

Characterization and source identification of sub-micron particles at the HKUST Supersite in Hong Kong

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ABSTRACT

Particle size distribution measurements were conducted continuously at a 30-second interval using the Fast Mobility Particle Sizer (FMPS) in August, September, November and December of 2011 at a coastal background site in Hong Kong. Concurrent measurements of CO, NO_x, O₃, SO₂ and volatile organic compounds (VOCs) were used to determine the causes of high particle number concentration (PNC) events. In all sampling months, PNC were usually higher in the evening, likely resulting from the arrival of upwind air pollutants as wind direction changed in the late afternoon. On the more polluted days, the PNC were usually higher around noon, particularly in August, similar to the diurnal trend of O₃. The mode diameter at noon was smaller than in other time periods in all sampling months, further highlighting the role of secondary formation at this urban background site. A prolonged period of pollution episode occurred in late August. High PNC resulted from the arrival of pollution laden air from the PRD region or super regions. In December, new particle formation followed by subsequent growth accounted for most of the polluted days. Overall, meteorology was the most important

parameter affecting particle concentrations and formation at this Hong Kong background site.

Key word: Sub-micron particles; FMPS; New particle formation; PNC

INTRODUCTION

Current air quality standards for particulate matter (PM) are based on mass concentration - the integration of particle mass concentration below a certain aerodynamic diameter. However, the health effects of ultrafine PM (diameter <100 nm) have raised public concerns in the last decade. Ultrafine particles (UFPs) are very small and they contribute little to particle mass. Recent epidemiological and toxicological in-vitro and in-vivo studies have attributed greater risk to exposure to UFPs compared to particles of greater sizes (Li et al. 2003; Sager and Castranova 2009). In particular, UFPs are able to cross the blood-brain and alveolar-capillary barriers (Oberdorster and Utell 2002), thereby inducing neurological toxicity and inflammation (Kleinman et al. 2008; Wang et al. 2009; Morgan et al. 2011). In recognition of the higher toxicity of ultrafine particles compared to aerosols in the accumulation and coarse modes, particle number emission limit was introduced in the Euro V/VI emission standards. In urban environments, particles with diameter < 500 nm account for more than 95% of particle number concentration (PNC) (Hudda et al. 2010; Woo et al. 2001). Since poor correlation has been reported between PNC (dominated by UFPs) and PM_{2.5} mass concentrations (dominated by Aiken mode particles) (Sardar et al. 2005), there is an urgent need to quantify exposure to sub-micron particles, and investigate their sources and formation mechanism in order to better characterize exposure.

Due to the different physical characteristics, UFPs have high spatial and temporal heterogeneity. PNC can range from hundreds of particles in remote regions (Guyon et al. 2003) to hundreds of thousands of particles per cm³ in urban areas (Zhu et al. 2002; Shi et al. 2001). Lianou et al. (2007) reported much higher spatial variation in PNC than that in particulate mass concentrations. UFP concentrations can decay exponentially with distance from sources such as freeways (Zhu et al. 2002). Thus, the gradient of UFP concentration can be strong given their short lifetimes and the proximity to sources is important in determining their concentrations (Sioutas et al. 2005). Depending on ambient conditions and atmospheric processes in the vicinity of the measurement location, lifetime of the sub-micron aerosols can vary from seconds to hours. Their transient nature could be amplified in urban environment due to dominant primary emissions and rapid atmospheric processing. Thus, time resolution can be critical for the quantification of

particle size distribution (PSD). A common way to determine particle size distributions is through electrical mobility analysis. The Scanning Mobility Particle Sizer (SMPS) has been the most widely used tool to measure airborne PSD since its introduction ([Wang and Flagan 1990](#)). Particles entering the SMPS are neutralized and selected using electrical classification by the Differential Mobility Analyzer (DMA). Particles of a given electrical mobility then go to a Condensation Particle Counter (CPC) where particle concentrations are determined at that size. By scanning the voltage continuously, a full PSD can be built up. The Fast Mobility Particle Sizer (FMPS) is a more recent development of mobility sizer that uses an alternative particle sizing method. While the SMPS requires the scanning of particles in different voltages, the FMPS is based on the parallel measuring principle in electrical aerosol spectrometry ([Tammet et al. 2002](#)). The FMPS (TSI Model 3091) consists of a corona charger, two classification columns, and 32 electrometers. The high voltage between the two columns carries the particles to the electrometers where the particle concentration is inferred from the current recorded by each of the electrometer. The simultaneous quantification of various electrical mobility allows rapid measurement (on a timescale of seconds) of the FMPS. As a result, it has been employed to provide greater temporal resolution of PSD in many applications including laboratory studies ([Hosseini et al. 2010](#)), emission source testing ([Stabile et al. 2013](#); [Brand et al. 2013](#)), and monitoring measurements ([Kozawa et al. 2012](#)). Many studies were carried out to compare the size distribution measured between the SMPS and the FMPS. Although the total number concentrations appeared to be comparable, FMPS tends to underestimate particle size relative to SMPS and Aerosol Mass Spectrometer (AMS). By comparing three SMPS and one FMPS, [Asbach et al. \(2009\)](#) showed that the FMPS size distribution shifted towards smaller particle sizes. Similar results are shown in a more recent study, where the FMPS was generally well correlated with the SMPS in their middle size ranges, with divergences at the lower (below 50 nm) diameter ([Price et al. 2014](#)). Furthermore, [Jeong and Evans \(2009\)](#) observed the common presence of the 10.7 nm peak in their experiments, suggesting potential artifacts resulting from the calibration of the FMPS electrometers or the data inversion algorithm ([Jeong and Evans 2009](#)). More recently, [Lee et al.](#) has compared the size characterization of ambient aerosol by the

FMPS with the SMPS and the Aerodyne AMS (Lee et al. 2013a). Results showed that the FMPS significantly underestimated particle size by 40-50% compared to the SMPS.

Hong Kong, located at the southeast tip of the Pearl River Delta (PRD) Region, is a highly developed urban city. It has a population of 7.2 millions residing in 258 km² of urban or built-up land (Census and Statistics Department, 2011). Same as many other metropolitan cities, Hong Kong suffers from serious air pollution problems, particularly for ozone (O₃) and PM. Air pollution originates from local sources including coal-fired power plants and traffic emissions, as well as regional transport from the neighboring manufacturing and industrial facilities in the PRD region. Due to its sub-tropical and monsoonal climate, Hong Kong has hot wet summers and relatively cool dry winters. Air pollution episodes were often recorded in late summer and early fall, when the high temperatures and light winds were conducive to the formation and accumulation of air pollutants. To quantify the contribution of different sources (i.e. primary emission sources, atmospheric processes and regional transport) to ultrafine particles, PSD measurement was conducted at a coastal background site in Hong Kong. The goals of this study are to: (1) advance our understanding on the sources of these sub-micron particles, and (2) identify the favorable conditions for the formation and accumulation of ultrafine particles in Hong Kong.

METHODS

Sampling description

To encompass a wider range of meteorological conditions, the sampling campaign was conducted in August and September as the summer season, November and December of 2011 as the winter season. The sampling site is the Hong Kong University of Science and Technology (HKUST) Air Quality Research Supersite, located on the shorefront of the HKUST campus in the Hong Kong suburban area. As seen in Figure 1, the sampling site is approximately 30 meters west of the shorefront, about 3 kilometers northeast of the nearest populated town of Po Lam and 8-12 kilometers east of the highly developed Kowloon area. In addition to onshore marine emissions, this site can also be impacted by local anthropogenic activities, particularly when the land breeze is strong. Under certain meteorological conditions, air mass could also originate from long range transport. Sitting on the windward side of Hong Kong, it is a suitable location to study the

background air quality and the transportation of pollutants into Hong Kong. There is no major emission source near the site and the traffic volume is low on campus. The effects of meteorology, local emissions, and long-range transport on the aerosol abundance and composition of NR-PM₁ (non-refractory components in particulate matter less than 1 micron) at this site have been presented elsewhere (Lee et al. 2013a; Li et al. 2013; Li et al. 2014; Li et al. 2015). The average percentage contributions of sulfate (organic) to NR-PM₁ in May, Sep, Nov 2011 and Feb 2012 are 51.8 (27.6)%, 55.8 (26.3)%, 44.7 (37.4)%, and 40.1 (33.3)%, respectively. The oxygenated organics (low-volatility oxygenated organic aerosol (LVOOA) and semi-volatile oxygenated organic aerosol (SVOOA)) and hydrocarbon-like organic aerosol (HOA) account for typically 80% and 20% of the organic aerosol (Li et al. 2014). The high sulfate and oxygenated organic aerosol (OOA) contributions reflect the fact that this receptor site is affected mainly by regional pollution within the PRD and super-regional pollution from long range transport outside the PRD area (Wu et al. 2013). Hygroscopic growth factor and cloud condensation activity of ambient aerosols at the site have been reported (Yeung et al. 2014; Meng et al. 2014).

Instrument

PSD was measured using a FMPS (TSI model 3091, TSI Inc., Shoreview, MN, USA) with the impactor and charger needles cleaned every 3-5 days. Ambient air was sampled at 16.67 liter per minute (LPM) through a PM_{2.5} cyclone on the roof that removes coarse particles into a stainless steel sampling port supplying the FMPS, AMS, a hygroscopic tandem differential mobility analyzer (HTDMA) and cloud condensation nuclei counter (CCNC). The FMPS drew air at a flow rate of 10 LPM from the sampling port. PSDs were obtained every second, and the reported size distribution was averaged at a 30-second interval by the data acquisition. The FMPS does not allow for adjustments/size calibration by default. Lee et al. (2013a) evaluated the sizing performance of the FMPS by cross-validation with another SMPS on-site. The evaluation reported an underestimation of the FMPS by 40-50%, and suggested a post-correction method for the FMPS measurements (Lee et al. 2013a). Such correction is applied in this study and the reported size in this paper has been corrected using the linear regression as suggested by Lee et al. (2013a).

Various gas analyzers were used to measure criteria gaseous pollutants including CO (300A, API Inc.), O₃ (400E, Teledyne Instruments Inc.), SO₂ (100A, API Inc.), and NO-NO₂-NO_x (200E, Teledyne Instruments Inc.). Continuous measurements of VOCs were determined by online VOC gas chromatography (Syntech Spectras GC 955, Series 600/800, the Netherlands). The system collected and analyzed ambient sample every 30 minutes.

PMF model simulation

USEPA positive matrix factorization (PMF) model (version 3.0) was applied to evaluate the source contributions of ultra-fine particles in the present study. It has been widely used to apportion the source contributions of ambient particle in various environments (Bullock et al. 2008; Saarikoski et al. 2008; Friend et al. 2012). It is a mathematical receptor model that reduces large number of variables to interpretable source types using multivariate factor analysis. More details of the fundamentals and assumptions of the PMF modeling can be found in the literature (Paatero 1997). In this study, tracers of different sources were selected for the model input. For example, CO, C₃-C₄ and aromatics were used as the tracers of combustion processes, and aromatics could be also emitted from solvent usage, while O₃ was used as the tracer for secondary formation through photochemical reactions. The uncertainties for each species were determined as the sum of 5% of VOC concentration and two times the MDL of the species (Paatero 2000). All the species for the input was categorized as “strong”. The number of factors and the source profiles in the PMF model were chosen based on the results from the previous studies (Guo et al. 2011a; Ling et al. 2011; Friend et al. 2012).

RESULTS

3.1 Diurnal trends

Table 1 shows the monthly average of the daily PNC (calculated as the sum of particles between 7.8 and 499 nm) in the sampling months. September had a monthly concentration of 3002 cm⁻³, which is significantly lower than other months ($p < 0.05$). August and December showed higher monthly PNC, both at around 4000 cm⁻³. Figure 2 a-d show the averaged diurnal variations of PNC in all sampling months. PNC started to rise at ~7am and continued until early or late afternoon. The daytime diurnal trends of

PNC are very similar to those of O₃, especially in the December, suggesting the role of photochemical oxidation in particle formation. Furthermore, the diurnal trends of PNC were consistent in the 4 sampling months, indicating photochemically-induced particle formation takes place at a wide range of atmospheric conditions (temperature, relative humidity, etc) in Hong Kong. PNC started to increase later in the morning in November and December than in August and September, consistent with the trends of O₃ concentrations. Subsequent to the high levels in the afternoon, PNC either continued to increase until the evening (November), or experienced another peak in the evening (August, September and December). The evening peak occurred from 6 to 8 pm, when O₃ values had declined to the background levels. Therefore, while photochemical oxidation could account for the PNC afternoon peaks, PNC peaks in the evening may arise from another potential source.

In examining the high resolution Aerosol Mass Spectrometer (HR-AMS) data for May, Sept, Nov 2011 and Feb 2012, [Li et al. \(2015\)](#) found that the oxygen-to-carbon atomic ratio (O:C) and average carbon oxidation state (OS_C) of the organic aerosols (OA) showed little variation in autumn and winter, when the long-range transport of oxidized organics dominated, whereas they peaked in the afternoon in spring and summer, when locally produced secondary organic aerosol prevailed. Hence, although local photochemical oxidation may not be responsible for the enhanced oxygenation of OA all the time, it likely accounted for the PNC afternoon peaks in all seasons.

To investigate the contribution of vehicular emissions to the measured PNC, the diurnal variations of propene and *n*-butane are also plotted in Figure 2 e-h. Previous source apportionment studies concluded that propene and *n*-butane predominantly arise from vehicular fuel combustion in Hong Kong ([Guo et al. 2004a, 2004b](#)). The highest concentrations of propene and *n*-butane found in August indicated that air pollution caused by vehicular combustion might be more severe than in other months. During the 4 sampling months, propene and *n*-butane showed peak concentrations from 8 to 9 am, likely resulting from morning traffic. Although the sampling site is distant from urban centers, it is impacted by local traffic serving the University and the nearby low-density residential areas. It is also possible that winds have brought in traffic emissions from off campus. Clear Water Bay Road and Hiram's Highway are the two major roads closet to

the sampling site. Both of these roads see significant commuting traffic (both private vehicles and public transportation) during rush hour (about 7-9 am in the morning and about 6-8 pm in the evening). On weekends, both roads have significant leisure traffic (Lee et al., 2013b). Public transportation around the sampling site is mostly diesel and liquefied petroleum gas (LPG) minibuses, diesel buses, and to a lesser extent LPG taxis. Despite the morning peaks of *n*-butane and propene, no significant morning peaks were observed for PNC, suggesting local traffic is not a significant source of particle pollution. In the afternoon, a trough occurred from noon to 4 pm for both propene and *n*-butane, somewhat similar to the diurnal pattern of CO, which was due to the influence of photochemical reactions and the development of the boundary layer height (Guo et al. 2009; Gilman et al. 2009). At ~5 pm, the levels of *n*-butane and propene started to increase again, and remained high until later at night, which were caused by the anthropogenic emissions and the lower boundary layer. Overall, vehicular emissions were a dominant source of anthropogenic VOC at this site. Although the VOC peak in the morning did not coincide with the PNC trend, they both experienced a peak in the evening, suggesting possible contribution of anthropogenic emission to UFPs at the sampling site.

3.1.1 Summer Diurnal Trends

To examine the sources and formation mechanisms of sub-micron particles under different atmospheric conditions, the sampling days were segregated into four quartiles (i.e. approximately 6-7 sampling days per quartile depending on the total sampling days in each month) based on the median of daily PNC in each month. The first quartile is denoted as "clean days", and the last quartile as "polluted days". The concentration (dN/dlogDp) was averaged for four time periods: morning (7-10 am); noon (12-3 pm); evening (5-8 pm) and midnight (11 pm-2 am).

Figures 3a and 3c show the PSD on the cleaner days in August and September, respectively. The monthly averages over all periods in each month are also shown for comparison. In both months, evening periods had the highest concentrations among the four time periods. As mentioned previously, the higher average PNC in the evening was possibly due to evening rush hour, and/or arrival of pollutants from urban areas. Morning periods, on the other hand, were fairly clean, indicating morning rush hour was not a

dominant source of sub-micron particles at the site. In general, the mode diameter appeared to be slightly larger in September than in August on the cleaner days, suggesting that particles in September might be more aged. This is consistent with the observed lowest PNC in September (Figure 2f) as more aged aerosol means that no obvious primary emissions and/or new particle formation (NPF) occurred in September. Overall, the size distribution profiles were similar in the four time periods, highlighting the absence of a dominant particle source nor a strong impact of meteorology on the PSD of sub-micron particles atmospheric processes of particle formation on the relatively clean days in August and September.

Figures 3b and 3d show the PSD on polluted days. The size distribution profiles were distinct in the four time periods. In August, the morning concentration was the lowest ($p < 0.05$), with a mode diameter at around 160 nm, similar to those on cleaner days. As the day progressed, noon concentrations became considerably higher, and the mode diameter shifted to the smaller size (~ 60 nm). The higher levels of small size particles at noon likely resulted from photochemically initiated reactions. However, the mode diameter (~ 60 nm) was larger than the nucleation mode particles (< 10 nm) indicating that there was no NPF locally but regionally followed by transportation to the sampling site. PNC continued to increase and reached the highest concentration in the evening, approaching a log normal distribution with mode diameter at ~ 100 nm and a slight shoulder at around 50 nm. The PSD was very similar between evening and midnight, suggesting the high level at midnight was the carry-over from the evening period, and was amplified due to the lower mixing layer at night. Note that in Hong Kong, the daytime temperature and relative humidity are rather similar to the nighttime values. For example, the average temperature and relative humidity were 31.0 ± 0.2 °C and $70.8 \pm 0.5\%$ during daytime hours (0600-1800, local time), respectively, while the average values were 28.4 ± 0.1 °C and $81.5 \pm 0.6\%$ for nighttime hours, respectively, in August.

Although less pronounced, similar diurnal characteristics were found in September, with the lowest PNC value observed in the morning. At noon, PNC increased gradually and shifted to the smaller size, presenting a bimodal pattern with relatively higher levels from about 7 to 20 nm. In addition, the PNC peak at noon was found at mode diameter of ~ 160 nm, similar to that observed in the morning, while the peaks were at ~ 100 nm in the

evening and at midnight. The relatively higher PNC present at the small sizes at noon suggested the influence of NPF, while the larger mode diameter at noon could be due to the combined influence of NPF and the imposed air pollutants transported from urban areas with the prevailing southerly winds observed at noon (data not shown). Overall, the size distribution was distinct between cleaner and polluted days. On polluted days, the mode diameter was shifted to the smaller size likely due to the formation of smaller particles compared to cleaner days. High concentrations, likely resulting from photochemical reaction, were observed at noon on the polluted days, and they were more pronounced in summer.

3.1.2 Winter Diurnal Trends

Figure 4a shows the PSD on the cleaner days in November. In the morning, PNC was low with a mode diameter at ~100 nm. As the day progressed, the concentration increased slightly at noon. In addition to the major peak observed at 100 nm, a minor peak was present at 30 nm, likely attributed to photochemical oxidation around noon. Among the four periods, PNC was the highest in the evening, perhaps related to the transport of traffic related air pollutants to the sampling site. Moreover, the bimodal distribution at noon was gradually transformed into a single modal distribution in the evening, further indicating there were specific emission sources affecting the PSD in the evening. At midnight, the PNC decreased to the levels similar to those observed in the morning. In December, the diurnal profiles of the cleaner days (Figure 4c) were similar to those in November. In the morning, a dominant peak occurred at the mode diameter of 150 nm. The PNC level was the highest among the 4 months. As seen in Figure 2, CO levels were the highest in December, reaching above 0.5 ppm in the morning. As suggested by the larger mode diameter, primary emission might not account for the increased concentration in the morning. Thus, the higher concentration on the cleaner days in December was likely due to an overall low mixing height and limited atmospheric dilution. Similar to the cleaner days in November, another peak occurred at a smaller size diameter (~30 nm) at noon. This minor peak is also the most pronounced in clean days in December among the four months considered. In the evening, the concentration was the highest among the four periods but the peak became more flat, indicating comparable abundance of the minor peak at 30 nm and the major peak at 100 nm. The midnight

distribution was similar to the evening's, suggesting the carry-over effect as the wind speed was fairly low (< 1 m/s) at night.

The diurnal trends of polluted days in November (Figure 4b) appeared to be very similar to the ones on cleaner days, with the concentrations approximately 2 times higher.

In December, the morning concentration was the lowest and similar to that on cleaner days (Figure 4c and d). On the other hand, the noontime size distributions were very distinct from other periods/other months. NPF, to be discussed in more detail in the next section, accounted for 1 out of 6 polluted days in November and 4 out of 5 polluted days in December. Profiles on the polluted days in December appeared to show the process of vapor condensation and coagulations as particles evolved from noon to evening.

3.2 Episode Events

Certain meteorological conditions are conducive to the formation and/or accumulation of atmospheric particles. In this section, an episode event is defined as consecutive 2 or more days with daily PNC exceeding the sum of monthly average PNC and half a standard deviation. The occurrence of such events is usually induced/facilitated by meteorology that favors the formation and/or the accumulation of aerosols. The study of such events can advance our understanding on the atmospheric conditions contributing to particle formation in Hong Kong.

A prolonged episode event occurred from August 25 to 31, 2011 (herein referred as the summer episode) with an average daily PNC of 6970 ± 1196 cm⁻³ (Figure 5). In summer, Hong Kong is under high temperature and humidity and usually experiences unstable weather including thunderstorms, brief showers, and sunny conditions. On August 24 and 25, Hong Kong was affected by a low pressure trough. From August 26 to 28, a continental air stream brought along fine and hot weather to Hong Kong. Due to the high temperature (33-35 °C maximum daily temperature) and relatively low wind speed in the region, high levels of NO_x, CO, SO₂ and PM were observed at all air quality monitoring stations, including 3 roadside and 12 general monitoring stations (Hong Kong Environmental Protection Department, <http://epic.epd.gov.hk/ca/uid/airdata>). During the episode event, the wind was mainly from the north. To investigate the transport pathways of the air masses arriving at the HKUST site during this period, we analyzed the 72-h back trajectory using HYSPLIT 4 (Hybrid Single-Particle Lagrangian Integrated

Trajectory) model (Draxler and Hess 1998). Figure 6 shows the trajectory results of the air masses. It can be seen that the air masses originated mainly from Anhui, Henan, Hubei and Hunan provinces in mainland China, as evident from the simultaneous increase of NO_x and CO (Figure 5). As a result, high PNC (> 10,000 / cm³) occurred in the evening from August 25 to 29 (Figure 5). The increase in mode diameter (to around 100 nm) further confirms the contribution of aged aerosols to the higher PNC in the evening on these days. The fine and hot weather continued to intensify from August 29 to 31, with temperature reaching record high (maximum daily temperature = 36 °C). PNC started to increase at around 10 am and peaked at noon on these days – a trend similar to that of O₃. On August 29, another PNC peak occurred in the evening, as with the concurrent raise of NO_x and CO. The evening PNC peaks concurred with the trends of NO_x, SO₂ and CO, indicating the arrival of pollution-laden air at the site. On August 30 and 31, although the evening PNC peaks were still present, they were less pronounced. Overall, both the arrival of regional air pollutants and secondary aerosol formation contributed to the high PNC observed in the summer episode.

Another episode was observed from December 24 to 25, 2011, herein referred as the winter episode. Figure 7 depicts PNC as a function of time and particle diameter. The apparent ‘banana’ shape from 10 am to noon indicated NPF followed by subsequent growth. On these two days, Hong Kong was under the influence of dry winter monsoon that brought along low temperature, relative humidity and increased radiation. The effect of temperature was evident in NPF event in many previous studies (Boy and Kulmala 2002; Komppula et al. 2006). In particular, Guo et al. (2012) observed higher contribution of sulfuric acid to formation events on days with lower temperature and suggested that the low temperature might facilitate the nucleation of sulfuric acid with water vapor at the beginning of formation events. Note that NPF followed by growth was also clearly evident on November 23, December 8 and 10.

Table 2 shows the meteorological parameters, daily SO₂ and PNC levels on the days of NPF events, as well as on the preceding and following days. The daily SO₂ levels were not significantly higher on NPF days ($p > 0.05$). Guo et al. (2012) observed NPF events on 12 of 35 days at a mountain site in Hong Kong, and found that the average concentration of SO₂ was slightly higher on NPF event days (5.2 ppbv) than on non-NPF

days (4.2 ppbv). However, on non-NPF days with higher PN, SO₂ mixing ratio was higher than on NPF days, and they concluded that only a “significant amount” of SO₂ was needed for formation events (Guo et al. 2012). The daily average SO₂ level was as low as 3.1 ppbv on December 8 (a NPF day), further confirming that SO₂ level is not the only factor associated with NPF events. Interestingly, relative humidity and solar radiation seem to play a more important role than temperature in NPF events. On days with similar temperature, NPF occurred when relative humidity dropped by more than 7% and radiation increased by $> 40 \text{ W m}^{-2}$. This sudden decrease in relative humidity and increase in infrared radiation (IR) was associated with the arrival of dry winter monsoon. Pierce et al. reported particle formation events often occurred under sunny conditions and clean-air flow, although new-particle formation sometimes occurred when air flow came from the polluted regions (Pierce et al. 2014). Similar observations were found in Korea, where strong NPF events were associated with cold and dry air mass from the Asian continent (Kim et al. 2013).

Overall, the pollution episode in summer is distinctly different from that in winter. In summer, pollution occurred under the influence of continental air stream that brought along high temperature and rather stagnant conditions. At the sampling site, PNC increased simultaneously with other gaseous pollutants. On the other hand, new particle formation, under rather clean ambient atmosphere, was responsible for the high PNC observed in winter.

To further apportion the origins of ultrafine PM, the PMF model was applied to the dataset of non-methane hydrocarbons (NMHCs), sub-micron particles and O₃. It should be noted that three categories of sub-micron particles, including size 1 (7.8-20 nm), size 2 (20-100 nm) and size 3 (100-500 nm) were used as input for the PMF model to further investigate the contributions of NPF. Based on the calculated statistical parameters and the prior-knowledge about emission source profiles specified to Hong Kong, a five-factor model (Figure 8) that best reproduced the observed particle concentrations was chosen to represent the optimum modeling result. The first factor was dominated by isoprene (~95%), and was identified as biogenic emissions. The second factor contained most of the measured *m*-xylene, *p*-xylene and *o*-xylene, was identified as solvent use emissions. The contributions of this factor to the PNC were negligible, with percentage of about 1%.

Factor 3, with the dominance of benzene, and certain amounts of CO, propene, toluene, *n*-hexane, *n*-heptane and ethylbenzene, was associated with gasoline emissions. In addition, certain amount of O₃ was present in this profile, which might be due to the fact that some species from this source contributed to O₃ formation. On the other hand, approximately 30% of the measured PNC lied in this factor, which was mainly within the range of 20-500 nm. Majority (~39%) of the PNC was associated with factor 4, with high percentage of ultrafine PM with the range of 7.8-20 nm (about 95%), high contribution of O₃ (~60%), and certain amounts of PNC with the ranges of 20-100 nm (~30%) and 100-500 nm (~40%). Therefore, this source was assigned as secondary formation. To investigate the potential formation mechanism for the new particle formation, the concentrations of H₂SO₄ vapor calculated according to the method in [Guo et al. \(2012\)](#) was further input into the PMF model. It was found that in the source of secondary formation, size 1 was highly correlated with the concentration of H₂SO₄ vapor (data not shown), consistent with those at the mountain site in Hong Kong ([Guo et al. 2012](#)), suggesting H₂SO₄ vapor plays an important role on NPF. The last factor was dominated by propane (~55%), propene (~30%), *n*/*i*-butanes (~95%), and *n*-heptane, with certain amount of CO. Previous studies have identified these species in the composition of diesel emissions in Hong Kong ([Ho et al. 2009](#); [Tsai et al. 2007](#)). In addition, high percentages of propane and *n*/*i*-butanes could be also emitted from LPG usage ([Guo et al. 2011b](#)). Therefore, this factor was considered as LPG usage and diesel vehicle exhaust, with ~22% contributions to PNC. Furthermore, the contributions of secondary formation during warm and cold months were compared based on the PMF-extracted results for each sample ([Guo et al. 2011a](#)). It was found that the contributions of secondary formation to PNC in December were 1.25 times those in August ($p < 0.05$), although the solar radiation was higher and more favorable to photochemical reactions in summer. Previous study demonstrated that solar radiation was not the key factor influencing the processes of new particle formation, low temperature and low humidity under cool and dry weather might be more important for particle nucleation in the atmosphere ([Guo et al. 2012](#); [Wang et al. 2014](#)). Overall, results from the PMF model suggest that during the sampling period (i.e. August, September, November and December of 2011), vehicular emissions, including gasoline, diesel and LPG usage (likely transported from elsewhere)

and photochemical formation are two most important contributors to the observed PNC at the sampling site.

CONCLUSIONS

To investigate the favorable conditions for the formation and accumulation of ultrafine particles, the size distribution profiles were obtained at the HKUST supersite using the FMPS. The concurrent measurements of VOCs and various gas pollutants allowed the characterization of sources and formation mechanisms of ultrafine particles under different air flows (continental vs. oceanic, sea-land breezes, etc.). In the background site examined, secondary formation accounted for the higher PNC around noon, while transported aged aerosols from upwind locations contributed to the observed PNC in the evening or later at night. From August 25 to 31, a prolonged period of pollution episode occurred. The arrival of pollution-laden air from the region led to higher PNC levels. In November/December, formation of nucleation mode particles accounted for most of the polluted days. In conclusion, meteorology played a critical role in the levels of ultrafine particles at this background site. Vehicular emissions, regional transport and photochemical formation were the three most important contributors to the observed PNC at the sampling site.

ACKNOWLEDGEMENT

This project was supported by the Environmental Conservation Fund (ECF) (project number ECWW09EG04), the Hong Kong Research Grants Council (600413, PolyU5154/13E and PolyU152052/14E), and the Public Policy Research Scheme of Hong Kong (2013.A6.012.13A). We also thank the HK Environmental Protection Department for the provision of VOC and gases data.

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