Characteristics of airborne particle number size distributions in a coastal-urban environment

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\textbf{ABSTRACT}

Particle number size distributions are among the most important parameters in trying to understand the characteristics of particle population. Atmospheric particles were measured in an interaction of mixed environments in the Southeastern coastal city of Wollongong, Australia, during a comprehensive field campaign known as Measurements of Urban, Marine and Biogenic Air (MUMBA). MUMBA ran in summer season between 21\textsuperscript{st} December 2012 and 15\textsuperscript{th} February 2013. Particle number concentrations measured during this campaign were indicative of the interplay between marine environments and urban air which met the objective of this campaign. Particle number size distributions ranging from 14 nm to 660 nm in diameter, as measured by Scanning Mobility Particle Sizer (SMPS) in this study, were grouped using Principal Component Analysis. Based on strong component loadings (value $\geq 0.75$), three different factors were identified (i) Small Factor ($N_S$): $15 \text{ nm} < D_p < 50 \text{ nm}$, (ii) Medium Factor ($N_M$): $60 \text{ nm} < D_p < 150 \text{ nm}$ and (iii) Large Factor ($N_L$): $210 \text{ nm} < D_p < 450 \text{ nm}$. The three factors describe 89\% of the dataset cumulative variance. Particles in this region are dependent upon the interaction between the sources, and cannot be viewed as a simple mixture of biogenic and anthropogenic sources associated with various mechanical processes. The particles observed in the morning were found to be influenced by combustion emissions, presumably primarily from traffic, which is most obvious in $N_S$. The particle population during the day was found to be influenced by a mixture of marine sources and secondary aerosols production initiated by photochemical oxidation. The local steel works and the urban environment were the major contributors of particles at night. Secondary organic aerosols were identified in this study by the mass ratio of organic carbon to elemental carbon (OC/EC). Biogenic sources influenced secondary organic aerosols formation as a moderate correlation ($R^2 = 0.6$) was observed between secondary organic aerosols mass and biogenic isoprene. The processes described in this paper are likely repeated at other coastal urban environments worldwide.

\textbf{1. Introduction}

Atmospheric aerosols are a complex local, regional and global issue. As reported by the IPCC (2014), aerosols continue to contribute the largest uncertainty to the global radiative forcing estimates. In addition, aerosols are the second largest factor after CO$_2$ influencing global radiative forcing, with the estimated value of $-0.9$ [−1.9 to −0.1]W m$^{-2}$ (with the values in parenthesis representing the uncertainty). Aerosols have the ability to directly affect the global radiative forcing by scattering or/and absorption of solar radiation. Furthermore, smaller size aerosols (ultra-fine particles < 100 nm in diameter) can be activated as cloud condensation nuclei which can alter cloud albedo in what is referred to as aerosol indirect effect (IPCC, 2014; Dusek et al., 2006; Petters and Kreidenweis, 2007). Current health concerns relating to air quality are focused on the inhalation of ultra-fine particles as well as fine particles (particles with aerodynamic diameter less than 2.5 μm). Studies have shown a correlation between fine particulate matter and various health conditions, particularly respiratory and cardiovascular disease (WHO et al., 2013; Pope III and Dockery, 2006; Sun et al., 2010). Fine particles are able to enter the respiratory system and reach deep into the lungs (Morawska et al., 2004). Toxicological data suggest that ultra-fine particles can cause adverse pulmonary and

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new particles by nucleation are known as secondary aerosols (Duh et al., 2015; Pöschl, 2005). The particle number and size distribution depend greatly on numerous factors. Particles in the atmosphere that are emitted directly from emission sources are known as primary aerosols. Meanwhile, particles formed from the conversion of gases emitted into the atmosphere into solids either by condensing on existing particles or forming new particles by nucleation are known as secondary aerosols (Duh et al., 2008; Harrison et al., 2012; Seinfeld and Pandis, 2016). Examples of sources of primary aerosols include incomplete combustion of fossil fuels, wind-driven or traffic-related suspension of road dust and sea salt (Kumar et al., 2010; Kim et al., 2015). Examples of secondary products are sulfate (e.g. from SO2), nitrate (e.g. from NOx) and aerosol organic carbon species (Kim et al., 2015). Meteorological conditions including wind speed, wind direction, temperature and solar radiation play an important role in the physical and chemical modification of airborne particles. Meteorology also defines the atmospheric stability and therefore impacts on the atmospheric vertical mixing. For example, wind circulation significantly modifies the near surface aerosols over the coastal area (O'Dowd et al., 2002). Lowering the temperature can lead to the transformation of gaseous compounds to liquid or solid phases due to a lowering of the equilibrium vapour pressure. Solar radiation promotes the photochemical processes which probably lead to the formation of new particles (Charron et al., 2004).

There have been a number of sampling efforts to measure particle size distributions in urban, rural and remote sites around the globe. However, most of those studies were conducted in the Northern Hemisphere (Kulmala et al., 2004). In the Southern Hemisphere, for example in Australia, air quality studies have focused on remote areas with the objective of studying the well-mixed background conditions in comparison to the Northern hemisphere (Fisher et al., 2015). Examples of aerosol studies in Australia include the work of Salimi et al. (2017), Cheung et al. (2011) and Mojia et al. (2007) focused on the urban environment. These studies focused on particle sizes ranging from 9 nm to 414 nm, 4 nm - 110 nm and 15 nm - 630 nm, respectively. Ristovski et al. (2010) studied particle sizes ranging from 5 nm to 168 nm in eucalyptus forests. Modini et al. (2009) studied particle sizes ranging from 4 nm to 165 nm in a sub-tropical clean marine site. Meanwhile, Cainey et al. (2007) studied two sets of particle sizes which ranged from 6 nm to 150 nm and from 14 nm to 700 nm at a clean marine mid-latitude site.

The study presented here uses data from a campaign that focused on the air quality in a coastal-urban environment that is surrounded by a large scale dense forest. There is a steep forested escarpment which begins about 3 km west of the measuring site. The forest covers 20 km (east to west) and 60 km (north to south) consisting of the different forest types, from sub-tropical rainforest to eucalypt trees and towering eucalypts. This forest is dominated by eucalypts (NSW, 2017; Paton-Walsh et al., 2017). This campaign was known as Measurements of Urban, Marine and Biogenic Air (MUMBA). Unlike Northern Hemisphere locations, the background atmosphere in this region is largely free of anthropogenic sources. This campaign was unique because unlike other studies which have been done in this region, the measurements cover the interaction of mixed emission from the ocean, forest and urban environments. To date, this environment has rarely been studied. More details on this campaign can be found in the work by Paton-Walsh et al. (2017) and Guérette et al. (2017). The main objective of the work presented here was to analyse the characteristics of the observed particle size distributions and their spatial-temporal changes within the study area as well as the identification of potential particle sources.

This study is important to provide better understanding of the aerosol microphysical properties especially the particle number size distribution and particle number concentration in a mixed environment. Classification of particle number concentrations using principal component analysis allow particle populations to be classified according to their observed characteristics. Furthermore, the impact of distant (greater than say 200 km) anthropogenic sources in this region are low. As illustrated by back trajectories (Fig. 1(b) and Supplementary, Fig. S4), the sampled air was largely free from aged (multi-day) anthropogenic sourced particles. This help to improve our understanding of the anthropogenic impacts on the particle population characteristics. Large biogenic sources close to urban areas on the coast are relatively common and this site offers the potential to study the interaction of biogenic volatile organic compounds with airborne particles.

2. Methodology

2.1. Background of the measurement site

The MUMBA campaign ran for approximately two months (21st December 2012 to 15th February 2013) during the local summer. The aerosol instruments, which are the focus of this paper, were deployed for only one month (covering the period of 16th January to 15th February 2013). The study area was the coastal city of Wollongong, located in the Illawarra region of New South Wales, Australia, approximately 80 km south of Sydney. The main measurement site of the MUMBA campaign was positioned at 34.397°S and 150.900°E, within the University of Wollongong, Campus East (Fig. 1(a)). The site is an urban area, located near highways, train lines and housing. To the northwest of the site, there is a suburb (Fairy Meadow) which contains a large strip of commercial and industrial activity. A coastal nature reserve called Puckey’s Estate Reserve, dominated by wetland areas, is located to the east of the site. There is a sports park known as Thomas Dalton Park immediately northeast of the site.

Approximately 10 km south from the site is Port Kembla, an active industrial suburb and harbour with a large local steel works industry, and 3 km south from the site is the Wollongong central business district. There is also a large scale forest nature reserve, known as the Illawarra Escarpment conservation area, on steep slopes approximately 3 km to the west of the site.

Fig. 1(b) illustrates that the site received air masses from the ocean most of the time during the campaign as shown by four clusters of 48-h backward trajectories (as discussed in more detail in section 2.2.3). This implies that other than local sources, the monitoring site was also influenced by oceanic sources. During the campaign, high average particle number concentrations were observed in the south and northeast sector. Under low wind speed conditions, high average particle number concentrations were observed in the southwest and southeast (Fig. 1(c)). Factors that contribute to this observation are discussed in Section 3.3. We also studied the spatial distribution of particles population using median number concentration. Both average and median number concentration gave similar observations (details not included in this work). The temperature measured during the campaign ranged from 14 °C to 44 °C. Fig. 1(d) shows the diurnal cycle of temperature, global irradiance, wind speed and wind direction where hourly mean values were used in these plots. The mean diurnal temperature ranged between 20 °C and 24 °C. In general, clear days were experienced...
during the campaign which resulted in a mean global irradiance of 700 W m$^{-2}$ at noon. Low wind speeds generally occurred in the morning, increasing in the middle of the day and decreasing for the rest of the day. The general pattern in wind direction observed during the campaign was westerly winds observed overnight and early in the morning and easterly winds in the middle of the day (Fig. 1 (d)). Full details of the meteorological conditions during the campaign are given in the study by Paton-Walsh et al. (2017).

### 2.2. Instrumentation and data processing

#### 2.2.1. Particle number size distribution and carbonaceous aerosol

A large range of instruments were used to study atmospheric composition during the campaign. Paton-Walsh et al. (2017) and Guérette et al. (2017) have described in detail the instrumentation as well as the data processing. Data obtained from this campaign have been published online at PANGAEA (https://doi.pangaea.de/10.1594/PANGAEA.871982). Particle number size distribution was measured by a Scanning Mobility Particle Sizer (SMPS). This instrument measures the number of particles within 64 size bins with electrical equivalent diameters from 14 nm to 660 nm. It consists of an electrostatic classifier (TSI model 3080, USA), a differential mobility analyser (TSI model 3081, USA) and a condensation particle counter (TSI model 3772, USA). Sampling of the particle number size distribution was performed at ambient relative humidity (i.e. no drying was performed) and instruments were housed inside at temperatures within a few degrees of ambient, but within instrument operational limits. Measurement of particle populations in ambient conditions allows more accurate exploration of the dataset relative to ambient conditions. Sampling close to ambient temperature also avoids issues associated with hygroscopic growth during sampling. Daily instrument checks were performed during the campaign which involved tests for leaks (zero check), flow rates (for later flow rate corrections) and other instrument parameters such as butanol levels and sample distribution assessments. Size distribution inversions were performed using the instruments built-in software export tool deployed within the Aerosol Instrument Management software suite. Quality control/assurance procedures involved corrections for flow rate deviations (a factor of 1.24), corrections for inlet losses (factor of 0.90), as well as removal of periods when instrument parameters were out of specification.
In addition to particle number range from 14 nm to 660 nm, total particle concentrations with a diameter larger than 3 nm (CN₃) were measured using an Ultrafine Condensation Particle Counter (TSI model 3776, USA). Fine particle mass (with an aerodynamic diameter of less than 2.5 μm, PM₂.₅) were measured by an eSampler aerosol monitor (model 9800, Met One Instruments, USA). The eSampler makes two measurements; continuous real-time particle loadings are obtained by light scattering measurements, calibrated using a gravimetric measurement of the cumulative particle loading on filters changed weekly. Carbonaceous aerosol samples (elemental carbon (EC) and organic carbon (OC)) were obtained from filter samples of total PM₂.₅ aerosol which were collected using an Ecotech High Volume Air Sampler (model 3000). EC and OC were measured and analysed in the lab after the campaign using a Thermal Optical Carbon Analyser (model 2001A, Met One Instruments, USA).

2.2.2. Trace gases, physical parameters and traffic data

Additional data were used to assist in the interpretation of the aerosol data. These data included (a) NOₓ, CO and O₃ (b) volatile organic compounds and (c) meteorological parameters (temperature (°C), relative humidity (%), wind speed (m s⁻¹) and wind direction (°) together with global irradiance (W m⁻²) (details in Paton-Walsh et al. (2017) and Guérette et al. (2017)). The global irradiance was measured at the University of Wollongong, 2 km southwest of the campaign site. Traffic volume (number of vehicles per hour) reported with hourly resolution was obtained from the Roads and Maritime Services, New South Wales Government agency. The traffic data were collected from the three nearby traffic volume viewer sites (Fig. 1a). The particle number size distribution, trace gases and meteorological data used in this study were converted into 10-min averaged data for analysis and figure plotting. All data represented here are in Australian Eastern Standard Time (AEST (UTC + 10)) although summer time was in operation.

2.2.3. Multivariate analysis and HYSPLIT

Multivariate analysis (Principal Component Analysis, PCA) was used to determine the most significant particle diameters that account for the variance in the observed particle size distributions. PCA is capable of reducing the dimensionality, transforming a set of inter-correlated variables into a set of uncorrelated variables. In this present work, the variables are particle size distributions. PCA analysis was run using the Statistical Package for the Social Sciences (SPSS) statistics Base software version 21 (IBM, USA).

The paths of air masses were estimated using the Hybrid-Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler et al., 2016; Draxler and Rolph, 2003). The input data for the model were reanalysis datasets available from NOAA’s Air Resources Laboratory archive. The application of back trajectories in this study provides a regional scale view of the origin of air masses arriving at the measuring site. 48-h backward trajectories were used to determine the origin of air masses at the study area using gridded meteorological data at six-hour time intervals, with the calculation beginning at 100 m and 500 m above ground level. Four clusters were obtained in this study and each cluster is indicated by different line colours in Fig. 1(b) and Supplementary, Fig. S4. Details of the trajectory cluster analysis are given in Draxler et al. (2016).

3. Results and discussion

There are three major aims discussed in this present work. The first is the characterisation of the particle number size distribution (cm⁻³) and particle mass (μg m⁻³) (Section 3.1). The second is the identification of emission sources of particles (Section 3.2) and the third is understanding the variability in terms of temporal and spatial variation of particle number which is presented in Section 3.3.

3.1. Particle number size distribution

The campaign site experienced the interaction of biogenic, marine and urban sources during the campaign. This interaction resulted in a variety of atmospheric conditions from clean to polluted air and mixing of primary emissions from different sources as well as secondary production from precursor emissions. Results from this study are compared with other studies which are shown in Table 1. Hussein et al. (2004) has reported that ultra-fine particles contributed 80% of the total particle number count, especially in urban air. Harrison et al. (2011) stated that ultra-fine particles significantly contribute to the total particle number concentration. Information on ultra-fine particles in this study (PNC between 3 nm and 100 nm) was determined by using total CN₃ data measured by the ultrafine CPC and the PNC measured by SMPS as illustrated in Equations (1)–(3). Particles from 3 nm to 14 nm (abbreviated as “a”) was obtained by subtracting total PNC from total CN₃. Then “a” added to the sum of particle number from 14 nm to 100 nm (abbreviated as “b”) to get PNC between 3 nm and 100 nm (abbreviated as “c”).

\[ a = \text{Total CN}_3 - \text{Total PNC} \]
\[ b = \text{sum of PNC from PNC}_{14} \text{ to PNC}_{100} \]
\[ c = a + b \]

The mean and median of particle number concentration for the size range 3 nm–100 nm over the period of 16th January 2013 to 15th February 2013 was \(7.1 \times 10^3\) cm⁻³ and \(5.2 \times 10^3\) cm⁻³, respectively.

<table>
<thead>
<tr>
<th>Study</th>
<th>Site</th>
<th>Size (nm)</th>
<th>PNC a (cm⁻³)</th>
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<td>7.0</td>
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<table>
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<th>Size (nm)</th>
<th>PNC b (cm⁻³)</th>
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<td>14–673</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 1

Comparison between this study other studies. PNC is particle number concentration. NA is not available.

Mean Median Quartile, Q1 (25% percentile) Quartile, Q3 (75% percentile)
Ultra-fine particles made a large contribution to the total number concentration. The number size distributions of average particles number (Supplementary, Fig. S1 (b)) illustrates that ultra-fine particles dominated the particle population. The value obtained in this study is comparable to the value reported by Cheung et al. (2011) for a subtropical urban environment in Australia from January to December 2009 (Table 1).

The 10-min average particle number concentration over the size range of 14 nm–660 nm measured in this present work ranged between $3.6 \times 10^4$ cm$^{-3}$ and $1.8 \times 10^6$ cm$^{-3}$ and the mean and median value were $5.2 \times 10^4$ cm$^{-3}$ and $3.1 \times 10^5$ cm$^{-3}$, respectively. Comparison between the particle number concentration obtained in this study and other studies at coastal environments is shown in Table 1. The mean values obtained in this study are comparable to a study by Peng et al. (2014) from October to November 2011 in China and by Sorribas et al. (2011) at a coastal-rural environment in Spain between August 2004 and July 2006. The mean value of particles number range from 14 nm to 660 nm in this study was lower than the study by Pey et al. (2008) at the coastal-urban environment in Barcelona from November 2003 to December 2004, with a mean value of $16.9 \times 10^5$ cm$^{-3}$. With this comparison, one can conclude that the particle number concentrations observed during this campaign fell within the particle number concentration observed elsewhere in marine and urban environments.

The daily average mass concentration of PM$_{2.5}$ measured during the aerosol phase of the MUMBA campaign was 6.1 μg m$^{-3}$ with a maximum daily average of 22.1 μg m$^{-3}$. The daily average of PM$_{2.5}$ measured nearby by the Office of Environment and Heritage (OEH) for the same time period was 6.2 μg m$^{-3}$. The OEH station is located approximately 3 km from the MUMBA campaign site. This suggests that the two sites are comparable in terms of the sources they are exposed to. The daily average of PM$_{2.5}$ obtained in this study was always below the maximum allowable daily average as specified in the Australian National Environment Protection (Ambient Air Quality) Measure (Air NEPM) which is (25 μg m$^{-3}$, not to be exceeded) and the United States Environmental Protection Agency, US EPA (35 μg m$^{-3}$, 98th percentile, averaged over 3 years).

Principal component analysis (PCA) with varimax rotation was then performed on the total particle number size range (14 nm - 660 nm) measured by the SMPS in order to identify the characteristics of the particles. This analysis is another alternative way to determine particle size classification. This practice allows particles classification to be determined by the characteristics of the particle population measured during the campaign. Eigenvalues of more than one are used in the varimax rotation to obtain the significant factors (Kim and Mueller, 1987). Distribution of component loadings obtained from PCA are illustrated in Fig. 2. Component loadings (factor loadings), reflect the correlation between the factors and variables. In this study, strong component loadings value (≥ 0.75 Liu et al. (2003)) that is only those sizes where one PCA component dominated, were chosen for result interpretation.

Three factors that describe 89% of the cumulative variance were identified. Given their distribution, Factor 1 is labelled as the Small Factor ($N_{S}$) (14 nm < $D_{p}$ < 50 nm), Factor 2 is labelled as the Medium Factor ($N_{M}$) (60 nm < $D_{p}$ < 150 nm) and Factor 3 is labelled as the Large Factor ($N_{L}$) (210 nm < $D_{p}$ < 450 nm). Both Factor 1 and Factor 2 describes 31% of the variability meanwhile, Factor 3 describes 27%. The Small, Medium and Large factors used in this study are approximately equivalent to Nucleation mode, Aitken mode and Accumulation mode, respectively. Temporal and spatial variations in these factors are discussed in Section 3.3.

3.2. Identification of emission sources

The determination of probable sources has been studied by relating the particle number concentrations to carbonaceous aerosols concentrations. The characteristics of carbonaceous aerosols can be generally interpreted by considering organic carbon (OC), elemental carbon (EC) and the sum of these, Total Carbon (TC = OC + EC). EC is a primary pollutant released into the atmosphere mainly during the incomplete combustion of fossil fuels and biomass. OC is formed from both primary sources and secondary formation processes (Tian et al., 2013). Measurements of OC and EC have been made during the campaign using a PM$_{2.5}$ high volume sampler (details in Paton-Walsh et al. (2017)). The high volume sampling times were morning (4:00 to 9:00) and afternoon (10:00 to 18:00). Overall, the average mass of PM$_{2.5}$ in the morning and afternoon was comparable. The percentage of total carbon in PM$_{2.5}$ was higher in the morning compared to the afternoon (Supplementary, Table S1). This observation is attributed to the higher concentrations of EC measured, presumably due to the morning traffic. This coincided with the clear morning maximum observed in combustion products such as CO, NO$_x$, benzene and toluene as well as the motor vehicles diurnal pattern (Fig. 3).

According to a study by Turpin and Huntzicker (1995), the sources of carbonaceous particles can be qualitatively estimated by determining the relationship between the OC and EC concentrations. The correlation between the OC and EC should be higher when a major fraction of both OC and EC are emitted by a dominant primary source (e.g., biomass burning, coal combustion or motor vehicular exhaust). Lin et al. (2009) used measurements at a coastal and urban area in Taiwan to define a good correlation between OC and EC with $R^2$ value is equal to 0.8 or more. They defined a weak correlation for $R^2$ is ≤ 0.4. In the present

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**Fig. 2.** Distribution of component loadings on the entire 10-min average particle number concentration. Only component loadings that are equal to and greater than 0.75 are used to interpret the results. Note: x-axis is in log scale.
study, the $R^2$ value obtained for OC to EC was 0.3 (n = 35) for the aerosol measurement period. This value suggests that there is a possibility that OC and EC are not predominantly from a common source. Similar observations were made by Na et al. (2004) in a semi-rural area in California. However, Cao et al. (2007) observed a good correlation between OC and EC at Qingdao and Xiamen (both developing coastal cities in China) with $R^2$ value of 0.78 and 0.87, respectively.

The mass ratio of OC to EC (OC/EC) provides information about the emission sources of aerosols. The mean (median) value of OC/EC in this study is 6.9 (5.0). This value is comparable with the measurement made at a semi-rural area in the California by Na et al. (2004) with a mean value of 6.1. However, the mean OC/EC value obtained in this study is higher than reported by Cao et al. (2007) in Qingdao and Xiamen, of 3.5. Weijers and Schaap (2013) and Pachauri et al. (2013) have concluded that there is a formation of SOA if the OC/EC ratio exceeds 1.0.

Table 2

<table>
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<tr>
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<th>SOA</th>
<th>$R^2$</th>
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<td>SOA, Bioiso</td>
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<td>Afternoon</td>
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<tr>
<td>Afternoon</td>
<td>Morning</td>
<td>0.007</td>
<td></td>
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</table>

Total Isoprene = Biogenic Isoprene + Anthropogenic Isoprene

The anthropogenic isoprene contribution calculation (Eq. (6)) has been determined by using the method proposed by Borbon et al. (2001) and Duane et al. (2002) which assumes that anthropogenic isoprene is 5% of Benzene. The calculation of biogenic and anthropogenic isoprene is presented in Table S2, supplementary materials. The percentages of the average anthropogenic isoprene in the morning and in the afternoon were 3.2% and 1.6%, respectively. $R^2$ values observed between SOA and biogenic isoprene were stronger than between SOA and anthropogenic isoprene (Table 2), indicating that biogenic isoprene played a stronger role than anthropogenic isoprene in the formation of SOA during the aerosol measurements period of the campaign. Paton-Walsh et al. (2017) has reported that there were biogenic influences as there are high levels of isoprene and monoterpenes observed which are important for both ozone (O$_3$) formation and secondary organic aerosol formation in the region. The biogenic sources (e.g. isoprene and monoterpenes) were from a nearby forested region which is dominated by eucalypt forest. A study by Emmerson et al. (2016) which focuses on current estimates of biogenic emission from eucalypts for southeastern Australia highlights the potential of eucalypts forest to emit isoprene and monoterpenes.

3.3. Temporal and spatial variation of particle number

Fig. 3 presents the diurnal patterns of the particle number concentration for the Small ($N_s$), Medium ($N_{M}$) and Large ($N_L$) factors. We also studied the diurnal variation of total particle number concentration, $N_T$ (Supplementary, Fig. S1 (a)). $N_s$ and $N_L$ show similar patterns because $N_s$ contributes the most to the total particle number concentration as shown in the number size distributions of average particles number (Supplementary, Fig. S1 (b)). Data on 22$^{nd}$ January 2013 at different times were used to illustrate the effects of different sources on the number size distribution (Supplementary, Fig. S2). For reference, several trace gas species have also been included. Three different time frames were created based on the observed particles’ temporal variation (Fig. 3) as well as matching the high volume sampler time periods. The three time frames used are: (i) Morning (4:00 to 9:00); (ii) Afternoon (10:00 to 18:00) and (iii) Night (21:00 to 23:00). These time period definitions will be used for further analyses.

Bivariate polar plots are a useful way to show the variation of a variable's concentration with wind speed and wind direction in polar coordinates. Wind direction together with wind speed can effectively cluster and discriminate different emission sources. Hence, together with the time series, bivariate polar plots have also been used to study the distribution of the particle number (Figs. 4-6). In a bivariate polar plot, wind speed is plotted as the distance from origin and wind direction as the angle. The colour is the average value of the variable (Carslaw and Ropkins, 2012; Uria-Tellaetxe and Carslaw, 2014). Plots using the median (instead of the mean) and using a log-scale gave similar results to Figs. 4-6 and are not shown here.
morning compared to in the afternoon (Supplementary, Table S1). This conclusion is in line with the inference drawn from the EC observations, where higher EC concentrations are observed in the morning compared to in the afternoon (Supplementary, Table S1) presumably due to fossil fuel use. A study by Mejia et al. (2007) observed similar morning peak around 6:00 to 10:00 at the suburban area of Brisbane, Australia. Particle number distribution on the 22nd January 2013 at 5:00 and 6:00 (Supplementary, Fig. S2) showed two peaks. The first peak was approximately at 20 nm and the second peak was approximately at 50 nm. Observed peaks are more likely to be driven by morning traffic. Large particles were also measured on this day, however at much lower concentrations than seen for the smaller particles (Supplementary, Fig. S2).

Overall, we conclude that all three factors were influenced by morning traffic emissions, presumably from traffic. The obvious peak observed in \( N_s \) can be attributed to road traffic as well as growth of \( N_M \) into bigger size particles. A clear maximum concentration followed by a significant decrease in \( N_s \) and combustion products in the morning but not observed in \( N_s \) and \( N_M \) factors, indicate that \( N_S \) and \( N_M \) factors were influenced by other undefined sources. This observation could be also caused by the accumulation of pollutants overnight.

Morawska et al. (2008) reported that particles with size range from 20 nm to 130 nm in suburban Brisbane, Queensland came from vehicle emission. Ristovski et al. (2006) found that particles ranging from 20 nm to 60 nm and 20 nm to 130 nm are related to petrol and diesel engine exhaust, respectively. Harris and Maricq (2001) conclude that particle mean size diameters in the range of 40 nm to 80 nm correspond to petrol fuelled engines while, 60 nm to 120 nm correspond to diesel fuelled engines. Other studies, including Kittelson et al. (2000) reported that particles with size ranging from 50 nm to 300 nm are related to vehicle emissions. Vu et al. (2015) state that particles ranging from 100 nm to 1000 nm in urban areas were from road vehicles mainly generated from the combustion of fuel and lubricants as well as growth of Aitken mode (30 nm < \( D_p < 100 \) nm). Pey et al. (2008) reported that diesel vehicles also emitted accumulation mode particles (50 nm < \( D_p < 1000 \) nm). Using these observations, one can expect for this current study, \( N_S \) (14 nm–50 nm) to be influenced by emission from petrol fuelled engines. \( N_M \) (60 nm–150 nm) and \( N_L \) (210 nm–450 nm) influenced by diesel engine emissions.

The dependence of \( N_S \), \( N_M \) and \( N_L \) on wind speed and direction in the morning (4:00 to 9:00) is shown in Fig. 4. \( N_S \) shows a high particle number concentration in the northwest and southeast. Observation in the northwest coincides with the location of commercial and industrial properties as well as main highways, roads and the South Coast train line. High particle number concentration in the northwest is not clear in \( N_M \) and \( N_M \) and we presume that is because there are additional sources masking the traffic pattern. Observations in the northeast are related to the transport of pollutants by the north easterly sea breezes carrying pollutants from sources in and around Sydney. Furthermore, observations in the southeast show the transport of pollutants by south easterly winds which carry pollutants from the industrial areas and the Wollongong central business district. The wind was blowing between southwest and southeast during this time frame (Supplementary, Fig. S3). \( N_S \) shows high particle number concentrations from the south. This is consistent with the location of an active industrial suburb and the Wollongong central business district.
3.3.2. Afternoon (10:00 to 18:00)

Afternoon peaks (≈ 11:00–14:00) (Fig. 3) coincide with the peak in global irradiance and ground level ozone concentration and so may be associated with photochemistry. This is also consistent with the observed increased concentrations of secondary organic aerosols (SOA) in the afternoon. The median value of SOA in the afternoon was approximately double the magnitude observed in the morning (Table S1). The generation of SOA is often photochemically initiated (Wang et al., 2016). Meteorological conditions also play a role in the observed afternoon peaks. Sea breezes carry various pollutants including particles as well as precursors for particle formation and growth from other locations to the monitoring station. This situation can affect the particle number distribution. North easterly sea breezes in the afternoon (Fig. S3) carry particles from the Sydney region which can contribute to the observed particle number concentration. Sorribas et al. (2015) also identified sea breeze effects in their study. However, at the same time, the sea breezes can dilute the concentration of particles if there is little urban influence in the incoming air. Decreases in the particle number concentration can also be caused by the greater vertical mixing due to higher solar heating. Particle number distribution on the 22nd January 2013 at 12 noon and 13:00 (Supplementary, Fig. S2) show peaks approximately from 50 nm to 60 nm. Observed peaks are probably influenced by SOA as well as sea breeze.

The spatial distribution of \( N_S \), \( N_M \) and \( N_L \) shows relatively high particle number concentrations coming from the northwest during this time (Fig. 5). This is consistent with the particle sources being near busy highways, roads and also the commercial and industrial areas located in the northwest of the monitoring station. Another potential source that could contribute to particle concentrations is biogenic emissions release from the Illawarra escarpment. The large Illawarra escarpment is dominated by Eucalypt species. Eucalypts are among the highest emitters of biogenic volatile organic compounds in southeastern Australia (Winters et al., 2009; Emmerson et al., 2016). Although the measurement site rarely experienced northwest winds during the aerosol campaign period (Fig. S3), high particle number was measured when we experienced this situation. All factors show reasonably high particle number concentrations at low wind speed from the southeast as well as from the southwest for small and medium factors. These observations were likely driven by local sources of particles.

3.3.3. Night (21:00 to 23:00)

The night peak (22:00–23:00) which is clearly observed in \( N_S \) but is also evident in \( N_M \) and \( N_L \) (Fig. 3) is probably linked to the accumulation of particles from traffic and industrial activities. Peaks at around 20 nm–30 nm were observed on 22nd January 2013 at 22:00 and 23:00 (Supplementary, Fig. S2) which is consistent with the peak observed in \( N_S \) from the diurnal pattern. High particle number concentrations were
observed in winds from the south for all three size factors as illustrated in the spatial distribution plots (Fig. 6). The source is likely to be from Port Kembla, an active industrial area, and the Wollongong central business district.

Fig. 6. Dependence of mean particle number concentration (# cm⁻³), wind speed and wind direction of Small (N₃), Medium (N₄) and Large (N₅) factors in the Night (21:00 to 23:00). Wind speed and wind direction are represented by the concentric circles and coloured shape, respectively. Average particles counts are illustrated by the colour bar. Note that the colour scale varies between plots. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

4. Summary and conclusions

A measurement of the particle number size distribution was conducted over the period of 16th January 2013 to 15th February 2013 in the coastal city of Wollongong, Australia. Particle number concentrations measured during the aerosol measurements period of the MUMBA campaign were influenced by marine and urban air. During the measurement period, the average value recorded from the 10-min average particle number concentration over the size range of 14 nm–660 nm was 5.2 × 10³ cm⁻³. Diurnal variation of the three factors (small, medium and large) obtained from the principal component analysis showed the influence of combustion emission, particularly traffic emissions on particle number concentration during morning peak hours. Overall, distinct sources of particle number were identified which were traffic emissions, industrial activities and marine aerosol. In terms of diurnal cycle, traffic emissions dominated in the morning, photochemical reactions, marine aerosol and local sources particles dominated in the afternoon. Emission from industrial and central business activities dominated at night. The weak correlation between organic carbon and elemental carbon suggests that the population of carbonaceous aerosols were influenced by secondary organic aerosol rather than primary sources such as fossil fuel. In relation to wind direction, particle number concentrations were strongly influenced by sea breezes that carry particles from sources in and around Sydney (north easterly winds) as well as Port Kembla Steel Works and the urban areas (winds from the south). The study shows that meteorological conditions, local and transported sources have a definite influence on the particle population. However, instruments are needed in future research to measure additional aerosol information, such as elemental concentrations. This would improve our knowledge and understanding of aerosol sources and their formation. Future studies on the influence of rainfall on the number size distribution are also needed to understand the characteristics of particle populations. Hopefully, in the future, there will be more studies focusing on this type of environment, where urban sources mix with natural emissions. This study provides a useful stepping stone towards our understanding of complex mixed natural and urban environments, because the atmospheric processes described in this study are likely to be replicated in many other coastal cities worldwide.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2018.05.031.

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