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Size spectra and source apportionment of fine particulates in tropical urban environment during southwest monsoon season

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Abstract

In this study, we carried out high time-resolution measurements of particle number concentration and size distribution (5-1000 nm) in Singapore, which represents a tropical urban environment. The measurements were taken during the southwest monsoon season in 2017 using a fast-response differential mobility spectrometer at a sampling rate of 1 Hz. In the measurement, short-lived nucleation events were found prominent at early afternoon because of the abundant incoming radiation that enhances the photochemical reactions in atmosphere. For the first time in the region, a five-factor positive matrix

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factorization approach was applied to the size spectra data. Based on PM number concentration, two sources within nucleation mode (<30 nm) were resolved and account for 43% of total number concentration, which is higher than the available monitoring data in other big cities. Among the sources, O_3 -related atmospheric photochemical reactions with peak size at 10-12 nm is a unique factor and prominent in early afternoon nucleation events. The findings of this work can serve as a baseline for assessing influence of local and cross-border airborne PM emissions during various seasons in the future.

Short-lived nucleation is found prominent in tropical urban environment. A unique source is discovered correlated with O_3 .

Keywords: PM emission, source apportionment, PMF, Southeast Asia

1. Introduction

Air pollution is a major urban problem and presents a big challenge for the sustainable development of modern cities. Long-term exposure to ambient fine particulates (<1000 nm) is associated with increased mortality and morbidity from cardiovascular and pulmonary diseases [39, 47]. Epidemiological studies have also demonstrated that ultrafine particles (<100 nm) from particulate matter (PM) emissions may have severe adverse health effects, considering their larger likelihood of penetration and higher surface area per unit volume to adsorb organic compounds [7, 19].

Currently, air quality is measured and controlled in mass concentration as the standard metric. However, these metric does not consider the spec-

tra of particle sizes, specifically the contribution of fine particulates. Fine particulates are inhalable particles that have significant influence on human health and visibility degradation [38]. Among them, ultrafine particles are negligible in mass but comprise the major proportion (80%) in total number concentration from ambient PM measurement [24]. Thus, in order to generate relevant and reasonable regulations, it is important to understand the size distribution and number concentration of fine particulates in the air, as well understanding the extent to which different emitters contribute to these particles.

Tropical urban regions in Southeast Asia are reported to have serious air pollution issues from airborne PM emissions in recent years [13, 15, 37], while relevant studies remain sparse. For these densely populated cities, particulate matter is emitted from a diverse mixture of mobile sources (air, ground and marine transportation) and stationary (industrial) sources. In Singapore, for example, five major sources for $PM_{2.5}$ aerosols were identified in 2001 as solid dust, metallurgical industry, biomass fires/local traffic, sea-salt and oil combustion, from a principal component analysis on chemical species data [3]. Later studies attribute the burning of biomass (in bush fires) in Sumatra as a major source of local airborne $PM_{2.5}$ emissions [25, 36]. A typical report on PM_{10} particles in 2013 haze event shows that particles larger than 0.2 mm in diameter is remarkably higher than those on normal days [11]. Besides, traffic-related $PM_{2.5}$ emissions and the exposure to daily commuting have also been studied [42, 44]. The gasoline-powered vehicles are found to make a higher contribution to $PM_{2.5}$ aerosol components than the diesel-powered vehicles in traffic emissions [48]. From these most recent literatures, the

contribution of bush fires is no longer the most concerning source in Singapore and a new and comprehensive re-assessment of the sources of airborne PM emissions is needed, which can work as a baseline for studies and regulations
40 on local air quality.

Another significant factor contributing fine particulates in modern cities is the nucleation event, which occurs in both clean and polluted environments by homogeneous nucleation or heterogamous nucleation [6]. Strong nucleation events are usually observed at high temperature, solar radiation,
45 low relative humidity (RH) and low-condensation sink conditions [4, 21]. It has been suggested that the nucleation events could be caused by local precursors from traffic, ship or aircraft emissions [20].

Positive Matrix Factorization (PMF) is an established method developed by Paatero [34, 35] that has previously been used to apportion the sources
50 of airborne PM emissions by analyzing the chemical composition of the samples [10, 18, 40]. Recently, the method was also found effective on particle number concentration and size distribution (PNSD) data [31, 33], which has received much attention with a rapid increase in publications. The method is based on the assumption that different sources will produce characteristic
55 size distributions, just like fingerprints. The measured particle size distribution can then be described as a sum of characteristic size distributions from different sources. Up to now, the PMF analysis on particle size distribution has been performed in major cities in the world, including London, New York city and Beijing. A list of PNSD source profiles from those studies has been
60 reviewed in detail [45].

This study aims to investigate the possible sources of airborne PM emis-

sions in Singapore during the southwest monsoon in 2017, which represents a typical tropical urban environment in Southeast Asia. This period is of particular interest because no major external pollution sources (like land/forest fires) were reported in 2017 [2], which is unique for the region as heavy pollutions from forest fires were prevailing during the southwest monsoon season in the previous years [4]. The resulting PM characteristics and sources can thus be considered as a baseline for Singapore emissions. In this research, the particle size distribution between 5 nm-1000 nm was measured at 1 Hz frequency. For the first time in the region, real-time PNSD spectra were measured and used to perform the source apportionment by PMF with combined meteorological data and bivariate conditional probability function (CPF) analysis. The major five source profiles and their contributions were determined and quantified.

2. Experimental methodology

2.1. On-site sampling

The sampling campaign was carried out during 2017 southwest monsoon season in Singapore from 31 July to 8 October (36 days). In this study, the measurement was mainly carried out on weekdays, only six days of measurement was done on weekends. The site was selected at the open terrace at the third floor of a building ($1^{\circ}18'13.8''\text{N}$, $103^{\circ}46'25.76''\text{E}$), which is shown in the map in Fig. 1. From the sampling site, the AYE Expressway is 30 m away in the south, the Clementi road is 50 m away in the west and the West Coast Highway is about 1.5 km away in the south and southwest. The AYE Expressway is the major link of east and west Singapore and the Clementi

road is an arterial road from north to south. As one of the busiest harbors in the world, 145147 cargo ships (>75 GT) arrived Singapore harbor in 2017 (www.mpa.gov.sg). The closest harbor (Pasir Panjang terminal) is located at 2 km away in the south. A large industrial park is located 6 km away in the southwest (only a small part shown in the map). The industrial park is specialized for petrochemical industry. In addition, a power plant is located at about 20 km in the northeast of the site (not shown in the figure). The plant could play a role in cross-border emissions considering the limited land area of Singapore.

A DMS500 (Cambustion Ltd., Cambridge) fast-response differential mobility spectrometer was used in this study. DMS has been widely used in both engine emission studies and environment measurements. Detailed description of DMS can be found in previous studies [1, 5, 23]. It is capable of measuring particle number contribution and size distribution (PNSD) from 5-1000 nm at a maximum frequency of 10 Hz. The DMS 500 was calibrated by using NaCl aerosol (50 nm and 100 nm), NIST traceable certified Nanospheres (PSL, 296 nm, 600 nm and 903 nm) and soot aerosol (50 nm, 100 nm and 200 nm). The particle size was calibrated against a DMA (TSI 3082), with concentration indicated by a standard aerosol electrometer (Keithley 617). In this study, the measurement was recorded at 1 Hz to improve the signal/noise ratio. The fast response time (1s) of DMS can provide a real-time measurement of airborne PM emissions. During the measurement, the autozero of electrometer was performed once an hour to maintain the measurement sensitivity. The diffusion correction and bimodal agglomerates mode correction were used in the setup software. The meteorological conditions

were recorded at the NUS Geography weather station every 5 min, including atmospheric pressure, air temperature, relative humidity, rainfall, solar irradiance, wind speed and wind direction (*inetapps.nus.edu.sg/fas/geog/*). The station is at a distance of 700 m to south from the sampling site and
 115 at a height of about 67 m above sea level. Pollutant mass concentrations of PM_{10} , $\text{PM}_{2.5}$, O_3 , NO_2 , SO_2 and CO are provided by Singapore National Environment Agency (NEA) south monitoring station that is 5 km from the sampling site (*data.gov.sg/group/environment*).

Figure 1: Map of studied area.

2.2. Data processing

120 Data were collected and managed by MongoDB 3.4, which is an open-source database tool widely used in statistics and scientific research. In total, 3,272,112 valid PNSD spectra were stored in the database, along with meteorological information recorded during the measurement campaign. Data

analysis was performed in Matlab R2016B and R 3.4.3, using the Openair
125 package [9].

PMF analysis was performed by using the US EPA PMF 5 [30], this latest
version incorporates three error estimation (EE) methods for analyzing fac-
tor solutions, i.e., classical bootstrap (BS), displacement of factor elements
(DISP) and bootstrap enhanced by displacement (BS-DISP). Mathemati-
130 cally, PMF is a tool that decomposes a large matrix (i.e., measured data)
into two smaller non-negative matrices (i.e., factor contributions and factor
profiles). For the observation matrix X ,

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where g_{ik} represents the contributions of factor k to sample i ; f_{kj} depicts
the factor profiles of factor k in size bin j ; e_{ij} is the residual for sample i in
135 the size bin j . PMF solves the problem by minimizing the sum of weighted
least squares, Q :

$$\{g, f\} = \arg \min_{g, f} Q \quad (2)$$

with

$$Q = \sum_{i=1} \sum_{j=1} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \quad (3)$$

where u_{ij} represents measurement uncertainties. The uncertainties of
DMS data were estimated from the method detection limit (MDL) [30], which

140 is provided by the instrument manufacturer (Cambustion Ltd., Cambridge)

$$u_{ij} = \begin{cases} \frac{5}{6}\text{MDL}, & x_{ij} \leq \text{MDL} \\ \sqrt{(\varepsilon x_{ij})^2 + (0.5\text{MDL})^2}, & x_{ij} > \text{MDL} \end{cases} \quad (4)$$

where the error fraction ε was determined by a trial and error approach from 5%-15% [1, 46]. An optimization of ε was carefully conducted based on the EPA manual and literature reports [26, 28], i.e., (1) Reducing the number of size bins with low signal-to-noise (S/N) ratios; (2) Reducing the
145 number of size bins with large absolute scaled residuals (a threshold of 3 was used); (3) the best calculated value for Q with respect to the expected value calculated as suggested by [8]; In this case, best PMF outputs were found when $\varepsilon = 10\%$. Based on the signal-noise ratio, we categorize the species as bad if the signal-noise ratio is less than 0.5 (no bad species in this study)
150 and weak if the signal-noise ratio is greater than 0.5 but less than 3 (specific criteria due to higher measurement uncertainty for particles smaller than 10 nm).

The choice of the number of factors is a compromise between too many factors that may split a real source into multiple none-existing sources, and
155 too few factors that may combine different real sources. In this work, the best solutions were selected from testing from 3 to 7 factors under the guideline of EPA manual and literature reports [26, 28], i.e., (1) Evaluating the possible pollutant sources in Singapore and their impacts; (2) Obtaining convergence and stable Q over all the runs; (3) Obtaining a good fitting for total particle
160 number concentration ($R^2 > 0.9$, slope $\rightarrow 1$); (4) Reducing the number of

samples with large absolute scaled residual (a threshold of 3 was used); (5)
the best calculated value for Q with respect to the expected value [8]; (6)
Adopting the statistics tools provided by the software (BS, DISP and BS-
DISP). In general, BS intervals include effects mainly from random errors
165 and DISP intervals include effects mainly from rotational ambiguity. BS-
DISP combines the strength of robustness to data errors and the strength of
rotational uncertainty.

Bivariate conditional probability function (CPF) analysis was adopted to
analyze the impacts of wind on source apportionment results [43]. The CPF
170 is defined as,

$$P(C \geq C_0 | \Delta\theta, \Delta\nu) = \frac{m_{C \geq C_0, \Delta\theta, \Delta\nu}}{n_{\Delta\theta, \Delta\nu}} \quad (5)$$

where m is the number of samples in the wind sector $\Delta\theta$ with wind
speed interval $\Delta\nu$ having number concentration C no less than a threshold
value C_0 , and n is the total number of samples in the same wind direction-
speed interval $\Delta\theta, \Delta\nu$. The threshold criterion was set at 75th percentile
175 considering the sample size in this study.

3. Results and Discussion

3.1. Diurnal and nocturnal patterns

In Singapore, the typically tropical climate features for high tempera-
ture and high humidity. During the measurement campaign, the recorded
180 mean temperature is $27.4 \pm 1.6^\circ\text{C}$ and the mean relative humidity (RH) is
 $77.0 \pm 9.4\%$. The southwest monsoon is one of the two major monsoon seasons
in Singapore and generally prevails from June to early October (according

to the report at *weather.gov.sg/climate-climate-of-singapore*). The wind rose diagram for the measurement period is shown in Fig. 2. The mean wind
 185 speed is 1.8 ± 1.6 m/s, which can be categorized as calm to light breeze. The winds are mostly from the south, developed over the island of Sumatra in the south or Straits of Malacca in the west. In the studied area, the diurnal pattern of the weather is prominent due to the strong influence of solar radiation in tropical area [4]. As shown in Fig. 3a, temperature starts to increase from
 190 26.3°C in the morning as the sun rises, and reaches a peak at 28.7°C at 13:00 hrs, then it decreases till the next morning. The lowest temperature of a day is generally between 6:00-7:00 hrs just before the sunrise. The variation of humidity shows the opposite pattern to the temperature. Generally, at 7:00 hrs in the morning RH reaches a peak at 81.4%, it then decreases to the
 195 lowest point of a day at 69.6% as temperature rises. At nighttime (19:00-6:00 hrs), RH remains higher than 75.0% and increases till the next morning. The diurnal pattern of incoming radiation is presented in Fig. 3b, showing that radiation is abundant in Singapore and remains high from 10:00-15:00 hrs above 300 W/m^2 . The incoming radiation is the driving force for the rise of
 200 temperature and the drop of RH during daytime (7:00-18:00 hrs).

The diurnal and nocturnal pattern of PNSD spectra (5 nm-1000 nm) is presented in Fig. 3b. The plot corresponds to an average of the daily spectra obtained during the measurement campaign. It is observed that 90.2% of the particles in number concentration is attributed to ultrafine particles (<100
 205 nm) in this study, which is consistent with the observation in other big cities across the world [22]. During daytime, from 8:00-15:00 hrs, ultrafine particles significantly emerge, which can be due to both primary emissions and

Figure 2: Wind rose diagram during the southwest monsoon. The color of the bars represents wind speed range and the length represents the frequency of counts under the wind speed range.

secondary formation, such as traffic and gas-to-particle conversion (GTP) [4, 20]. The latter could indicate the occurrence of nucleation events, also
 210 called new particle formation (NPF) events [12, 41]. The nucleation events are favored by high radiation conditions, because they are driven by photochemical reactions in the atmosphere [45]. In Fig. 3b, the emerging of ultrafine particles also coincides with the time when incoming radiation is prominent, temperature is high and RH is low. Interestingly, no further size
 215 growth can be seen for these ultrafine particles in the spectra, which indicates that these nucleation events could be short-lived [20, 41]. During these short-lived nucleation events, the existing large particles in submicron and micron ranges, which are named condensation sinks (CS), can absorb the precursor gases and suppress the small particle growth. In Singapore, CS

220 are reported to be higher than most of the studies from other parts of the world [4]. Similar short-lived nucleation events have been also reported in Brisbane, Australia, in a subtropical urban environment [12].

Figure 3: Top: hourly pattern of temperature and relative humidity; Bottom: contour of PNSD and the hourly pattern of incoming radiation. The shaded area represents the 95% confidence interval.

For a more detailed analysis, the measured particle size distribution can be divided into three regions, i.e., nucleation mode (5-30 nm), Aitken mode
 225 (30-100 nm) and accumulation mode (100-1000 nm) [45]. Such classification is useful for the identification of the possible sources of airborne PM emissions, prior to a source apportionment study. Fig. 4a presents the time evolution of the number concentration of particles in different modes (all the concentrations are above instrument sensitivity). The daily total number
 230 concentration is dominated (>85%) by nucleation and Aitken mode particles that are smaller than 100 nm. The contribution of accumulation mode particles on total number concentration is negligible, although they dominate (>90%) the volume based concentration as observed in Fig. 4b. Here the di-

urnal and nocturnal pattern for volume concentration is calculated assuming
 235 that the particles are all spherical. Temporal trend in mass concentrations of
 PM₁₀, PM_{2.5}, O₃, NO₂, SO₂ and CO are plotted in **Fig. S1** for complemen-
 tary analysis of trend based on the mean data provided by NEA for certain
 pollutants.

Three major peaks are observed from the diurnal and nocturnal pattern
 240 of total number concentration. The first peak at 9:00 hrs has a value of
 3.67×10^4 #/cc, comprising a combined contribution from the Aitken mode
 and nucleation mode particles, with a slightly larger contribution from the
 former. The peak occurs during morning traffic rush hours, which entails
 that the high concentration of nucleation and Aitken mode particles could
 245 result from the traffic emissions. This peak is supported by the concur-
 rent peak at 9:00 hrs in hourly CO concentration in **Fig. S1**. The sec-
 ond peak falls between 12:00-15:00 hrs with the highest value of 3.98×10^4
 #/cc. Overall, the early afternoon peak is dominated by the nucleation
 mode particles. The sharp peak demonstrates a rapid increase in the num-
 250 ber of particles that can be attributed mainly to abundant incoming ra-
 diation, highest temperature and lowest RH of the day shown in Fig. 3b.
 Considering the sparse traffic at that time (Clementi Avenue 2 into AYE,
<https://www.onemotoring.com.sg/content/onemotoring/en.html>), these nu-
 cleation mode particles should be formed in the atmosphere mainly via sec-
 255 ondary processes of photooxidation converting gas to particles. The forma-
 tion of these secondary aerosols is substantiated by the concurrently increas-
 ing concentration of O₃ in **Fig. S1**, demonstrating prominent atmospheric
 photooxidation. The last peak occurs at 20:00 hrs with a concentration of

2.71 $\times 10^4$ #/cc. This peak also coincides with increasing concentrations in
260 both CO and NO₂ in **Fig. S1**, suggesting emissions of combustion processes
from traffic emissions and industry combustion.

A similar trend was observed in a study performed in 2008-2009 in Sin-
gapore [4] for southwest monsoon season, with three peaks at 8:00-9:00 hrs,
14:00 hrs and 17:00-19:00 hrs. While in the northeast monsoon season, there
265 were no early afternoon peaks found in the same study. In India, the after-
noon peaks (12:00-18:00 hrs) were also reported in the city Pune and Kan-
pur [21], where these nucleation events last longer and particles could further
grow into accumulation mode. Another joint research performed in Barcelona
(Spain), Madrid (Spain) and Brisbane (Australia) proposed that the three-
270 peak PNSD spectra is typical phenomenon for high-insolation cities [6]. Our
study in Singapore could be the evidence for this assumption.

In contrast to the number concentration, the volume concentration has
far less variation and remains at 12-16 $\mu\text{m}^3/\text{cc}$. This is expected since the
total volume concentration of airborne PM emissions is mainly contributed
275 by larger particles, or accumulation mode particles. The results are much
lower than the peak values reported in 2013 haze period in Singapore that
was above 100 $\mu\text{m}^3/\text{cc}$ [11]. A low point of total volume concentration (12
 $\mu\text{m}^3/\text{cc}$) can also be found around 12:00 hrs, which could be the result of more
dilution due to the expanded boundary layer [1] and associated high wind
280 speed at noon (> 3.1 m/s at 12:00-14:00 hrs). The dip in the total volume
concentration around noon time is consistent with the mass concentration
trend in both hourly PM_{2.5} and PM₁₀ pattern in **Fig. S1**.

Figure 4: Hourly number (a) and volume (b) concentration under different modes: nucleation mode ($D_p < 30$ nm), Aitken mode ($30 < D_p < 100$ nm) and accumulation mode ($100 < D_p < 1000$ nm). The shaded area represents the 95% confidence interval.

3.2. Source apportionment on PNSD

From the above analysis, the PNSD in Singapore is mainly composed of ultrafine particles at nucleation mode and Aitken mode. The diurnal and nocturnal pattern of the particle concentration shows correlation with traffic rush hours and meteorological variations. In order to better understand the key processes and possible sources of airborne PM emissions, a source apportionment study was performed in this section based on particle number concentration and size distribution.

Here, the data obtained from DMS were averaged to 5 min resolution to minimize undesirable noise and retain high time resolution synchronizing with the meteorological data [1]. Three hours' data were missing on Oct.8th night due to power outage and were excluded from the modeling. Considering the frequent occurrence of nucleation events in the region, we set a high percentile at 99.9% to exclude outliers and two size distributions recorded on Sep.30th were excluded. As a result, 7174 samples of PNSD each with 38 size

bins are prepared as the input file for PMF analysis. Each size bin is evenly logarithmically spaced, where the logarithmic difference between each size
 300 bin is 1/16. Total particle number concentration of all samples was also used in the data input file as an indicator and assigned in the software. Due to the low signal-noise ratio, weak variables were assigned an uncertainty of 300%. Thus, the data input file has 7174 rows (samples) and 39 columns (number concentration at different size bins and total number concentration). The
 305 uncertainty input file has the same dimension of matrix as data input file.

In order to determine the optimal number of factors, the model (robust mode) was operated with 3 to 7 factors in this study. The 5-factor solution was selected as the most physically plausible case, and the sum of weighted least squares Q is closer to the expected value calculated as suggested by [8].
 310 For solutions having a number of factors smaller than 5, Qs are considerably larger than the expected values which is a result of unresolved sources. In those cases, a large number of size bins show large scaled residuals and a poor fitting of total number concentration ($R^2 < 0.9$). For solutions having a number of factors larger than 5, Qs are lower than the expected value,
 315 and the spurious factors appear without distinct physical meaning. These spurious factors only exhibit a negligible contribution to the total particle number concentration. In addition, the 5-factor solution is robust through the in-built error estimation (50 BS runs), while 4-factor solution has two base factors and 6-factor solution has one base factor that were not fully matched.
 320 No significant rotational ambiguities were found through DISP (dQmax=4) and BS-DISP (dQmax=0.5) estimation. A summary of key parameters in the process is presented in **Table. S1**.

The results of PMF are presented in Fig. 5. Each row corresponds to a factor. The left column are particle size profiles in number (solid line) and
 325 volume concentration (dash line); the middle column are temporal patterns of factor contributions (the shaded area represents the 95% confidence interval); the right column are the results of bivariate CPF analysis, where both wind speed (ws) and wind direction (wd) data were used to plot the CPF probability. For direct comparison between different factors, all factor
 330 contributions were normalized and the axis limits were set at fixed values for most cases. A summary of the factors with related processes and potential sources is shown in Table 1.

Table 1: Summary of the factors with related processes and potential sources.

	Contribution¹	Size range	Major processes	Potential sources
Factor 1	35%(N), 12%(V)	Aitken	Primary emissions	Aged traffic, industry
Factor 2	13%(N), 2%(V)	Nucleation	Atmospheric photochemical reactions	O ₃ -related precursors
Factor 3	30%(N), 1%(V)	Nucleation	Secondary emissions	Fresh traffic, industry
Factor 4	4%(N), 53%(V)	Accumulation	Mixture, urban background	Marine aerosols, secondary aerosols
Factor 5	18%(N), 32%(V)	Aitken	Combustion-related	Fuel combustion

¹ Contribution to particle total number concentration (N) and total volume concentration (V).

Factor 1 is the largest contributor to total number concentration, accounting for 35%. It is also the third largest contributor (12%) to total

Figure 5: Left: Factor profiles in number (solid line) and volume concentration (dash line). Middle: temporal pattern of factor contributions, the shaded area represents the 95% confidence interval. Right: the results of bivariate CPF analysis for each factor.

335 volume concentration. From the size distribution pattern, the mode size for
 the major sharp peak in number concentration is at 42-49 nm in the Aitken
 mode, with minor peak at 6-7 nm. In volume concentration, there are two
 peaks; the major peak is at 100-116 nm and the minor one is at 487-562 nm.
 From the temporal trend in Fig. 5, the factor is prominent in the morning
 340 (8:00-11:00 hrs) and then remains at a high level (above 1.0) until 21:00 hrs.
 The peak at morning traffic rush hours in temporal trend implies that the
 factor could be related to traffic emissions. Aged traffic-related particles are
 reported to be around 50 nm in big cities, and generally accounts for a major
 part in total number concentration ($>30\%$) [17, 29, 46]. Besides, consider-
 345 ing the CPF results, factor 1 can be associated with the winds mainly from
 southwest, where industry park (petrochemical refinery), harbor (shipping)
 and the West Coast Highway exist. Similar size distribution patterns are
 also reported to represent industrial activities in Ostrava (mode size at 45
 nm), Kuwait City (mode size at 42 nm) and Rochester (mode size at 40-50
 350 nm) [1, 26, 32]. therefore, in the studied area, factor 1 could be a mixture of
 both aged traffic and industrial emissions.

Factor 2 has a contribution of 13% to total number concentration, and a
 negligible contribution (2%) to total volume concentration. From the size dis-
 tribution pattern, the mode size for the sharp peak in number concentration
 355 is at 10-12 nm, within the nucleation mode. From the temporal pattern, the
 factor has a very high normalized contribution (>1.5) from 12:00-15:00 hrs
 and remains weak through the rest of the day. Based on previous analysis of
 particle diurnal pattern, factor 2 is strongly related to the short-lived nucle-
 ation events that occur at early afternoon, mainly caused by photochemical

360 reactions in the atmosphere. From the CPF results, it shows association
 with a wide range of wind directions from north, west and south. Consis-
 tent temporal trend in O_3 concentration (shown in **Fig. S1**) demonstrates
 prominent photooxidation of volatile organic compounds at early afternoon.
 This can also be verified from the Pearson correlation, as factor 2 has very
 365 strong positive correlation ($r=0.86$, $p\text{-value} < 0.01$) with incoming radiation
 and strong positive correlation with O_3 ($r=0.77$, $p\text{-value} < 0.01$). Hence,
 factor 2 can be attributed to nucleation events mainly driven by atmospheric
 photochemical reactions. Such factor is rarely reported in literature and the
 peak particle size of factor 2 is smaller than the O_3 -rich secondary aerosol
 370 reported in other cities at about 50 nm [29, 32].

Factor 3 is the second largest contributor to total number concentration
 (30%), while its contribution to volume concentration (1%) is almost negli-
 gible. From the size distribution pattern, the mode size for the single sharp
 peak in number concentration is at 15-20 nm, within the nucleation mode.
 375 From the temporal pattern, the factor is prominent at multiple time peri-
 ods, including early morning (6:00 hrs), morning traffic hour (9:00-10:00 hrs),
 early afternoon (12:00-14:00 hrs) and late afternoon traffic hour (19:00-20:00
 hrs). Compared to factor 2, it has a broader temporal pattern and corre-
 lates well with both morning traffic and afternoon rush hours. Based on
 380 above facts, factor 3 can be linked with secondary emissions from combus-
 tion. The precursor gases from possible sources like fresh traffic and industry
 form these particles through nucleation. Several studies have also reported
 similar nucleation mode particles from fresh road traffic and industry emis-
 sions [1, 17, 26, 32]. From the CPF results, it shows an association with the

385 winds at lower speed from west and at higher speed (>4 m/s) from north,
which may correspond to fresh traffic emissions at nearby expressways and
possible precursors transported from north.

Factor 4 is the largest contributor (53%) to total volume concentration but
plays a small part in number concentration (4%). From the size distribution
390 pattern, the mode size for the major peak in number concentration is at 100-
116 nm, within accumulation mode; and minor peaks exist at 6-7 nm and
21-27 nm. In volume concentration, the mode size for the single peak is at
487-562 nm. More than 70% of accumulation mode particles at 300-1000 nm
are attributed to factor 4. From the temporal pattern, the factor remains
395 relatively invariable during the day and night, and reaches the lowest level at
the noon, which could be due to the highest planetary boundary layer at the
noon that substantially affected by the vertical temperature profile [14]. In
terms of size distribution and temporal pattern, factor 4 could be the mixture
of transported particles from exhaust emissions and secondary aerosols, which
400 serve as the urban background in the studied area [1, 26]. In CPF analysis, it
associates with wind from the south at high speed (> 4 m/s), where sea and
harbor exist. Possible source of factor 4 could involve sea salt particles in
accumulation mode. Typical mode sizes of sea salt particles are reported at
100 nm from film droplets (break-up droplets) evaporation [27], and above
405 1000 nm from the evaporation of complete droplets [45], which is beyond the
measurement range of this study.

Factor 5 is the third largest contributor to total number concentration,
and accounts for 18%. It is also the second largest contributor (32%) to the
total volume concentration. From the size distribution pattern, the mode size

410 for the major peak in number concentration is at 75-87 nm, within Aitken
 mode; and a minor peak exists at about 15 nm. In volume concentration, the
 peak is at around 154-178 nm and from the profile there could be a second
 peak coarse particles larger than 1000 nm which is beyond the measurement
 limit in this study. From the temporal pattern, the factor has peaks at the
 415 early morning between 4:00-8:00 hrs, and is prominent at nighttime, before
 8:00 and after 20:00 hrs. This is consistent with the temporal trend in NO₂
 and CO concentration (shown in **Fig. S1**), and can also be verified from
 the Pearson correlation, as factor 5 has strong positive correlation with CO
 ($r=0.69$, $p\text{-value} < 0.01$) and moderate positive correlation with NO₂ ($r=0.46$,
 420 $p\text{-value} < 0.03$). This factor could be related to the primary emission of fuel
 combustion considering the typical particle size distribution, as the mode
 size is reported at 70-80 nm for stationary combustion in Augsburg [16]
 and at 100 nm for fuel combustion in Beijing [46]. In CPF analysis, it
 shows an association with low speed winds from wide range of directions and
 425 winds from northeast at high wind speeds (> 4 m/s), which may indicate
 combustion emissions from both nearby areas and cross-border sources.

Based on above analysis, five factors were resolved and identified as aged
 traffic and industrial emissions (35%), atmospheric photochemical reactions
 (13%), fresh traffic emissions (30%), urban background (4%) and fuel com-
 430 bustion (18%). Among the five factors, two factors (atmospheric photo-
 chemical reactions and fresh traffic emissions) are closely related to the nu-
 cleation events frequently found in the morning and early afternoon, which
 together account for 43% of total number concentration of particles. This
 percentage is higher than that in other big cities with available monitoring

435 data [17, 29, 46]. In terms of Aitken mode particles in the studied area, they show characteristics of aged traffic, industrial emissions and fuel combustion. For accumulation mode particles, marine aerosols (sea salt) and secondary aerosols are the major contributors present in the urban background, which can be important components of mass concentration of PM_{10} and $PM_{2.5}$. Notably, from the CPF results, some cross-border emitters in the northeast are 440 likely to be significant pollution sources at high wind speeds. Future measurements and chemical analyses of multi-pollutants are recommended to verify and elucidate potential source characteristics and related atmospheric processes.

445 4. Conclusions

In this study, particle number concentration and size distribution in the size range of 5-1000 nm were measured during the southwest monsoon season in 2017 in Singapore. PMF using particle number concentration and size distribution data was performed for the first time in the region. Results of 450 this investigation can be considered as a baseline for Singapore airborne PM emissions. From this study, particles in the nucleation mode are discovered as the largest contributor to the total number concentration. Nucleation events were found prominent in the diurnal pattern of PM spectra because of the abundant radiation.

455 Five major sources were identified with PMF modeling: aged traffic and industrial emissions, atmospheric photochemical reactions, fresh traffic emissions, urban background and fuel combustion. The airborne PM emissions in tropical urban environment are found to have 43% of particles originated from

nucleation-related processes, which is higher than the available monitoring
460 data in other big cities. Among them, O₃-related atmospheric photochemical
reactions with peak size at 10-12 nm is a unique factor prominent in early
afternoon. The source analysis in this study could be a reference for future
studies in Southeast Asia and other tropical large cities.

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Supplementary Information

Size spectra and source apportionment of fine particulates in tropical urban environment during southwest monsoon season

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- 2. Figure S1.** Temporal trend in mass concentrations of PM₁₀, PM_{2.5}, O₃, NO₂, SO₂ and CO during the measurement campaign (mg/m³ for CO and µg/m³ for the rest). PM₁₀, PM_{2.5} and SO₂ are presented by 24-hour mean value. O₃ and CO are presented by 8-hour mean value. NO₂ is presented by 1-hour mean value. Data are provided by NEA from data.gov.sg/group/environment.

Table S1 Key parameters in PMF solutions with different factor numbers.

	3 factors	4 factors	5 factors	6 factors	7 factors
Qexpected (Qe)	229463	222254	215045	207836	200627
Qrobust (Qr)	688816	417538	224770	142128	88535
Qr/Qe	3.00	1.88	1.05	0.68	0.44
R² (total con.)	0.795	0.827	0.943	0.957	0.965
Slope (total con.)	0.791	0.809	0.922	0.933	0.941
BS (<100%)	-	2	0	1	-
DISP swaps	-	0	0	0	-
BS-DISP swaps	-	0	0	0	-

Figure S1. Temporal trend in mass concentrations of PM_{10} , $\text{PM}_{2.5}$, O_3 , NO_2 , SO_2 and CO during the measurement campaign (mg/m^3 for CO and $\mu\text{g}/\text{m}^3$ for the rest). The shaded area represents the 95% confidence interval.