OM was also associated with the stir fry of side dishes, in the light of rising fractions of saccharides and oleic acid. Differently, making lunch and dinner resulted in much less pronounced increases of these air pollutants, though more dishes were made. A plausible explanation was the effect of the range hood, which was turned on during both cooking periods. We compared the indoor mixing ratios (or concentrations) of some representative air pollutants with and without range hood exhaust during 2 cooking practices, when the range hood 219 was turned on intermittently. As shown in Table S3, the indoor levels of these species were reduced 220 by  $4\% - 81\%$  with the range hood exhaust, confirming the effectiveness of the range hood in removing cooking emissions from the apartment. Besides, the fraction of oleic acid increased markedly during making lunch and dinner, due to the use of larger amount of oil than in making breakfast.

224 The occupant smoked in the apartment at  $\sim$ 12:20 and  $\sim$ 18:00, causing tremendous rise in the concentrations of PM1-OM and nitrate, as well as the mixing ratios of many VOCs and CO. Saccharides experienced the largest enhancements among the OA markers that were quantified, thereby an obvious increase of the proportion in the total concentration of OA makers. A ritual candle was burned during 22:21–22:40 in the kitchen. Correspondingly, we observed notable increases of NO, NO2, SO2, CO and *n*-alkanes (especially even *n*-alkanes). Spraying air freshener 230 in the morning  $(\sim 10:25)$  was responsible for the enhancements of formaldehyde and acetaldehyde. Lastly, makeup in the morning and eating fruit (persimmon) & drinking tea in the afternoon did

- not cause significant changes in the mixing ratios (or concentrations) of air pollutants discussed here. However, the use of camphor oil as a repellent in the makeup substantially increased the
- signal intensity of monoterpenes (see section 3.3).
- Furthermore, we calculated the net increments (NIC) of the 12 quantifiable aldehydes during
- 236 individual indoor activities, with the formula of NIC =  $C_{W/A}$   $C_{W/OA}$ .  $C_{W/A}$  and  $C_{W/OA}$  represent
- 237 the mixing ratios with and without the presence of indoor activities, respectively.  $C_{w/A}$  were the
- averages over the rising, plateau (if any) and decline periods of the mixing ratios, and the time
- 239 frames for calculating  $C_{w/o A}$  were the periods before the activities within the same hours the

 activities were conducted. Since the sampling switched to outdoor air in odd hours, the decline periods were not complete in some cases. Therefore, the NICs were somewhat overestimated. However, we do not think this had a great impact on the fractions of individual aldehydes in the total NIC of the 12 aldehydes, bearing in mind the discrepancies in decay rates of different aldehydes.

 Figure 4 shows the total NIC of the 12 aldehydes during individual indoor activities and the apportionments. Overall, painting ranked the first in the total NIC, followed by incense burning 247 and smoking. Ritual candle burning had the lowest NIC of aldehydes. Butanal contributed 54.6% to the total NIC during painting, which even played more predominant role (82.1%) in the total NIC attributable to cleaning. Pentanal, formaldehyde and butanal were the main aldehydes emitted from incense burning (smoking), contributing 40.9% (43.5%), 17.1% (12.1%) and 14.3% (16.6%) to the total NIC, respectively. Emissions from spraying air freshener mainly consisted of formaldehyde, butanal and propanal. Hexanal accounted for 72.2% of the total NIC of the 12 aldehydes in emissions of scented candle burning. Pentanal, formaldehyde and hexanal were the main constituents of cooking emissions. While hexanal dominated the total NIC during the use of camphor oil, other aldehydes (such as heptanal, propanal and decanal) also made considerable contributions. The total NIC during ritual candle burning was mainly attributed to formaldehyde (44.6%), propanal (15.4%), decanal (14.1%) and acrolein (10.3%). It should be noted that the pie areas in Figure 4 are proportional to the total emissions of the 12 aldehydes instead of all VOCs. Many VOCs with great enhancements in some activities were not quantified, such as ethanol in spraying air freshener and monoterpenes in cleaning and camphor oil use (see section 3.3).

 Similarly, the NICs of particle-phase air pollutants were calculated, as shown in Figure 5. 262 Activities that did not cause significant changes in PM<sub>1</sub> compositions are not discussed. It is 263 striking that the PM<sub>1</sub>-OM contributed more than 95% of the total NIC of PM<sub>1</sub> during cooking and all the activities involving combustion except scented candle burning. The burning of scented 265 candles only increased PM<sub>1</sub> concentration by  $5.2 \pm 1.7 \,\mu g \,\text{m}^3$  on average, which was 6.6–37 times 266 lower than the NICs of PM<sub>1</sub> caused by the other activities. During scented candle burning,  $76\pm0.4\%$ 267 of the NIC of PM<sub>1</sub> was attributed to PM<sub>1</sub>-OM (NIC:  $4.0 \pm 1.7 \mu$ g m<sup>-3</sup>), with the rest contributed by 268 sulfate (~16%) and ammonium (~7%). In contrast, incense burning caused the largest NIC of PM<sub>1</sub>-269 OM (189 ± 45 μg m<sup>-3</sup>), followed by smoking (119 ± 15 μg m<sup>-3</sup>), cooking (41 ± 7.3 μg m<sup>-3</sup>) and 270 ritual candle burning  $(33 \pm 7 \mu g m^{-3})$ . While continuous emissions were observed during the other 271 combustion activities, scented candle burning mainly led to enhancement of  $PM_1$ -OM in the ignition and extinction states, with much higher concentrations in the extinction state. This was due to the emissions of larger size particles in the smoldering phase immediately after the candle was extinguished (Manoukian et al., 2013). For ritual candle burning, smoke plumes were discernable even in the flaming phase, which might explain the different emission patterns. Furthermore, we investigated the elemental compositions of PM1-OM detected by AMS in indoor activities. The hydrogen to carbon atomic ratios (H:C) and oxygen to carbon atomic ratios (O:C) 278 are plotted in the right panel of Figure 5. Highest H:C ratios  $(1.94\pm0.02)$  and lowest O:C ratios  $(0.23\pm0.02)$  were observed during ritual candle burning. The features, especially the proximity of 280 average H:C ratio to that in long acyclic alkanes  $(\sim 2)$ , indicated strong emissions of high saturation molecules (such as alkanes) from ritual candle burning (Heald et al., 2010). In contrast, incense

- 282 burning witnessed the lowest H:C ratios  $(1.76\pm0.01)$  and highest O:C ratios  $(0.42\pm0.01)$ , implying multiple oxygen-containing functional groups in the molecules emitted from incense burning (Heald et al., 2010). These inferences are verified by the enhancement ratios (ERs) of speciated
- OA markers below, while the NICs of them will be presented in a subsequent paper.

#### **3.3. Enhancement ratios**

 Since many air pollutants (especially VOCs) that were not quantified experienced significant enhancements in signal intensities during some indoor activities, neglecting them might lead to incomplete or even biased understandings on emission characteristics of indoor activities. To make use of the unquantified species, the ERs are calculated for all the detected air pollutants following 291 the formula of ER =  $C_{W/A}/C_{W/O A}$ . While  $C_{W/A}$  and  $C_{W/O A}$  have been defined for the quantified species, they represent the signal intensities for the unquantified species with and without the indoor activities, respectively. Limited by the time resolution of 1 hour for TAG data, we 294 calculated  $C_{w/o A}$  on the days without activity and in the same hours as  $C_{w/A}$  was calculated.

 Table 2 lists the top 5 ERs for indoor gaseous and particulate air pollutants. Cooking resulted in 296 high ERs for inorganic trace gases (NO, CO and NO<sub>2</sub>), due to the combustion of natural gas (Singer et al., 2017). Ethanol also had an ER of 1.9, which was caused by the occasional use of alcohol- containing ingredients, such as fermented rice. Cyclohexane was measured in cooking emissions with the emission rates lower than many other VOCs (e.g. formaldehyde, acetaldehyde and 2- butanone) in previous studies (Alves et al., 2015; He et al., 2020). The reason for the high ER of cyclohexane in this study is unknown. The particle-phase species with high ERs in cooking included linoleic acid, cholesterol, arabinitol/xylitol, β-sitosterol and oleic acid. Linoleic acid, β- sitosterol and oleic acid were most likely derived from the oils (corn oil and peanut oil) and ingredients (Zhao et al., 2007). Cholesterol and arabinitol/xylitol were mainly derived from the 305 ingredients, because they were enhanced when fried eggs  $\&$  fishes and stir-fried vegetables were made, respectively. The most noteworthy gaseous air pollutant during smoking was 2,5- dimethylfuran whose ER was 4.3. 2,5-dimethylfuran was proposed as an excellent marker for smoking in blood and breath samples (Ashley et al., 1996; Castellanos et al., 2019). In particle phase, the iso-/anteiso-alkanes were observed with high ERs during smoking, consistent with previous studies (Cass, 1998). Stigmasterol, which had the highst ER (269), is one of the most abundant plant sterols and has often been detected with great abundance in smoking emissions (Rogge et al., 1994). Simple sugars (e.g. fructose, glucose and sucrose) are important components and common additives in tobacco, presenting at levels of up to 20% in tobacco by mass (Jansen et 314 al., 2014). This explained the notable enhancement of fructose isomers (ER = 162) during smoking. The gaseous air pollutants differentiating incense burning from the other activities were benzene, propene and acetaldehyde. Vanillic acid and syringic acid, pyrolysis products of lignin (Simoneit et al., 1993), were unique markers of incense burning, with the ER of 108 and 80, respectively. While C28–C34 even *n*-alkanes were significantly enhanced during the burning of both scented candle and ritual candle, the former witnessed enhancements of fatty acids (stearic acid and 320 palmitic acid), β-sitosterol and fructose isomers, in contrast to the  $C_{27}-C_{35}$  odd alkanes with 321 different structures for the latter. It should be noted that the higher ERs for  $C_{28}-C_{34}$  even *n*-alkanes 322 were due to the lower  $C_{w/o A}$ . In fact, the NIC of C<sub>27</sub>–C<sub>35</sub> odd *n*-alkanes was comparable to that of  C28–C34 even *n*-alkanes for both candles, consistent with the emissions of paraffin candles (Fine et al., 1999). The high ERs of alkanes in ritual candle burning were roughly consistent with the H:C ratio of 1.94±0.02 detected by AMS. Besides, the gaseous air pollutants with top 5 ERs were also different (except NO) for the burning of two types of candles.

 The other indoor activities did not lead to significant increases of particle-phase air pollutants, but the signal intensities of some VOCs were obviously enhanced. For example, the ER of monoterpenes (limonene/α-pinene/β-pinene) reached 196, 10 and 3.7, when we used camphor oil, air freshener and cleaning agents, respectively. Air freshener was also a strong source of ethanol (ER = 129). Styrene, formaldehyde and linalool/geraniol with ERs of 3.0–7.5 were widely detected in air freshener spray (Kim et al., 2015; Steinemann, 2017). Painting caused tremendous enhancements of aromatics and acrolein. Studies confirmed considerable emissions of aromatics in paint applications (Yuan et al., 2010). Acrolein, as a combustion by-product of organics (Seaman et al., 2007), however was not identified to be associated with painting. The reason for its enhancement is unknown and should be referenced with caution.

### **3.4. Chemical evolution of cooking emissions**

 Chemical evolution of indoor air pollutants has significant impacts on the fate and subsequent health risk of primary emissions. In this study, the aging of cooking emissions provided some insights into the indoor heterogeneous chemistry. Studies (Vesna et al., 2009; Zeng et al., 2020) indicated that unsaturated fatty acids (e.g. oleic acid and linoleic acid) were prone to be oxidized by O3 and OH radical via heterogeneous reactions. The oxidation products, i.e. nonanal and nonanoic acid were too volatile to be measured by TAG. Azelaic acid and 9-oxononanoic acid, the other two oxidation products of cooking emissions, were reasonably detected. However, simultaneous enhancements of azelaic acid and oleic acid were observed during cooking, 346 indicating the primary emissions of azelaic acid, which was confirmed by previous studies (He et al., 2004). Therefore, we select 9-oxononanoic acid as a representative of the oxidation products. Since 9-oxononanoic acid was not quantified due to lack of standard, the IS-scaled peak areas were used in the analyses below.

350 Figure  $6(a)$ –(b) shows the diurnal patterns of 9-oxononanoic acid and O<sub>3</sub>. The average IS-scaled 351 peak area of 9-oxononanoic acid indoors  $(0.97\pm0.11)$  was significantly  $(p<0.01)$  higher than that outdoors (0.72±0.11). For both indoor and outdoor profiles, bimodal distributions were observed with one peak in the afternoon and the other peak in the evening. The daytime variations of 9- oxononanoic acid coincided fairly well with the patterns of O3. It is expected that the indoor OH had the peak at noon, when the ambient OH reached highest levels and the HONO photolysis indoors was most intensive driven by the elevated HONO levels during making lunch and strongest sunlight that penetrated windows. Therefore, the afternoon peak of 9-oxononanoic acid was likely explained by the OH-initiated oxidations of cooking emissions and the peak delay relative to OH might be due to the oxidation processes of several generations (Zeng et al., 2020). However, the 360 possible O<sub>3</sub>-involved formation pathways could not be excluded (Vesna et al., 2009). It seemed that O3 alone was not accountable for the higher levels of 9-oxononanoic acid indoors and in the evening, where and when the O3 mixing ratios were relatively low. A plausible explanation was that the abundance of precursors was another influencing factor. For example, oleic acid was more

 abundant in indoor air, and reached its highest concentrations in making dinner, which fueled the production of 9-oxononanoic acid in the evening. Besides, the high levels of indoor 9-oxononanoic acid might be partially explained by OH-initiated oxidations, especially when HONO levels were elevated after cooking. The factors influencing the yields of 9-oxononanoic acid are also worth exploring.

 Furthermore, we examined the levels of 9-oxononanoic acid and oleic acid in the indoor samples collected during cooking and two hours later. A marginal increase (*p*=0.29) was identified for 9- 371 oxononanoic acid within the 2 hours when oleic acid decreased remarkably (Figure  $6(c)$ ). As a 372 result, the ratio of 9-oxononanoic acid/oleic acid went up (Figure  $6(d)$ ). At the same time, the 373 decrease of oleic acid/stearic acid ratio ( $Figure 6(d)$ ) was a sign of chemical aging of cooking 374 emissions, because oleic acid is more reactive than stearic acid (Wang et al., 2020). It is noteworthy that some indoor activities were occasionally conducted 2 hours after cooking, which might interfere with the chemical compositions of TAG samples. However, the conclusion will still hold even if all the samples subject to interference of other activities are filtered out.

 In general, there was no activity with intensive emissions after making dinner till the next morning, except for a few times of candle burning. Therefore, it provided a good opportunity to look into the continuous variations of the fingerprints of cooking emissions and the chemical evolution. As 381 shown in Figures  $6(e)$ –(f), the level of 9-oxononanoic acid gradually increased after cooking, reaching the maximum 4–8 hours later when oleic acid decreased to the lowest level. We noticed 383 that the increase rate of 9-oxononanoic acid within the first 2 hours  $(9.4\% \text{ hr}^{-1})$  was much lower 384 than the decrease rate of oleic acid  $(-45.8\% \text{ hr}^{-1})$ . This might be due to the fact that 9-oxononanoic acid is not the first-generation product of the unsaturated fatty acids (Vesna et al., 2009), hence time difference between the degradation of the initial precursors and production of 9-oxononanoic acid. As expected, the ratio of 9-oxononanoic acid/oleic acid increased within the first 10 hours, and decreased subsequently due to some fresh emissions of oleic acid in making breakfast and decay of 9-oxononanoic acid. A continuous decline was observed for the ratio of oleic acid/stearic acid, till the last 2 hours. Overall, the dynamic characteristics of all the fingerprints analyzed from TAG data clearly indicated the chemical aging of cooking emissions, even at night.

## **4. Conclusions**

 Indoor air quality is a big health concern in Hong Kong, where people have to endure long working hours, small living space and a wide range of indoor sources of air pollutants. This study focused on air pollution in Hong Kong homes, one of the most important indoor environments. We deployed a set of online instruments in a residence for 3–4 occupants. Air pollutants in gas and particle phases were chemically characterized at molecular level and improved time resolutions. The origins for most of the primary and secondary air pollutants were unambiguously distinguishable, based on not only the established knowledge but also the stratified I/O ratios with 1 as the benchmark. While the presence of indoor activities was an essential reason for the higher concentrations of primary air pollutants indoors, aldehydes had I/O ratios higher than 1 even in absence of any activity. Emission characteristics of 9 indoor activities were thoroughly revealed. Painting and incense burning had the highest emissions of aldehydes and PM1-OM, respectively. The molecular fingerprints of individual indoor activities were identified, such as linoleic acid and  oleic acid in cooking emissions, and 9-oxononanoic acid as one of their oxidation products. Based on the evolutions of relevant fingerprints, the chemical aging of cooking emissions indoors was clearly indicated. The high apartment rent, large sizes of the instruments and intensive labor in transferring, deploying and maintaining the instruments hamper widespread application of the online measurements in more dwellings. However, the indoor sources and chemistry examined are

- expected to be ubiquitous in this region. Therefore, this study gives unprecedented insights into the dynamic profiles and chemical evolutions of air pollutants that may be present in ordinary
- Hong Kong homes, and is also a prototype for more in-depth indoor air quality studies.
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# **References**

- Alvarez EG, Amedro D, Afif C, et al. Unexpectedly high indoor hydroxyl radical concentrations associated with nitrous acid. *Proc Natl Acad Sci USA*. 2013;**110**: 13294-13299.
- Ashley DL, Bonin MA, Hamar B, McGeehin M. Using the blood concentration of 2,5- dimethylfuran as a marker for smoking. *Int Arch Occup Environ Health*. 1996; **68**:183-187.
- Alves CA, Evtyugina M, Cerqueira M, Nunes T, Duarte M, Vicente E. Volatile organic compounds emitted by the stacks of restaurants. *Air Qual Atmos Health*. 2015; **8**: 401-412.
- Ault AP, Grassian VH, Carslaw N, et al. Indoor Surface Chemistry: Developing a Molecular Picture of Reactions on Indoor Interfaces. *Chem*. 2020; **6**: 3203-3218.
- Ai ZT, Mak CM, Cui DJ. On-site measurements of ventilation performance and indoor air quality in naturally ventilated high-rise residential buildings in Hong Kong. *Indoor Built Environ*. 2015; **24**: 214-224.
- Blondeau P, Iordache V, Poupard O, Genin D, Allard F. Relationship between outdoor and indoor air quality in eight French schools. *Indoor air*. 2005; **15**: 2-12.
- Baumann MG, Lorenz LF, Batterman SA, Zhang GZ. Aldehyde emissions from particleboard and
- medium density fiberboard products. *For Prod J*. 2000; **50**: 75-82.
- Blando JD, Turpin BJ. Secondary organic aerosol formation in cloud and fog droplets: a literature
- evaluation of plausibility. *Atmospheric Environ*. 2000; **34**: 1623-1632.
- Cass GR. Organic molecular tracers for particulate air pollution sources. *Trends Analyt Chem*. 1998; **17**: 356-366.
- Chi R, Chen C, Li H, Pan L, Zhao B, Deng F, Guo X. Different health effects of indoor‐and 443 outdoor - originated PM2. 5 on cardiopulmonary function in COPD patients and healthy elderly adults. *Indoor air*. 2019; **29**: 192-201.
- Carslaw N, Fletcher L, Heard D, Ingham T, Walker H. Significant OH production under surface cleaning and air cleaning conditions: Impact on indoor air quality. *Indoor Air*. 2017; **27**: 1091- 1100.
- Castellanos M, Suñer R, Fernández-Real JM, Sanchez JM. 2,5-dimethylfuran as a validated biomarker of smoking status. *Nicotine Tob Res*. 2019; **21**: 828-834.
- Chen C, Zhao B, Weschler CJ. Indoor Exposure to 'Outdoor PM10": Assessing Its Influence on the
- Relationship Between PM10 and Short-term Mortality in US Cities. *Epidemiology*. 2012; **23**: 870-
- 878.
- Ezzati M. Indoor air pollution and health in developing countries. *Lancet*. 2005; **366**:104-106.
- Fine PM, Cass GR, Simoneit BR. Characterization of fine particle emissions from burning church candles. *Environ Sci Technol*. 1999; **33**: 2352-2362.
- Gligorovski S, Abbatt JP. An indoor chemical cocktail. *Science*. 2018; **359**: 632-633.
- Guo H, Kwok NH, Cheng HR, Lee SC, Hung WT, Li YS. Formaldehyde and volatile organic compounds in Hong Kong homes: concentrations and impact factors. *Indoor air*. 2009; **19**: 206- 217.
- Guo H, Lee SC, Ho KF, Wang XM, Zou SC. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmospheric Environ*. 2003; **37**: 5307-5317.
- Guo H, Lee SC, Li WM, Cao JJ. Source characterization of BTEX in indoor microenvironments in Hong Kong. *Atmospheric Environ*. 2003; **37**: 73-82.
- Gandolfo A, Rouyer L, Wortham H, Gligorovski S. The influence of wall temperature on NO2 removal and HONO levels released by indoor photocatalytic paints. *Appl. Catal. B-Environ.* 2017; **209**: 429-436.
- Godish T, Spengler JD. Relationships between ventilation and indoor air quality: a review. *Indoor Air*. 1996; **6**: 135-145.
- Hu D, Bian Q, Li TW, Lau AK, Yu JZ. Contributions of isoprene, monoterpenes, β-caryophyllene,
- and toluene to secondary organic aerosols in Hong Kong during the summer of 2006. *J Geophys*
- *Res Atmos*. 2008; **113**: doi:10.1029/2008JD010437.
- Habre R, Coull B, Moshier E, et al. Sources of indoor air pollution in New York City residences
- of asthmatic children. *J Expo Sci Environ Epidemiol*. 2014; **24**: 269-278.
- He LY, Hu M, Huang XF, Yu BD, Zhang YH, Liu DQ. Measurement of emissions of fine particulate organic matter from Chinese cooking. *Atmospheric Environ*. 2004; **38**: 6557-6564.
- Heald CL, Kroll JH, Jimenez JL, et al. A simplified description of the evolution of organic aerosol composition in the atmosphere. *Geophys. Res. Lett*. 2010; **37**: doi:10.1029/2010GL042737.
- He WQ, Shi AJ, Shao X, Nie L, Wang TY, Li GH. Insights into the comprehensive characteristics of volatile organic compounds from multiple cooking emissions and after reatment control technologies application. *Atmospheric Environ*. 2020; **240**: 117646.
- Huang RJ, Zhang Y, Bozzetti C, et al. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature*. 2014; **514**: 218-222.
- Institute for Health Metrics and Evaluation (IHME). Findings from the Global Burden of Disease Study 2017. Seattle, WA: IHME, 2018.
- Jansen E, Cremers J, Borst S, Talhout R. Simple determination of sugars in cigarettes. *J Anal Bioanal Tech*. 2014; **5**: 1.
- Kim S, Hong SH, Bong CK, Cho MH. Characterization of air freshener emission: the potential health effects. *J Toxicol Sci*. 2015; **40**: 535-550.
- Kristensen K, Lunderberg DM, Liu Y, et al. Sources and dynamics of semivolatile organic compounds in a single–family residence in northern California. *Indoor Air*. 2019; 29: 645-655.
- Krugly E, Martuzevicius D, Sidaraviciute R, et al. Characterization of particulate and vapor phase
- polycyclic aromatic hydrocarbons in indoor and outdoor air of primary schools. *Atmospheric*
- *Environ*. 2014; **82**: 298-306.
- Liu J, Deng H, Lakey PS, et al. Unexpectedly High Indoor HONO Concentrations Associated with Photochemical NO2 Transformation on Glass Windows. *Environ. Sci. Technol.* 2020; 54: 15680- 15688.
- Lyu X, Guo H, Yao D, et al. In Situ Measurements of Molecular Markers Facilitate Understanding of Dynamic Sources of Atmospheric Organic Aerosols. *Environ Sci Technol*. 2020; **54**:11058- 11069.
- Li Y, Huang X, Yu IT, Wong TW, Qian H. Role of air distribution in SARS transmission during the largest nosocomial outbreak in Hong Kong. *Indoor air*. 2005; **15**: 83-95.
- Lee SC, Li WM, Ao CH. Investigation of indoor air quality at residential homes in Hong Kong— case study. *Atmospheric Environ*. 2002; **36**: 225-237.
- Lee SC, Li WM, Chan LY. Indoor air quality at restaurants with different styles of cooking in metropolitan Hong Kong. *Sci Total Environ*. 2001; **279**: 181-193.
- Liu S, Li R, Wild RJ, et al. Contribution of human–related sources to indoor volatile organic compounds in a university classroom. *Indoor Air*. 2016; **26**: 925-938.
- Lee BP, Li YJ, Yu JZ, Louie PK, Chan CK. 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. *J Geophys Res Atmos*. 2015; **120**: 7040-7058.
- Liu Y, Misztal PK, Arata C, Weschler CJ, Nazaroff WW, Goldstein AH. Observing ozone
- chemistry in an occupied residence. *Proc. Natl. Acad. Sci. U.S.A.* 2021; **118**: e2018140118;
- doi.org/10.1073/pnas.2018140118.
- Liu Y, Misztal PK, Xiong J, et al. Characterizing sources and emissions of volatile organic compounds in a northern California residence using space- and time-resolved measurements. *Indoor Air*. 2019; **29**: 630-644.
- Lin X, Trainer M, Liu SC. On the nonlinearity of the tropospheric ozone production. *J Geophys Res Atmos*. 1988; **93**: 15879-15888.
- Morawska L, He C, Hitchins J, Mengersen K, Gilbert D. Characteristics of particle number and
- mass concentrations in residential houses in Brisbane, Australia. *Atmospheric Environ*. 2003; **37**: 4195-4203.
- Manoukian A, Quivet E, Temime-Roussel B, Nicolas M, Maupetit F, Wortham H. Emission
- characteristics of air pollutants from incense and candle burning in indoor atmospheres. *Environ. Sci. Pollut. Res.* 2013; **20**: 4659-4670.
- Polidori A, Turpin B, Meng QY, et al. Fine organic particulate matter dominates indoor-generated PM2.5 in RIOPA homes. *J Expo Sci Environ Epidemiol*. 2006; **16**: 321-331.
- Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BR. Sources of fine organic aerosol. 6. Cigaret smoke in the urban atmosphere. *Environ Sci Technol*. 1994; **28**: 1375-1388.
- Steinemann A. Ten questions concerning air fresheners and indoor built environments. *Build Environ*. 2017; **111**: 279-284.
- Seaman VY, Bennett DH, Cahill TM. Origin, occurrence, and source emission rate of acrolein in residential indoor air. *Environ Sci Technol*. 2007; **41**: 6940-6946.
- Salthammer T, Mentese S, Marutzky R. Formaldehyde in the indoor environment. *Chem Rev*. 2010; **110**: 2536-2572.
- Samet JM, Marbury MC, Spengler JD. Health effects and sources of indoor air pollution. Part I. *Am J Respir Crit Care Med*. 1987; **136**: 1486-1508.
- Singer BC, Pass RZ, Delp WW, Lorenzetti DM, Maddalena RL. Pollutant concentrations and emission rates from natural gas cooking burners without and with range hood exhaust in nine California homes. *Build Environ*. 2017; **122**: 215-229.
- Spengler JD, Sexton K. Indoor air pollution: a public health perspective. *Science*. 1983; **221**: 9-17.

Simoneit BR, Schauer JJ, Nolte CG, et al. Levoglucosan, a tracer for cellulose in biomass burning

and atmospheric particles. *Atmospheric Environ*. 1999; **33**: 173-182.

- Tong X, Chen XC, Chuang HC, Cao JJ, Ho SS, Lui KH, Ho KF. Characteristics and cytotoxicity
- of indoor fine particulate matter (PM2.5) and PM2.5-bound polycyclic aromatic hydrocarbons
- (PAHs) in Hong Kong. *Air Qual Atmos Health*. 2019; **12**: 1459-1468.
- The New York Times. Tiny Apartments and Punishing Work Hours: The Economic Roots of Hong
- Kong's Protests. https://www.nytimes.com/interactive/2019/07/22/world/asia/hong-kong-
- housing-inequality.html.
- Uhde E, Salthammer T. Impact of reaction products from building materials and furnishings on
- indoor air quality—a review of recent advances in indoor chemistry. *Atmospheric Environ*. 2007;
- **41**: 3111-3128.
- Weisel CP, Alimokhtari S, Sanders PF. Indoor air VOC concentrations in suburban and rural New Jersey. *Environ Sci Technol*. 2008; **42**: 8231-8238.
- Weschler CJ, Carslaw N. Indoor chemistry. *Environ Sci Technol*. 2018; **52**: 2419-2428.
- Wang C, Collins DB, Arata C, et al. Surface reservoirs dominate dynamic gas-surface partitioning of many indoor air constituents. *Sci Adv*. 2020; **6**: eaay8973.
- Wang Q, He X, Zhou M, et al. Hourly Measurements of Organic Molecular Markers in Urban
- Shanghai, China: Primary Organic Aerosol Source Identification and Observation of Cooking Aerosol Aging. *ACS Earth Space Chem*. 2020; **4**: 1670-1685.
- 560 Wang Y, Wang H, Guo H, et al. Long-term O<sub>3</sub>-precursor relationships in Hong Kong: field
- observation and model simulation. *Atmospheric Chem Phys*. 2017; **17**: 10919-10935.
- Yu IT, Li Y, Wong TW, et al. Evidence of airborne transmission of the severe acute respiratory syndrome virus. *N Engl J Med*. 2004; **350**: 1731-1739.
- Yuan B, Shao M, Lu S, Wang B. Source profiles of volatile organic compounds associated with solvent use in Beijing, China. *Atmospheric Environ*. 2010; **44**: 1919-1926.
- Zhu Y, Chan KL, Lam YF, et al. Analysis of spatial and temporal patterns of on-road NO2 concentrations in Hong Kong. *Atmos Meas Tech*. 2018; **11**: 6719-6734.
- Zhao Y, Chen C, Zhao B. Emission characteristics of PM2.5-bound chemicals from residential Chinese cooking. *Build Environ*. 2019; **149**: 623-629.
- Zhao Y, Hu M, Slanina S, Zhang Y. Chemical compositions of fine particulate organic matter emitted from Chinese cooking. *Environ Sci Technol*. 2007; **41**: 99-105.
- Zeng J, Yu Z, Mekic M, et al. Evolution of indoor cooking emissions captured by using secondary
- electrospray ionization high-resolution mass spectrometry. *Environ. Sci. Technol. Lett.* 2020; **7**:
- 76-81.