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Investigation into chemistry of new particle formation and growth in subtropical urban environment

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Abstract

The role of different chemical compounds, particularly organics, involved in the new particle formation (NPF) and its consequent growth are not fully understood. Therefore, this study was conducted to investigate the chemistry of aerosol particles during

- ⁵ NPF events in an urban subtropical environment. Aerosol chemical composition was measured along with particle number size distribution (PNSD) and several other air quality parameters at five sites across an urban subtropical environment. An Aerodyne compact Time-of-Flight Aerosol Mass Spectrometer (c-TOF-AMS) and a TSI Scanning Mobility Particle Sizer (SMPS) measured aerosol chemical composition and PNSD, re-
- spectively. Five NPF events, with growth rates in the range 3.3–4.6 nm, were detected at two sites. The NPF events happened on relatively warmer days with lower humidity and higher solar radiation. Temporal percent fractions of nitrate, sulphate, ammonium and organics were modelled using the Generalised Additive Model (GAM), with a basis of penalised spline. Percent fractions of organics increased after the NPF events, while
- ¹⁵ the mass fraction of ammonium and sulphate decreased. This uncovered the important role of organics in the growth of newly formed particles. Three organic markers, factors f_{43} , f_{44} and f_{57} , were calculated and the f_{44} vs. f_{43} trends were compared between nucleation and non-nucleation days. f_{44} vs. f_{43} followed a different pattern on nucleation days compared to non-nucleation days, whereby f_{43} decreased for vehicle emission generated particles, while both f_{44} and f_{43} decreased for NPF generated particles. It was found for the first time that vehicle generated and newly formed particles cluster in different locations on f_{44} vs. f_{43} plot and this finding can be used as a tool for source apportionment of measured particles.

1 Introduction

²⁵ Aerosol particles affect the Earth's climate, air quality and public health, both directly and indirectly (Stevens and Feingold, 2009; Lohmann and Feichter, 2005; Pope



II and Dockery, 2006). Knowledge about their formation, transformation and physical/chemical properties helps in understanding their effects on climate and human health. New particle formation (NPF; also known as nucleation) events have been observed in different locations, including coastal, forested, rural and urban areas (O'Dowd

- et al., 2002; Kulmala et al., 2007; Petäjä et al., 2007; Stanier et al., 2004; Woo et al., 2001; Salma et al., 2011; Cheung et al., 2011; Mejía and Morawska, 2009; Modini et al., 2009), and these events are one of the main sources of ultrafine particles (UFPs; particles smaller than 100 nm), in addition to combustion emitted particles. The significant increase in the number of UFPs after NPF events can potentially cause adverse
 effects on human health, given the increasing evidence of the toxicity of UFPs and their
- role in human mortality and morbidity (Donaldson et al., 2002; WHO, 2005; Ning et al., 2003).

Over the past years, the traditional view of the processes involved in NPF has been evolved in light of the recent breakthroughs in this field. The main findings leading to ¹⁵ the current understanding of NPF events were observations and theoretical prediction of molecular clusters and their size dependent growth via nano-Kohler-type processes (Kulmala et al., 2007, 2013, 2004). It is now understood that this process includes the following steps (I) production of low and extremely low volatile vapours as a results of chemical reaction in the gas phase; (II) clustering; (III) nucleation; (IV) activation of clusters by a different group of vapours; and (V) multicomponent condensation growth

of the activated clusters (Ehn et al., 2014; Riccobono et al., 2014; Kulmala et al., 2014). The chemistry and dynamics of UFPs during NPF events in urban environments have been investigated in only a handful of studies as it was thought that these events tend to happen more in pristine air. However, NPF events have been observed frequently
²⁵ in Brisbane, an urban area in Eastern Australia, and were associated with precursors emitted from traffic and solar radiation (Cheung et al., 2011). Cheung et al. (2011)

characterised the evolution of particle number size distribution (PNSD) in Brisbane and found 65 nucleation events over a one year period, with an average particle growth rate of 4.6 (nm h^{-1}). To date, no study has been conducted to identify the chemical



compounds responsible for NPF and growth using direct measurements in this area. More studies need to be carried out, particularly in less studied areas, using direct measurements techniques, in order to determine the species involved in NPF events and the nature of their contribution. To address this gap in knowledge, the main aim of this study was to determine the role of chemical species in NPF events in a subtropical urban environment.

2 Materials and methods

2.1 Background

This study was performed as part of the "Ultrafine Particles from Traffic Emissions and Children's Health" (UPTECH) project (UPTECH; Salimi et al., 2013). Air quality measurements were conducted for two consecutive weeks at each of 25 sites across the Brisbane Metropolitan Area, in Australia, during the period October 2010 to August 2012. Chemical composition of the aerosol particles were monitored in real-time at five sites, referred to as S1, S4, S11, S12 and S25.

15 2.2 Instrumentation

A TSI SMPS measured PNSD within the size range 9–414 nm. The SMPS system consisted of a TSI 3071 Differential Mobility Analyser (DMA) and a TSI 3782 water-based Condensation Particle Counter (CPC). Particle size detection accuracy of the SMPS system was calibrated at the start of measurements at each site using polystyrene la-

- tex (PSL) particles. In addition, the system sheath and aerosol flow rate were checked every second day. The measured PNSD data were corrected for diffusion loss inside the system and sampling tube. Further information regarding the SMPS's operating conditions and calibration can be found in (Salimi, 2014). An Aerodyne compact Timeof-Flight Aerosol Mass Spectrometer (c-ToF-AMS) was deployed to monitor the chem-
- $_{\rm 25}$ ical composition of aerosol particles in the $\rm PM_1$ fraction in real time. A detailed de-



scription of the sampling method and c-TOF-AMS operation can be found in Crilley et al. (Crilley et al., 2013). Briefly, the c-TOF-AMS was housed in a vacant room at each site and sampled for 2–3 weeks. The sampling interval was 5 min, alternating equally between particle time of flight and mass spectrometer modes. The instrument was calibrated for both ion efficiency and particle size at the beginning of measurements at each site, and ion efficiency calibration was also performed in the middle and at the end of measurement campaigns at each site. The issue related to particle size mentioned in (Crilley et al., 2013) has been fixed for this paper as it was a calculation error. All calibrations were performed according to the standard procedures proposed in the literature (Drewnick et al., 2005; Jayne et al., 2000; Jimenez et al., 2003c). Solar

¹⁰ In the literature (Drewnick et al., 2005; Jayne et al., 2000; Jimenez et al., 2003c). Solar radiation and other meteorological parameters were measured by a Monitor Sensors μ Smart Series weather station, a TSI 3781 water-based CPC was used for particle number concentration (PNC) measurements, and a TSI DustTrak measured particle mass concentration (PM_{2.5} and PM₁₀).

15 2.3 Data analysis

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Characterisation of New Particle Formation Events: NPF events were identified and classified using the procedure developed by Dal Maso et al. (2005). PNSD data were analysed to identify a distinct new mode of particles in the nucleation mode size range (particles with diameter less than 30 nm). If the mode grew in size and was persistent for more than one hour, it was assigned as a NPF event. Once identified, the growth rate of the nucleation events were calculated following the procedure described in (Creamean et al., 2011).

Condensation Sink: The surface area of aerosol particles that is available for condensation can be measured using condensation sink (CS). The CS determines the rate of condensation of gaseous molecules on pre-existing particles and is a function of PNSD (Pirjola et al., 1999; Lehtinen et al., 2003). CS, with unit s⁻¹, was calculated



using the following formula (Lehtinen et al., 2003):

$$CS = 2\pi D \int_{0}^{\infty} d_{p} \beta_{M}(d_{p}) n(d_{p}) dd_{p} = 2\pi D \sum_{i} \beta_{M_{i}} d_{p,i} N_{i}$$

Particle Size: Due to the difference in detection limit between the two instruments $(D_{va} = 50 \text{ nm} \text{ for AMS} \text{ and } D_m = 10 \text{ nm} \text{ for SMPS})$, measurement of the mass distribution for the smallest particles detected during each nucleation was delayed for the AMS in order for particles to grow to the detactable size. Ratio of mobility diameter (D_m) , measured by the SMPS, to D_{va} is a function of size, composition, shape and relative humidity for ambient particles. This ratio can be simplified to be equal to particle density, assuming that particles are spherical (Jimenez et al., 2003a). The newly formed particles were assumed to have the density of around 1.8 g cm⁻³ and therefore, $D_m/D_{va} = 1.8$ for newly formed particles (Zhang et al., 2004). Therefore, the AMS's lowest detection limit will be equivalent to a $D_m = 30 \text{ nm}$.

Particle Chemical Composition: Concentrations of sulphate, nitrate, organics and ammonium were measured by a c-TOF-AMS, as these have been identified as the main contributing species to the NPF events and subsequent particulate growth in lit-15 erature (Zhang et al., 2004). These data were processed and analysed using Squirrel v1.51 in Igor Pro v6.22. The organic aerosol (OA) can be divided into oxygenated OA (OOA) and hydrocarbon-like OA (HOA), based upon key m/z ions that have been shown to be surrogates for the different components. OOA can be separated further into low-volatility OOA (LV-OOA) and semi-volatile (SV-OOA). Two main ions, m/z 44 20 (CO_2^+) and m/z 43 (mostly $C_2H_3O^+$), can characterise the evolution of OA in the atmosphere (Ng et al., 2010b). The ratios of m/z 44 and m/z 43 to total signal in the component mass spectrum (f_{44} and f_{43} , respectively) can characterise the degree of oxidation of OA, since the SV-OOA component spectra have a lower f_{44} and higher f_{43} compared to LV-OOA. OA has been shown to occupy a triangular region of the f_{44} vs. 25

 f_{43} plot with younger OA occupying the lower part of the triangle, while more oxidised



(1)

and subsequently more aged OA are concentrated in the upper part (Ng et al., 2010b, 2011). Therefore, f_{43} and f_{44} were calculated and plotted against each other to determine the type and evolution of OA during NPF events. m/z 57 ions have been shown to be a tracer of HOA (primary organics from combustion sources) (Ng et al., 2010a) and therefore, f_{57} was calculated to investigate the OA originated from vehicle emissions.

Generalised Additive Model (GAM): The diurnal trends of chemical components and f_{57} were further analysed using the Generalised Additive Model, with a basis of penalised B-splines (Wood, 2003). This approach allows for the flexible estimation of non-linear relationships without assuming, a priori, the functional form of the non-linearity.

¹⁰ The resulting fitted smooth functions, and their 95 % confidence intervals, indicate the temporal trends of each chemical species and f_{57} .

3 Results and discussion

3.1 Identified new particle formations

After the analysis of PNSD measured at five sites, five NPF events were detected, where three events were observed in S12 and two in S25, while no events were observed at S1, S4 and S11. Therefore, we focused only on S12 and S25, for which the NPF growth rates varied from 3.3 to 4.6 (nm h⁻¹) (Table 1).

Figure 1 summarises the average solar radiation, relative humidity, temperature and CS for days with NPF events (nucleation days), as well as for the days where no NPF
events were observed (non-nucleation days) at S12 and S25. At both sites, nucleation days had higher solar radiation intensity compared to non-nucleation days, which is aligned with similar observations in the literature (Zhang et al., 2004). As expected, similar trends were observed for temperature as well. Lower relative humidity before the start of NPF events was observed on nucleation days compared to non-nucleation
days at S12, whereas higher relative humidity was observed on nucleation days after the start of NPF events. Lower relative humidity was observed on nucleation days



both before and after the start of nucleation at S25, which is in agreement with the observations made by others in similar environments (Birmili and Wiedensohler, 2000; Hamed et al., 2011). CS was found to be lower on nucleation days compared to non-nucleation days, about two hours before the start of nucleation at both sites. Similar

- ⁵ trends have been observed in other studies (Salma et al., 2011; Hussein et al., 2008). CS is a measure of the available surface area for condensation of vapours, as well as for the scavenging of particle clusters. A small CS is favourable for nucleation as it produces less surface area for vapours and newly formed clusters, in agreement with the observations in Fig. 1.
- Figure 2 illustrates the average mass concentration of organics, nitrate, sulphate and ammonium during nucleation and non-nucleation days at S12 and S25. Mass concentration of organics and nitrate followed relatively the same trend through the day until 4–5 p.m. (6–7 h after the start of the NPF event) at S12 and S25.

However, mass concentration of organics and nitrate increased dramatically between

3–10 p.m. on nucleation days, at higher rate compared to non-nucleation days at S12, and the same trend was observed at S25, with an hours delay in the increase of the mass concentration of organics and nitrate. Sulphate and ammonium mass concentration started to increase at 12 p.m., reached a peak and decreased subsequently, however, a significant increase was observed around 4 p.m.

20 3.2 Evolution of chemical composition of newly formed particles

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The analysis and interpretation of the chemical composition of the newly formed particles focusses mostly on the particles in the growth phase due to the lowest detection limit of the C-TOF AMS which does not permit to see them in the formation phase. However, the role of precursors on the NPF events can still be investigated as the condensable vapours responsible for NPF events do condense on pre-existing particles which are detectable by the instrument.

Figure 3 illustrates the evolution of PNSD and mass concentration of chemical species (organics, nitrate, sulphate and ammonium) during the three consecutive NPF



events at S12. In general, size distribution of the aerosol mass species followed the evolution of PNSD, with the exception of ammonium, which showed no particular trend throughout the nucleation events.

The mass concentration of sulphate increased significantly six hours after the start of ⁵ nucleation, when the nucleated particles grew and reached the AMS's lowest detection size limit. The mass concentration of nitrate and organics increased three hours after an increase in sulphate concentration was observed. The same trends were observed in the case of all three nucleation events. Time series of PNSD and mass concentration of particle species during two NPF events happening on two consecutive days at S25 ¹⁰ are illustrated in Fig. 4. Unlike the observations at S12, no distinctive trend in sulphate

- mass concentration was observed during the first event. However, organics and nitrate showed similar trends and ammonium did not display any distinctive trend. Sulphate followed similar trend to this during the events observed at S25.
- It has been previously determined in the literature that the main contributing species to NPF events and subsequent particulate growth are sulphate, nitrate, organics and ammonium (Zhang et al., 2004). Therefore, the percent fractions of each of these chemical species in the size range from 50 to 100 nm (D_{va}) were calculated by dividing the mass concentration of each chemical species by the total (sulphate + nitrate + ammonium + organics). The temporal trend of each species mass pre-
- ²⁰ cent fraction was modelled using the Generalised Additive Model (GAM) with a basis of penalised B-splines. Similar trends for all chemical species were observed at both sites. Ammonium, sulphate and nitrate mass fractions peaked around the start of nucleation and subsequently decreased after the event. However, organics followed the opposite trend, with a significant increase after the start of nucleation (Fig. 5). In other words,
- the fraction of organics increased and the fraction of ammonium, sulphate and nitrate decreased when the newly formed particles reaching the range 50–100 nm (D_{va}), indicating that organics were the main contributor to the growth of newly formed particles.

At S12, the magnitude of mass fractions changed from almost 50, 30, 10, and 10 % before the nucleation to 70, 20, 6, and 4 % after the event for organics, ammonium,



nitrate and sulphate respectively. At S25, the changes in mass fractions were more dramatic as they changed from 40, 40, 12, and 8% before the event to 85, 8, 5, and 2% after the nucleation occurred.

3.3 Role of organics

- 5 As indicated in the previous section, three significant NPF events were observed at S12 on three consecutive days, each event lasted for the rest of the day and was closely followed by the start of another event. In addition, the involvement of organics in NPF events at S12 was higher than at S25, therefore, further data analysis regarding the role of organics were performed at S12. Firstly, f_{43} and f_{44} were calculated for nucleation days and non-nucleation days. f_{44} was plotted against f_{43} at each hour of 10 the day, as well as the triangle space proposed by Ng et al. (2010b) (Figs. 6 and 7). SV-OOA components fell in the lower half of the triangle, while LV-OOA components were concentrated in the upper half. The base of the triangular region included a wide range of f_{43} , which represent less oxidised SV-OOA (Ng et al., 2010b). During the non-nucleation days, the OA was concentrated in the middle and right border of the 15 triangular region, which is the beginning of the LV-OOA region. As expected, the f_{AA} decreased during morning and afternoon rush hours, as the particles were younger and less oxidised, while, f_{43} remained almost unchanged during the day. OA components
- ²⁰ at which time f_{44} decreased while f_{43} remained unchanged.

During the nucleation days, several hours after the start of nucleation, when the particles grew enough to be detected by the AMS, f_{44} and f_{43} both decreased and the aerosol components reached the bottom left side of the triangular region. It is expected that the particles originating from nucleation events cluster somewhere at top of the

fell in the middle right side of the triangular region before the start of morning rush hour,

²⁵ triangle, however, as the particles measured in our study have been originating from nucleation events and primary vehicle emissions, they clustered at the middle right hand side of the triangle.



In order to assess the possible different clustering on f_{44} vs. f_{43} for nucleation days compared to non-nucleation days, *K*-means clustering technique (Hartigan and Wong, 1979) was applied on the whole f_{43} and f_{44} data. Nucleation and non-nucleation days were attributed to two separate clusters after the start of nucleation, while this distinction was not observed prior to the event.

After the start of nucleation and an increase in traffic density, OOA components moved toward the region defined for younger particles. However, during the nucleation events, both f_{44} and f_{43} decreased, while only f_{44} decreased when the particles were generated by the traffic during non-nucleation days (Fig. 8). Particles which originated from traffic emissions and NPF clustered at different locations inside the triangle, indicating that the f_{44} vs. f_{43} data can be used to assign a dominant source (traffic or NPF) of the OA.

It has been reported in the literature that f_{57} is associated with combustion generated primary organics (Canagaratna et al., 2004; Jimenez et al., 2003b). f_{57} was calculated and its diurnal variation was modelled using a GAM model with a basis of panelised Bspline. The results of the modelling showed that f_{57} followed exactly the same trend on nucleation and non-nucleation days, with an increase during the morning and afternoon rush hours. This shows the effect of vehicle generated particles both in nucleation and non-nucleation days and can explain the pattern observed in f_{44} vs. f_{43} plot during

20 nucleation days.

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4 Summary and conclusions

In summary, PNSD, chemical composition and meteorological parameters were measured at five sites across the Brisbane metropolitan area. Five NPF events, with growth rates ranging from 3.3–4.6 nm h⁻¹, were observed, and the NPF events happened on days with relatively lower humidity, and higher solar radiation and temperature than non-event days. Higher sulphate, nitrate, ammonium and organics were observed on nucleation days compared with days when no nucleation was observed. Percent frac-



tions of nitrate, sulphate, ammonium and organic chemical species were calculated and their diurnal trends were modelled using the GAM. Ammonium, sulphate and nitrate mass fractions increased before the start of nucleation, peaked around the start of nucleation and decreased after the event. Conversely, the organics percent fraction

- ⁵ increased significantly after the start of nucleation, indicating the important role of organics in the growth phase of NPF events. f_{44} and f_{43} were analysed to investigate the role of organics more in depth, as the f_{44} vs. f_{43} would reveal information regarding the level of oxidation and volatility of OOA. f_{43} and f_{44} both decreased after the start of nucleation, while f_{44} decreased only in case of particles generated from vehicle emission.
- ¹⁰ Aerosol particles generated by vehicle emissions and NPF events clustered in different locations on the f_{44} vs. f_{43} plot. This determined the application of the f_{44} vs. f_{43} plot for identification of the source/s and transformation of the OOA components as they clearly followed different patterns.
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Table 1. Average growth rates durin	ng the nucleation events.
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Site	start of event	end of event	$GR (nm h^{-1})$
s12	12 Aug 2011 11:00	13 Aug 2011 5:00	3.9
s12	13 Aug 2011 12:30	14 Aug 2011 6:20	4.6
s12	14 Aug 2011 15:20	15 Aug 2011 6:00	3.3
s25	25 Aug 2012 12:24	26 Aug 2012 2:14	4.3
s25	26 Aug 2012 12:00	27 Aug 2012 1:00	3.8





Figure 1. Average diurnal pattern of solar radiation (SR), humidity, temperature and condensation sink (CS) on nucleation and non-nucleation day at S12 and S25. Vertical dotted lines show the start of nucleation.





Figure 2. Average diurnal pattern of organics, nitrate, sulphate and ammonium concentrations on nucleation and non-nucleation days at S12 and S25. Vertical dotted lines show the start of nucleation.

















Figure 5. Mass fraction of each chemical species (sulphate, nitrate, ammonium and organics) during the nucleation events at s12 and s25. Vertical dashed lines represent the point at which the newly formed particles reached the AMS's lowest detection limit.











Figure 7. f_{44} vs. f_{43} at each hour of the day for all data measured at S12 during the nucleation days. The triangle from Ng et al. (2010b) is drawn as a visual aid. Nucleation starts around 10 a.m.





Figure 8. The pattern observed in f_{44} vs. f_{43} plot after the aerosol particles were dominated by either traffic or NPF events.





Figure 9. Diurnal variation of the f_{57} at S12 during the nucleation and non-nucleation days.

