# New Particle Formation Events Observed during the COALA-2020 Campaign

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**Abstract:**

Aerosols play an important role in atmospheric processes influencing cloud formation, scattering and absorbing solar radiation, and ~~as a part of the~~play an important role in chemical reactions affecting the abundance of trace gases in the atmosphere. Ultimately aerosols affect the radiative balance of the earth modifying climate. A large fraction of aerosols is formed through chemical reactions following gas-to-particulate processes in the atmosphere: nucleation, condensation and growth. Biogenic Secondary Organic Aerosols (BSOA) are formed when plant produced volatile organic compounds (VOCs) react in the atmosphere through heterogeneous reactions. ~~South east Australia is one~~One of the ~~locations with the~~ highest ~~emissions of biogenic VOCs~~BVOC emitting regions in the world~~,~~ is South-east Australia due to the high density of *Eucalyptus* species~~, which are high emitters of VOCs~~. The COALA-2020 (Characterizing Organics and Aerosol Loading over Australia) campaign worked towards a better understanding of biogenic VOCs in quasi-pristine conditions in the atmosphere and their role in particle formation.

The observations showed a highly reactive atmosphere with frequent new particle formation (NPF) occurring (50% days with data) often associated with pollution plumes. Analysis of NPF events ~~indicated~~suggested that $SO_2$ ~~and NOx~~ plumes likely triggered particle formation, while particle growth depended on available VOCs, ~~OH concentration~~hydroxyl radicals (influenced by relative humidity), and the presence of multiple $SO_2$ ~~and NOx~~ intrusions promoted growth of smaller clusters. Nighttime NPF events ~~correlated~~coincided with ~~NOx~~monoterpene ozonolysis. One nighttime NPF event showed potential isoprene nitrate oxidation enhancing growth, but the limited night-time data hindered conclusive interpretations. These findings highlight the significant role of biogenic VOCs, ~~especially isoprene,~~ in driving NPF and SOA formation in South-east Australia, even after major wildfires. The COALA-2020 campaign provided valuable insights into local atmospheric chemistry and its potential impact on regional air quality and climate. However, longer-term observations are crucial to understand seasonal variations, trends and extreme events.

**Keywords: COALA-2020; aerosols, BVOCs, NPF.**

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## 1. Introduction

~~Aerosols can influence our health (Annesi-Maesano et al., 2013; Shi et al., 2016) but also play an important role in regulating Earth's energy balance, the hydrological cycle and even the abundance of key chemical species in the atmosphere such as hydroxyl (OH) and indirectly greenhouse gases (e.g., Kerminen et al., 2012). The chemical composition, size and particle concentration determine the effects on health and the environment (Liu et al., 2016b; Pope and Dockery, 2006; Ren et al., 2017). Aerosols can be directly emitted (primary aerosols) or they can be product of interactions in the atmosphere (secondary aerosols) (Pöschl, 2005).~~

~~Secondary aerosols are produced via gas-to-particle transition, where reactive compounds in the atmosphere are oxidised to become low volatility organic compounds (LVOC). These compounds, along with sulfuric acid vapour are often involved in the nucleation process promoting clustering (e.g., Yu and Luo, 2009). Once the clusters (ultrafine particles) are formed, they can grow through coagulation and condensation potentially resulting in cloud condensation nuclei (CCN) (Dal Maso et al., 2005; Hussein et al., 2005; Kulmala et al., 2001). Usually, three distribution modes are used to classify the particle size distributions of ultrafine particles: the nucleation mode (<10 nm), the Aitken mode (10 - 100 nm) and the accumulation mode (> 100 nm). The formation of these molecular clusters and their subsequent growth to larger sizes is denominated new particle formation (NPF).~~

~~Biogenic VOCs play an important role in secondary organic aerosol (SOA) formation (e.g., Mahilang et al., 2021). Monoterpenes have higher SOA formation yields than isoprene (Friedman and Farmer, 2018; Riva et al., 2019; Zhang et al., 2018) but isoprene contributes more than half of the total BVOC emissions in the world making it an important SOA source too (e.g. Fry et al., 2018). Particularly the SOA yield of isoprene oxidised through $NO_3$ at night is reported to be several times the yield observed through the OH oxidation path (e.g. Ng et al., 2008). Recent studies suggest that in biogenic-rich regions isoprene-SOA yield can be much higher than previously reported when considering further oxidation of the products in low $NO_x$ environments (e.g. Liu et al., 2016a), promoting the formation of key condensing species.~~

~~The OH availability in the atmosphere is key to promoting SOA formation (e.g. Song et al., 2019). To form key condensing species, multiple oxidation steps must happen to the original VOC molecule. After a VOC molecule oxidises becoming a more complex and larger OVOC, it is less likely to be oxidised again, particularly when in the presence of other VOCs with higher OH reactivity (Kiendler-Scharr et al., 2009). This was recently demonstrated in different chamber and ambient studies where isoprene mole fractions were many times higher than monoterpenes. In these studies, isoprene scavenged OH, interrupting the formation of $C_{20}$ dimers and reducing the yield of highly oxygenated molecules (HOMs), thereby suppressing the nucleating process driving NPF (Heinritzi et al., 2020; Liu et al., 2016a). This effect is non-linear nor constant and will change with local conditions. High levels of $SO_2$ and VOCs in a humid atmosphere will enhance NPF (Nestorowicz et al., 2018; Song et al., 2019, p.20; Xu et al., 2021).~~

~~Understanding BVOC emissions and their role in SOA formation is important to accurately predict aerosol properties and their impact on climate. However, BVOC are poorly characterized under Australian conditions (Paton-Walsh et al., 2022). MEGAN emissions show south-east Australia as one of the BVOC hot-spots in the region (Guenther et al., 2012) but multiple modelling studies have shown that MEGAN emissions estimation might not be representing local conditions correctly in this region (Emmerson et al., 2016, 2018, 2019). Most of the Australian forested regions are dominated by high emitting *Eucalyptus* species (ABARES, 2019; Aydin~~

~~et al., 2014; Padhy and Varshney, 2005) that combined with periods of temperature and drought stress create the conditions to have high emissions/concentrations of BVOCs in the atmosphere (Emmerson et al., 2020; Fini et al., 2017; Ormeño et al., 2007). The emissions ratios of isoprene to other VOCs are poorly constrained and the local chemistry is not well understood.~~

~~The COALA-2020 campaign worked towards a better understanding of biogenic VOCs in quasi-pristine conditions in the atmosphere and their role in local atmospheric chemistry in south-east Australia. COALA-2020 was a collaborative effort between local institutions including the University of Wollongong, CSIRO, ANSTO, and the University of Sydney, and international peers from Georgia Institute of Technology, The University of California, Irvine, Nagoya University and Lancaster University. This part of the study focused on identifying and characterising NPF events after the "Black Summer" 2019-2020 Australian bushfire season. Here we aimed to identify~~Aerosols can influence our health (Annesi-Maesano et al., 2013; Shi et al., 2016) but also play an important role in regulating Earth's energy balance, the hydrological cycle and even the abundance of key chemical species in the atmosphere such as hydroxyl radical (OH) and indirectly greenhouse gases (e.g., Kerminen et al., 2012). The chemical composition, size and concentrations determine the effects on health and the environment (Liu et al., 2016b; Pope and Dockery, 2006; Ren et al., 2017). Aerosols can be directly emitted (primary aerosols) or they can be product of chemical reactions in the atmosphere (secondary aerosols) (Pöschl, 2005).

Secondary aerosols are produced via gas-to-particle transition. New Particle Formation (NPF) occurs when multiple reactions in the atmosphere create stable molecular clusters. Once the clusters are formed, they can grow through coagulation and condensation potentially resulting in cloud condensation nuclei (CCN) (Dal Maso et al., 2005; Hussein et al., 2005; Kulmala et al., 2001). Multiple factors determinate NPF in the atmosphere including atmosphere composition and boundary conditions (temperature, humidity, PBL height, turbulence) (Bousiotis et al., 2021; Wu et al., 2021a; Xu et al., 2021a). Sulfuric acid ($H_2SO_4$) is one of the main drivers of the nucleation process in the continental boundary layer, but it does not explain all growth and nucleation rates (Sihto et al., 2006). The presence of ammonia ($NH_3$), amines or ions in the atmosphere can enhance $H_2SO_4$ nucleation rates (Kirkby et al., 2023; Zhao et al., 2011; Zheng et al., 2015). High levels of $SO_2$ and Volatile Organic Compounds (VOCs) in a humid atmosphere will enhance NPF (Nestorowicz et al., 2018; Song et al., 2019, p.20; Xu et al., 2021b).

VOCs are a group of carbon-based gases emitted by biological and anthropogenic sources that are characterised by their high vapour pressure (Goldstein and Galbally, 2007; Kesselmeier and Staudt, 1999; Matsui, 2006). VOCs can undergo hydroxyl radical (OH), ozone or nitrate radical (NO3) oxidation in the gas phase, producing compounds of varying volatilities, and products with low enough volatility can contribute to NPF or partition to existing particles, resulting in particle growth.

The most common biogenic VOC (BVOC) is isoprene followed by monoterpenes. BVOCs play an important role in secondary organic aerosol (SOA) formation (e.g., Mahilang et al., 2021). VOCs have been associated with particle growth (Riipinen et al., 2012) but their role and the autoxidation mechanism was not understood until recently (Bianchi et al., 2019). Autoxidation of monoterpenes supports the particle growth process by generating highly oxygenated molecules (HOMs) via the formation of peroxy radicals (Bianchi et al., 2019; Kirkby et al., 2023; Lehtipalo et al., 2018, p.201). HOMs can be characterised as ultra-low VOCs (ULVOC) or extremely low VOCs (ELVOC) depending upon the saturation concentration at 298K.

While oxidation of monoterpenes produces higher SOA formation yields than isoprene resulting to the formation of ULVOC or ELVOC molecules during OH or ozonolysis oxidation(Friedman and Farmer, 2018; Lee et al., 2023; Luo et al., 2024; Riva et al., 2019; Zhang et al., 2018), under the right conditions, isoprene can also lead to SOA formation (e.g. Fry et al., 2018). Isoprene oxidation products can oxidise to LVOC promoting particle growth in the larger sizes (above 3 nm) (Heinritzi et al., 2020). For example, the SOA yield of isoprene oxidised with the nitrate radical at night generates several times the yield observed through the OH oxidation path (e.g. Ng et al., 2008). Recent studies suggest that in biogenic-rich regions isoprene-SOA yield in low $NO_x$ environments can be much higher than previously reported when considering further oxidation of the products (e.g. Liu et al., 2016a), promoting the formation of extremely low or low volatility organic compounds (ELVOC and LVOC respectively) important for particle grow.

Isoprene, monoterpenes, OH and nitrate radical and ozone availability in the atmosphere are key to promoting SOA formation (e.g. Song et al., 2019). As a VOC molecule oxidises it becomes more complex and a larger oxygenated VOC (OVOC),so is less likely to be oxidised again, particularly when in the presence of other VOCs with higher OH reactivity (Kiendler-Scharr et al., 2009). HOMs are key for nucleation, but HOM production in the atmosphere is limited by other reactions/byproducts. Isoprene NPF suppression is one of those cases in which isoprene oxidation products limit the formation of $C_{20}$ dimers and reduce the yield of highly oxygenated molecules (HOMs) in favour of weaker nucleators $C_{15}$ (Dada et al., 2023; Heinritzi et al., 2020; Liu et al., 2016a). This effect is non-linear nor constant and will change with local conditions.

Understanding BVOC emissions and their role in SOA formation is important to accurately predict aerosol properties and their impact on climate. However, BVOC are poorly characterized under Australian conditions (Paton-Walsh et al., 2022). MEGAN emissions show south-east Australia as one of the BVOC hot-spots in the region (Guenther et al., 2012) but multiple modelling studies have shown that MEGAN emissions estimation might not represent local conditions correctly in this region (Emmerson et al., 2016, 2018, 2019). Most of the Australian forested regions are dominated by high emitting *Eucalyptus* species (ABARES, 2019; Aydin et al., 2014; Padhy and Varshney, 2005) that combined with periods of high temperature and drought stress create the conditions for high emissions/concentrations of BVOCs in the atmosphere (Emmerson et al., 2020; Fini et al., 2017; Ormeño et al., 2007). The emissions ratios of isoprene to other VOCs are poorly constrained and the local chemistry is not well understood.

The COALA-2020 campaign worked towards a better understanding of biogenic VOCs in quasi-pristine conditions in the atmosphere and their role in local atmospheric chemistry in south-east Australia. COALA-2020 was a collaborative effort between local institutions including the University of Wollongong, CSIRO, ANSTO, and the University of Sydney, and international peers from Georgia Institute of Technology, The University of California, Irvine, Nagoya University and Lancaster University. This part of the study focused on identifying and characterising NPF events after the “Black Summer” 2019-2020 Australian bushfire season. Here we focus on identifying drivers and conditions in which NPF started or were enhanced in the local environment.

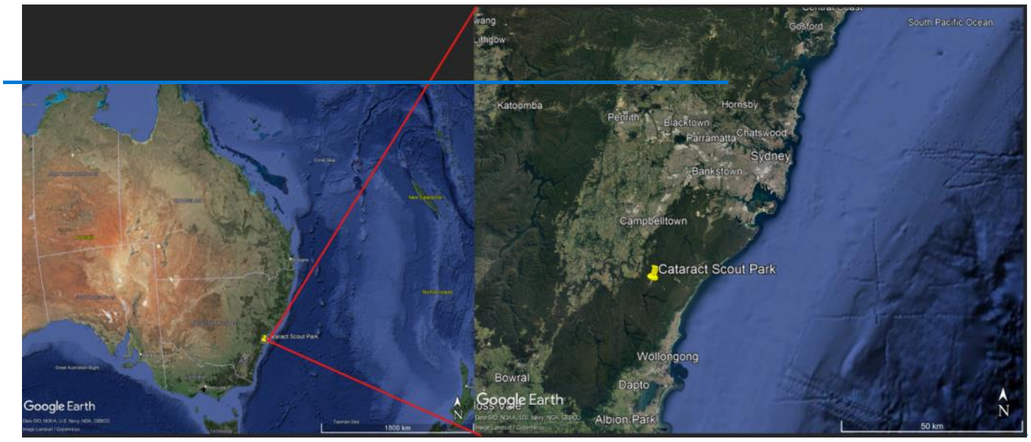
## 2. Materials and Methods

### 2.1 The COALA-2020 Campaign

The COALA-2020 campaign took place at Cataract Scout camp (34°14’44” S, 150°49’26” E) located 20 km north-northwest of Wollongong on the east coast of NSW, Australia. The site is surrounded by a heavily forested area mainly stocked by Eucalyptus species (see Figure 1). North of the sampling site is ~~the Appin Road,~~ a four-lane arterial road connecting the M1 motorway on the east coast with south-western Sydney. Other possible anthropogenic sources impacting the site are two underground coal mine heads, ~~the Appin Colliery (~~located 1.5 km to the northeast~~)~~ and ~~the West Cliff Colliery (~~2.5 km to the north). ~~Besides the close~~Further afield sources ~~it is important to note the proximity of~~include the Sydney suburban area (around 18 km north-west), Sydney city (45 km north), Wollongong urban area and Port Kembla steelworks in the southern part of Wollongong (28 km to the southeast).

The campaign was conducted ~~from~~17 January ~~17th until~~to 23 March~~ 23rd~~, 2020. The first period of the campaign (17 January to 5 February) was heavily impacted by smoke pollution from the bushfires affecting the region ~~until~~On 5 February ~~5th, when a~~A substantial rain event extinguished the fires and cleared the atmosphere of residual smoke pollution ~~(Mouat et al., 2022; Simmons et al., 2022). This period was~~(Mouat et al., 2022; Simmons et al., 2022). The smoke pollution period has been removed from the analysis presented here as we focus on understanding atmospheric processes during more normal conditions. Thus, this paper presents the analysis of BVOCs alongside anthropogenic emissions and their role in NPF during

**Formatted:** Font: (Default) +Body (Calibri), 12 pt, Not Italic, Font color: Auto, English (Australia) *the second part of the COALA-2020 ambient measurements campaign running from 5 February 5th until March 17th 2020.*



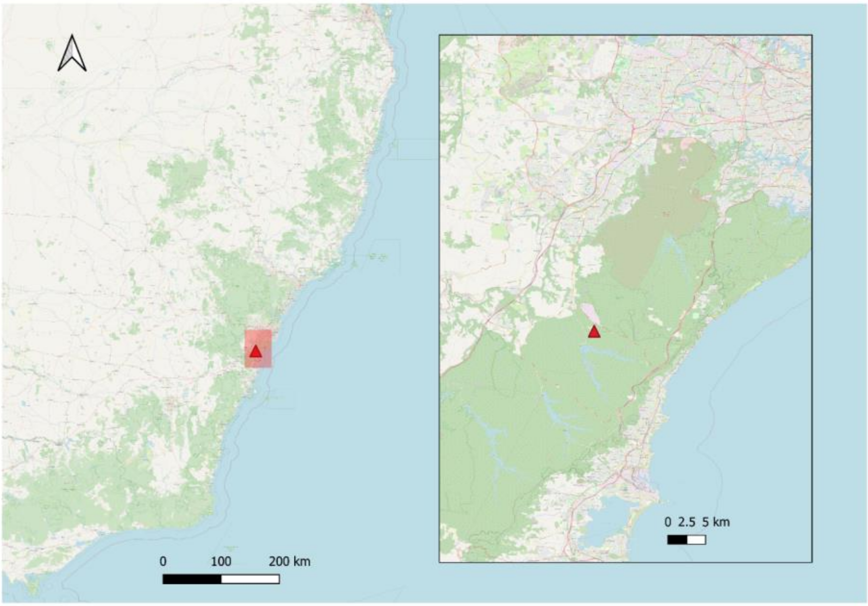


*Figure 1 Location of the sampling site, to Sydney, NSW in the north. The sampling site had four different climate control containers for the instruments, as well as a soil sampling site around 50 meters northeast from the main sampling site and the High-Vol PM filter. ~~Satellite view~~*

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## 2.2 Instrumentation

The instruments deployed in the campaign are presented in **Table 1**. They included an air quality monitoring station owned and operated by the NSW Government Department of Climate Change, Energy, the Environment and Water (DCCEEW), located approximately ~~10m~~10 m away from the main sampling line for VOCs. This station included measurements of temperature, windspeed and direction, PM$_{10}$, PM$_{2.5}$, O$_3$, SO$_2$, NO$_x$, CO and visibility. Inlet heights on this station were between 4.5m to 5.6 m above ground level. All NSW air quality monitoring stations are accredited by the National Association of Testing Authorities (Australia~~).~~ ~~Inlet heights on this station were between 4.5m to 5.6 m above ground level.~~), however it should be noted that these instruments are targeted at regulatory standards and are not research grade. In particular this means that measurements made close to the detection limits are likely to be inaccurate and should be interpreted as indicative measures rather than accurate quantitative measures of atmospheric concentrations.

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VOCs were measured using a Proton Transfer Reaction Mass Spectrometer (Ionicon PTR-ToF-MS 4000) which operated with a mass range spanning m/z = 18-256. The drift tube was held at a temperature of 70° C, pressure at 2.60 mbar, and an electric field to molecular number density ratio of 120 Td. The instrument was housed in a separate climate-controlled unit. Samples were drawn from an inlet on a 10 m mast through a 20 m long PTFE line using a bypass flow of 1.2-3 L min$^{-1}$. Calibrations were made on site using standardized cylinders containing 17 compounds including isoprene, monoterpenes, methyl vinyl ketone (MVK) & methacrolein (MACR), benzene, C$_8$-aromatics, and C$_9$-benzenes ~~(Mouat et al., 2022)~~(Mouat et al., 2022). Mass spectra were integrated to produce data at 1 minute temporal resolution. Mole fractions were further averaged on a five-minute basis.

A suite of aerosol instruments were operated within in the Atmospheric Integrated Research Facility for Boundaries and Oxidative eXperiment (AIRBOX) container ~~(Chen et al., 2019)~~(Chen et al., 2019). Sample air was drawn from a common aerosol bypass inlet. The inlet was located 5 m above ground level for the following instruments:

1. A Ultrafine Condensation Particle Counter (UCPC TSI 3776) was used to measure condensation nuclei number concentration greater than 3 nm (CN$_3$) (TSI Incorporated, Shoreview, MI, USA). The instrument was operated at a sample flow rate of 300 mL min$^{-1}$. Measurements were recorded at 1 Hz temporal resolution.

2. A Scanning Mobility Particle Sizer (SMPS) was used to measure aerosol size distribution between 14 and 670 nm mobility diameter. Full scans of this size range were recorded every five minutes. The system consisted of an X-ray aerosol neutralizer and 3071 Long Electrostatic Classifier (TSI Incorporated, Shoreview, MI, USA) coupled to a 3772 CPC (TSI Incorporated, Shoreview, MI, USA). Sample was drawn from the same inlet as used by the UCPC.

3. Chemical composition of aerosols with diameter smaller than 1 µm (PM$_1$) were taken using a Time-of-Flight Aerosol Chemical Speciation Monitor (ACSM; Aerodyne Research Inc., Billerica, MA, USA). Mass concentrations of organics (Org), sulphate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), and chloride (Cl$^-$) in the aerosol fraction 40-1000 nm vacuum aerodynamic diameter range, referred to as PM$_1$, are reported. Measurements were taken at 10-minute resolution. Sample air was drawn from

the aerosol inlet common to the CPC and SMPS and dried using a Nafion dryer to < 40% relative humidity before sampling.

*Table 1: Instruments deployed during the COALA 2020 campaign and included in the present analysis.*

| Name of parameter | Instrument type |
|---|---|
| $NO$ - $NO_2$ -$NO_x$ | API T204 |
| $O_3$ | Ecotech 9810 |
| $PM_{10}$ | Thermo (TEOM) 1405A |
| $PM_{2.5}$ | Thermo (BAM)5014i |
| $SO_2$ | API T100 |
| Black Carbon | Magee Scientific Aethalometer AE33 |
| VOCs | PTR-ToF-MS (Ionicon) |
| $CO$ - $CO_2$ - $CH_4$ - $N_2O$ | FTIR in situ analyser |
| $CN_3$ | TSI 3776 |
| Particle number size distribution (14 nm to 660 nm) | SMPS |
| $PM_1$ mass composition | Tof-ACSM, Aerodyne |
| Wind Speed and Wind Direction | 2D Ultrasonic anemometer |
| Temperature, Relative humidity | Vaisala HMP155 |
| Photosynthetic active radiation (PAR) | |

### 2.3 NPF Classification Method

~~The method proposed by Dal Maso et al. (2005) was used to classify the particle size distribution data. To apply the method the particle number density plots were made for each day during the campaign. Then the plots were visually inspected to determinate if there was an event. A day of data was classified as an *event* if there was nucleation, meaning growth up to 25nm for at least two hours.~~

The method proposed by Dal Maso et al. (2005) was used to classify the particle size distribution data. To apply the method the particle number density plots were made for each day during the campaign and the plots were visually inspected to identify if an event occurred on that day. A day of data was classified as an *event* if there was nucleation, and growth up to 25nm for at least two hours.

Once the events were classified, a logarithmic fit was applied to determine the ~~geometrical~~geometric diameter of each mode. The data was manually divided in chunks of 10 minutes to visually inspect and determine the number of modes and the geometrical diameter range of each event (nucleation <~~25nm~~25 nm, Aitken ~~25nm -100nm~~25 nm -100 nm, accumulation >100 nm). Once those parameters were defined and included in the code, each event was divided in periods of time with similar distribution modes.

For illustration a hypothetical event lasting two hours was divided in two: one hour with simultaneous two particle modes (nucleation and Aitken) and then one hour with just one particle mode (Aitken). This is done to estimate an accurate geometrical particle diameter based on the number of modes. This avoided the problems of changes in the number of modes in the sample. Finally, the data was merged again to have a time series of number of particles predicted with the fit, number of modes predicted and geometrical particle diameter.

The algorithm works by providing the number of modes observed in the input dataset. Then it selects the provided model equation for each mode number and iterates over a hundred fits looking for the best ~~one~~fit. The Bayesian Information Criterion (BIC) was used to identify the best fit, looking for the lowest values. Once the best fit was selected, the total particle number estimated by the model was compared with the sample record for each sample to assure it was within a 5 % difference compared to the total particle number reported in the sample. The result was then visually checked looking for the geometrical diameter and how it compares to the distribution size plots from the raw aerosol distribution size data. Once the model was considered representative and accurate enough, the growth rate for each event was determined using a simple linear regression of the change in the geometrical diameter in time from nucleation to Aitken and eventually to accumulation mode.

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## 3. Results and Discussion

### 3.1 Frequency of NPF Events

~~Of the forty days included in the analysis, fourteen (35%) showed clear NPF events, nine (22%) were considered undefined, eight (18%) didn't have enough data or were classified as a non-event and nine days (25%) didn't have any data. The percentage of days with NPF is similar to those of other sites in forested areas in the Northern Hemisphere (Kalkavouras et al., 2020; Uusitalo et al., 2021). On the days in which the particle growth pattern is not clear, the same chemical reactions driving the NPF events may also be influencing these particle clusters, but the pattern is obscured due to different factors influencing the chemistry and physically mixing the atmosphere. 35% of days with NPF events and 18% with undefined events implies a highly reactive atmosphere even in this rural area with relatively low anthropogenic influence.~~

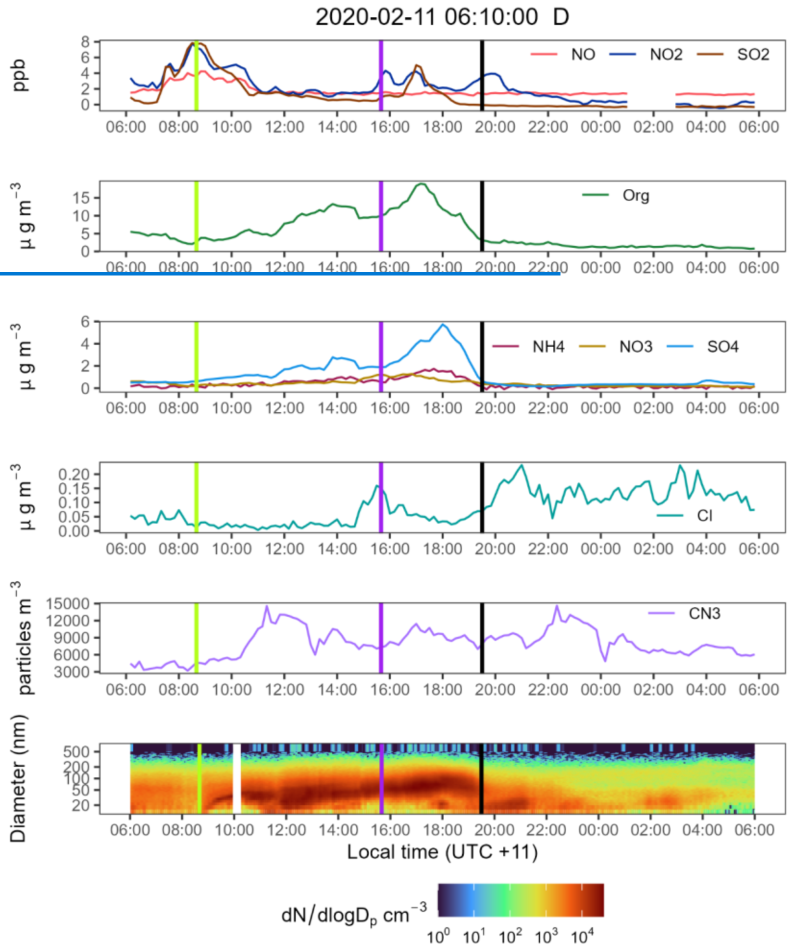
Of the 40 days included in the analysis, nine days didn't have any data. Of the 31 days with data, 14 (45%) showed clear NPF events, nine (29%) were considered undefined, eight (26%) didn't have enough data or were classified as a non-event The percentage of days with NPF is similar to those of other sites in forested areas in the Northern Hemisphere (Kalkavouras et al., 2020; Uusitalo et al., 2021). 45% of days with NPF events and 29% with undefined events implies a highly reactive atmosphere even in this rural area with some anthropogenic influence of mobile sources and occasionally coal-fired power plant in the Hunter Valley region.

An example of the time series of an NPF event is shown in Figure 2 for the event on 11 Feb 2020. The NPF commences at 8 am shortly before which a peak is observed in $SO_2$ and the $H_2SO4$ proxy (estimated using the rural proxy proposed by Dada et al. 2020). The shaded area in the plot highlights the growth period which is marked by an increase in mode diameter and condensation sink. Ozone also increases in this time. The increase in aerosol $SO_4$ and organics during this period shows the influence of this reaction chemistry on particles larger than 100 nm in the aerosol size distribution

### 3.2 Triggers for NPF Events

Of the fourteen days with NPF, five ~~were registered~~occurred during the night or early morning (before sunrise), and nine during the day. ~~The starting time of the event was important to mark which possible reactions might be driving the oxidation of products that eventually nucleate. Besides that, the~~The time series of $SO_2$, $NO_x$, ozone, VOCs and the aerosol composition were used to identify which variables triggered and influenced the aerosol formation and growth. Of the fourteen ~~events~~event days of NPF, eight ~~have~~days include VOC data and nine ~~have~~days include aerosol composition data~~. Only~~, noting that the composition data is not applicable to particles <100 nm and only three events led to accumulation sized particles (diameter >100 nm).

From the daily time series of all available variables over the 14 days of NPF events, it is evident that $SO_2$ ~~and $NO_x$ are probably triggering~~frequently triggers or at least ~~influencing~~influences the particle formation~~ most of the time. As an example~~. However, the ~~event on Feb 11th 2020, presented in Figure 2 shows how after there was a first $SO_2$ and $NO_x$ peak coming to ~~trigger for nighttime events is less clear. To group the ~~site at around 8:00 am, one hour later ~~common factors influencing NPFs for daytime and night-time events, a comparison of the ~~nucleation process starts. This event did not show a quick ~~growth ~~like several other events in~~rate was used to determine whether the ~~record possibly due to the early morning start time when there~~rates were ~~not enough VOCs to accelerate~~similar during the day and during the ~~nucleation and growth process. Later, once the temperature starts to increase, enhancing the VOCs emitted, and there is more OH available in the atmosphere, there will be higher density of particles in both nucleation and Aitken mode. This difference is reflected in the peak of particles captured in the $CN_3$ data around 11:00 am~~night.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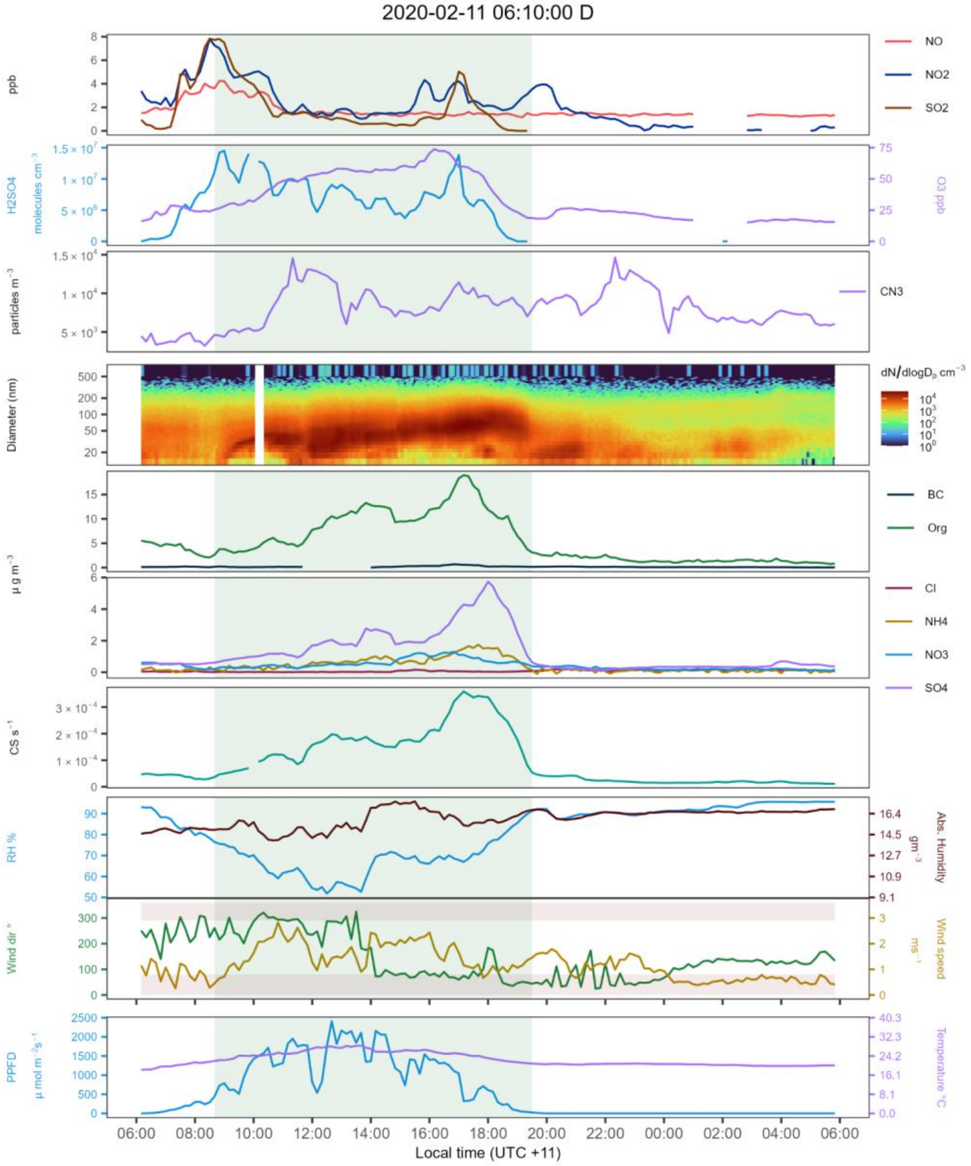

*Figure 2. Time series for all selected variables during the NPF event during 2020-02-11. NO = Nitric oxide, NO2 = Nitrogen dioxide, SO2 = Sulphur dioxide, H2SO4 = Sulphuric acid, O3 = Ozone, CN3 = Condensation Nuclei >3nm, CN3-CN14 = difference of CN3 minus the sum of*

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*all channels from the SMPS data. BC = Black carbon. Org = Organic mass fraction, NH4 = Ammonium mass fraction, NO3 = Nitrates mass fraction, SO4 = Sulphates mass fraction, Cl = Chloride mass fraction*~~*, CN3 = Condensation Nuclei >3nm.*~~*. CS = condensation sink. PFFD = Photosynthetic Photon Flux Density. VOCs mole fractions were not available during this specific event. Note how the fraction of organics, sulphates and ammonium increase with a positive correlation, dominating over the nitrate and chloride fractions until the end of the event.* ~~*The light green vertical line marks the NPF approximated starting time. The purple line marks the time were subsequent* $SO_2$ *emissions impacted the site. The black line represents the NPF approximated ending time.*~~*The light green area marks the NPF, and growth period mentioned in the analysis. the brown shade areas in the wind panel highlight areas where the wind comes from the nearby roads. Note that the NO values are close to detection limit and look biased high and hence should be interpreted as an indicative rather than accurate quantitative measure of atmospheric concentration.*

~~$SO_2$ appears to only affect daytime events, while $NO_x$ seems to have a shared role in both daytime and night-time events. Trying to group the common factors influencing NPFs on daytime and night-time events, a comparison of the growth rate was used to determinate if the rates were similar during the day and during the night.~~

### 3.3 Particle Growth Rates during daytime and nighttime events

The estimated growth rate is presented in Figure 3. Only four of the nine events during daytime (~~see~~ upper panel of Figure 3) had a representative Pearson coefficient ($R$>0.6), the remaining five events did not have a stable linear growth and are not shown in the plot. The events which showed unstable growth patterns suggests a highly variable condensation source, possibly resulting from changing $H_2SO_4$ concentrations. This is complicated further by changing wind directions.

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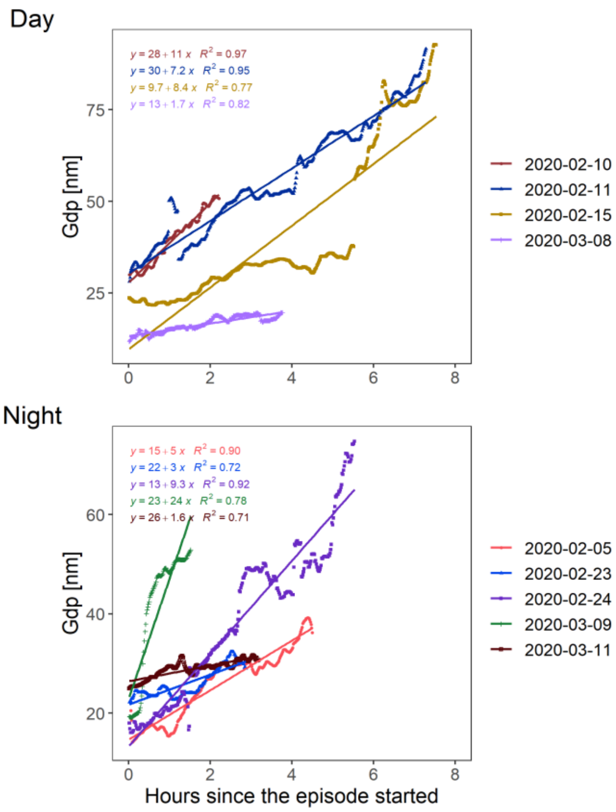

*Figure 3: Geometric particle diameter evolution in each event where the logarithmic fit converged. The top panel presents the daytime data (only four events converged to a statistically significant model). The bottom panel presents the nighttime events.*

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~~During these more unstable events the influence of plumes on the sampling site bringing $SO_2$ and $NO_x$ likely produced multiple reactions drastically changing the particle density in short periods of time or induced multiple formation events, making it harder to estimate the particle growth on these days using the same methodology.~~Some events highlight how the dynamic nature of daytime concentrations of $O_2$, $NO_2$ and $O_3$ complicate the analysis (see figure S1). Nonetheless, these events provide insight into the factors that may drive the growth and particle formation and so were included in all the analysis. Event 2020-02-15 in Figure 3 is an example of how the geometric particle diameter can change when there is rapid growth. The first part of the regression shows slower growth rate. After the 6th hour of slow growth, the rate increases substantially.

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~~Some events showed how the daytime concentrations of $SO_2$ and $NO_2$ were so dynamic that it might prove difficult to study a particular phenomenon when sampling in the ambient air (see figure S1). Nonetheless,~~

~~these events provide insight into the factors that may drive the growth and particle formation and so were included in all the analysis.~~

In contrast to the daytime events, all the night-time events were stable enough to ~~determinate~~determine the event growth rate. The growth rate varied considerably between events (see lower panel of Figure 3~~) and most likely reflects differences in the factors driving the particle formation between these episodes. The differences in the growth rate might be directly affected by the main oxidation pathways available at the time of the reaction. These reactions pathways might include VOC oxidation through nitrates ($NO_3$) oxidation path during the night, leftover isoprene or monoterpene oxidation and condensation over previously formed clusters, oxygenated VOCs (OVOCs) brought to the site and condensed on formed seeds or starting nucleation, or VOC oxidation through the ozone pathway. Some of these processes were observed during the campaign and will be further explored on the nighttime events section.~~

## ~~3.4 Daytime NPF Events~~

~~From the timeseries analysis of all daytime events (see Figure 2, 5-8 and supplementary figures S1-S5), four key points were identified for NPF in the area:~~

) and most likely reflects differences in the factors driving the particle formation between these episodes. The differences in the growth rate might be directly affected by the main oxidation pathways available at the time of the reaction. These reaction pathways might include isoprene oxidation by nitrate radical ($NO_3$) oxidation path during the night (Wu et al., 2021b), monoterpene ozonolysis and condensation over previously formed clusters(Liu et al., 2023; Wang et al., 2023), or oxygenated VOCs (OVOCs) brought to the site and condensed on formed seeds or starting nucleation(Bianchi et al., 2019; Higgins et al., 2022). Some of these processes were observed during the campaign and will be further explored on the nighttime events section.

## 3.4 Daytime NPF Events

From the timeseries analysis of all daytime events (see Figure 2, 5-8 and supplementary figures S1-S5), four key points were identified for NPF in the area:

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1. $SO_2$ ~~and $NO_2$~~ arriving at the site ~~triggers~~appears to trigger nucleation and growth events.
2. VOC availability ~~is needed for growth~~(monoterpenes and isoprene) enhances nucleation and growth.
3. The hours with high VOCs concentrations and higher oxidation capacity in the atmosphere ($OH$ concentrations are assumed to be higher during the hours with higher PAR ~~will~~) have ~~the highest~~higher particle ~~density~~number concentrations and ~~the highest frequency of the observed events~~generally guaranteed growth up to the accumulation mode.
4. ~~There might be nucleation~~Growth without the influence of $SO_2$ may occur~~and $NO_2$ in the atmosphere~~ but will do so at a slower ~~growth~~ rate.

During most of the daytime events $SO_2$ and $NO_2$ plumes impacted the site at some stage of each event.

On some occasions the $SO_2$ plume might last for a couple hours as shown in the first part of the event on Feb 11th 2020 (see Figure 2), whilst at other times there were multiple peaks of high $SO_2$ measured at the site ~~(~~as shown in several other events in the record (e.g. Figures S2, S3, S4). ~~Every time~~ However, subsequent nucleation was observed on every occasion that $SO_2$ ~~was first detected~~was observed above the detection limit at the site, ~~some nucleation commenced~~ growth occurred within 0 to 150 minutes after the ~~SO2~~$SO_2$ was first detected. ~~This~~The time window ~~of time matches the time needed to reach nucleation sized particles if we extrapolate the growth rate function from~~difference between events reflects the ~~daytime events previously discussed (see Figure 3).~~influence of conditions at the start of a particle growth event. To highlight this phenomenon a cross correlation between $SO_2$ and the aerosol mass of aerosol $S$~~$O_4$~~$O_4$ time series obtained from the tof-ACSM and the measured particle number concentration ($CN_3$) was applied. Figure 4 shows the Pearson correlation between $SO_2$ and the $CN_3$ and aerosol $SO_4$ in a window period of four hours i.e. starting two hours before the nucleation ~~started~~commenced and ending after the first two hours of the event. This time window ~~aims to capture~~captures the $SO_2$ influence on the particle formation. Each line/point shows the correlations at 0, 30, ~~6~~60, 90, 120 and 150 minutes lagged for each daytime event. The dotted blue lines show where the lagged correlation is significant at ($|r| > 0.5$).

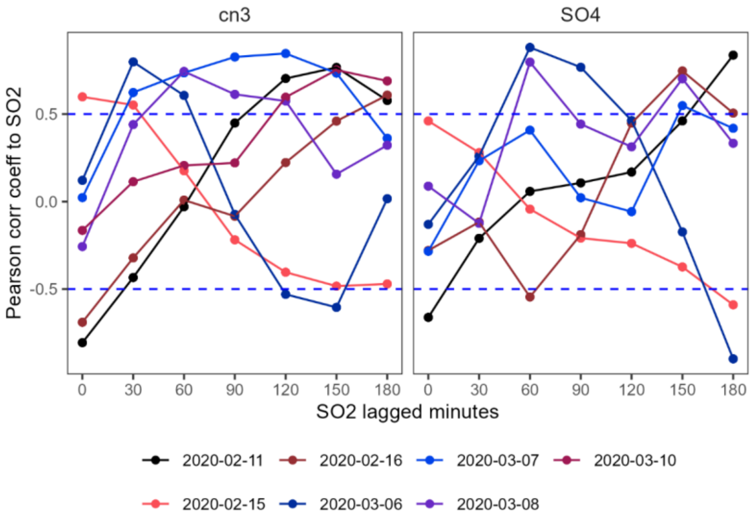

*Figure 4 : Pearson correlation values obtained from the cross correlation between $SO_2$ and $CN_3$ and $SO_4$ mass. The dashed lines represent the 0.5 threshold as a reference to identify significant correlations. Events on Feb 10th and March 11th did not follow this pattern and were removed from the plot.*

To interpret Figure 4, we can use the event on February 11th (black line) as an example. Here the correlation between $SO_2$ and $CN_3$ becomes significant (at $|r| > 0.5$) if the ~~aerosol data~~$SO_2$ time series is lagged 120

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minutes with respect to the aerosol data; and the correlation between $SO_2$ and aerosol $S$~~$O_4^{2-}$~~$O_4$ becomes significant after 3 hours. This means that if we move the $SO_2$ time series two hours forward it will be better correlated with the particle number concentration, accounting for the reaction time of $SO_2$ to produce $H_2S$~~$O_4^{2-}$ radicals~~$O_4$ and enhance/trigger the particle formation under the conditions in the atmosphere at the time. Usually, the $SO_2$ correlation with aerosol $S$~~$O_4^{2-}$ takes~~$O_4$ needs a longer lag time to be significant. This is a potential indication of the order in which the chemical reactions happen. First, we will see oxidation of the $SO_2$ to ~~$SO_4^{2-}$ and then nucleation.~~ $H_2SO_4$, then nucleation, and finally growth in mass when there is condensation or coagulation near CCN sizes. Using time series analysis as shown here can provide more evidence when the chemical mechanisms are known but observations of other variables are not available.

~~A similar result is observed for other events at different lagged times. The difference in the length of time necessary to achieve a significant correlation between $SO_2$ and the particle number seems to be related to the quantity of VOCs available after the $SO_2$ plume arrives at the site and how long the $SO_2$ is available in the atmosphere. Events on February 15th, March 06th and March 07th had the highest correlations in the first 30 minutes of lagging the $SO_2$ data. All these events had in common a relatively high isoprene mole fraction (>1 ppb) in the previous hour to the $SO_2$ coming to the site (see Figure S1, S2 and S5) or in the circumstances where VOC data were not available, conditions where isoprene mole fractions were assumed to be high (associated with weather conditions; i.e. high PAR and temperature see Figure S6). The event on March 8th also met this condition (see Figure S3), but the growth seems to be partially suppressed by other factors, as seen in the relatively low growth rate in Figure 4 compared to the other events.~~

~~The Feb 11th and Feb 16th events had similar arrival times for the $SO_2$~~ A similar result is observed for other events at different lagged times. The difference in the time necessary to achieve a significant correlation between $SO_2$ and the particle number seems to be related to the quantity of VOCs available when the $SO_2$ plume arrives at the site This matches our understanding of the process from nucleation to particle growth, at early hours we observed monoterpenes levels that are sufficient to promote nucleation through ozonolysis and HOM formation (Iyer et al., 2021; Wang et al., 2023) but potentially not enough to promote growth to larger sizes as it seems most of the particle growth observed could be related to isoprene levels. Later with higher temperatures, emissions of isoprene increase so that ELVOC or other OVOCs are potentially produced that contribute to growth in particle mass reflected in the increase of the sulphate fraction observed in the ACSM. Events on February 15th, March 06th and March 07th showed highest correlations in the first 30 minutes of lagging the $SO_2$ data. Common to all these events was a relatively high isoprene mole fraction and enhanced levels of monoterpenes (~1 ppb) in the hour before $SO_2$ being detected at the site (see Figure S1, S2 and S4) or in the circumstances where VOC data were not available, conditions where isoprene and monoterpenes mole fractions were assumed to be high by associated with weather conditions ( i.e. high PAR and temperature see Figure S5). The high levels of monoterpenes and subsequent ozonolysis could be driving the particle formation at these times. In this period H2SO4 is available to drive the nucleation and the HOM proxy (monoterpenes*ozone (e.g.: Zhang et al., 2024)) at it's highest values during the day potentially enhancing the effect.

The event on March 8th also met this condition (see Figure 5), although the event showed a relatively low growth rate. The isoprene and MACR + MVK concentrations in this event highlight the possibility of isoprene suppression (Heinritzi et al., 2020). The higher isoprene levels after 12:00, along with the increase of MACR

+MVK indicate isoprene oxidation through OH. This is the first step in the reaction chain to produce C15 dimers. Although the $CN_3$ data is not complete for the event, it is clear there was a decline of the number of particles in the smaller sizes at the same time as the oxidation products of isoprene increase. This is also supported using the HOM formation proxy (monoterpenes*ozone), where at the times with higher particle numbers, the HOMS proxy is higher and then when the particle number decreases the HOM proxy does it too while MACR+MVK products increase suggesting a change to a more isoprene driven chemistry. The organic and sulphate fraction increase as well as the condensation sink suggesting larger particle formation and conditions that favour condensation and coagulation instead of nucleation.

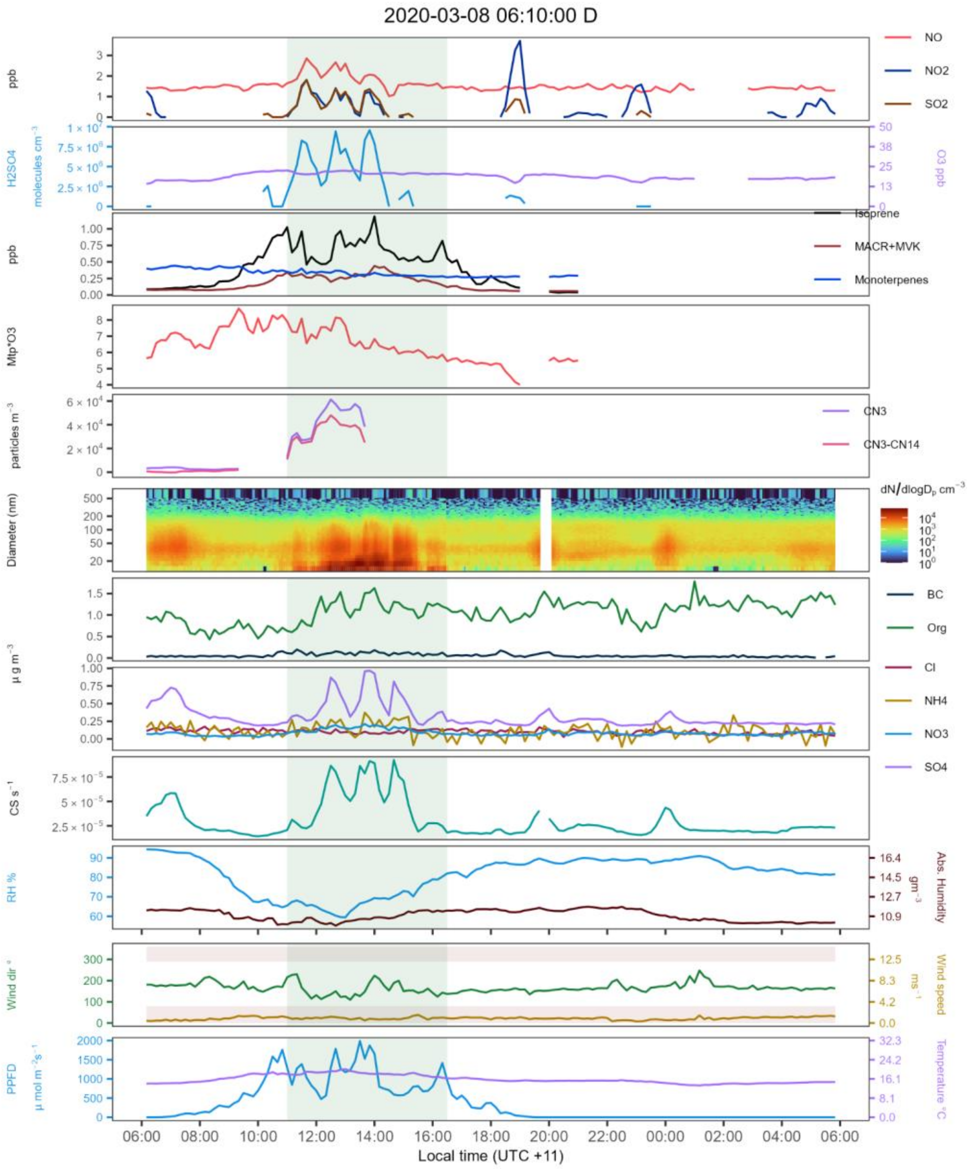

Figure 5 Time series of all selected variables during the NPF event during 2020-03-08. NO = Nitric oxide, NO2 = Nitrogen dioxide, SO2 = Sulphur dioxide, H2SO4 = Sulphuric acid, O3 = Ozone, MACR+MVK = isoprene ox. products methacrolein and methyl-vinyl-ketone, CN3 =

*Condensation Nuclei >3nm, CN3-CN14 = difference of CN3 minus the sum of all channels from the SMPS data. BC = Black carbon. Org = Organic mass fraction, NH4 = Ammonium mass fraction, NO3 = Nitrates mass fraction, SO4 = Sulphates mass fraction, Cl = Chloride mass fraction. CS = condensation sink. Mtp*ozone = HOM proxy product monoterpenes and ozone [ppb*ppb].*

The Feb 11th and Feb 16th events had similar arrival times for the $SO_2$ pollution (8:00 to 9:00) although the ~~VOC mole fractions were too low to enhance the particle formation and growth.~~photochemistry was not fully active yet (see $H_2SO_4$), monoterpenes levels were consistently high during all the campaign (~0.4 ppb based on the days with data), enough to promote nucleation. This presumption is supported by looking at the event on February 16th (see Figure S43). In this event, a first peak of $SO_2$ at 8:00 started ~~some particle formation but subsequent~~nucleation but then condensation or coagulation dominated favouring growth. The $CN_3$ -$CN_{14}$ data show that after that initial nucleation period the particle number is dominated by the >14nm fraction. Multiple $SO_2$ plumes came to site producing higher ratios of $H_2SO_4$, but it promoted growth to larger particles sizes particularly on the sulphates fraction that correlates with the $SO_2$ peaks ~~at 10:00 and 12:00 (times where generally VOCs are higher) led to a NPF event that eventually grew to accumulation sized~~. In the evening there were a couple of small particle bursts that were quickly coagulated on larger size particles.

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The event on March 10 (see Figure 6) shows high monoterpene concentrations that declined quickly just prior to the event being observed in the aerosol data. The aerosol growth phase is then observed to correlate with peaks in $SO_2$ and $NO_X$, as well as elevated levels of isoprene. Together, this suggests monoterpene ozonolysis initiated nucleation, followed by condensational growth via isoprene oxidation products.

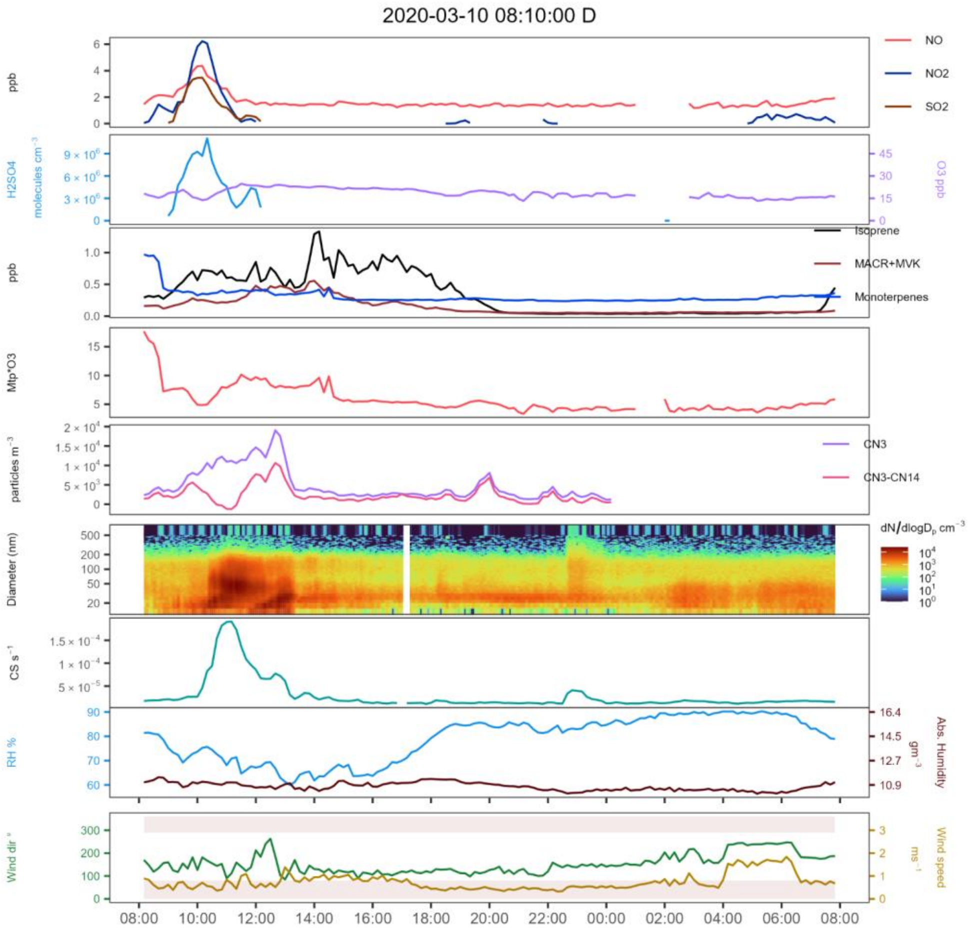

*Figure 6 Time series of all selected variables during the NPF event during 2020-03-10. The drop of $CN_3$ seem related to the lack of $SO_2$ after 11:00. NO = Nitric oxide, NO2 = Nitrogen dioxide, SO2 = Sulphur dioxide, H2SO4 = Sulphuric acid, O3 = Ozone, MACR+MVK = isoprene ox. products methacrolein and methyl-vinyl-ketone, CN3 = Condensation Nuclei >3nm, CN3-CN14 = difference of CN3 minus the sum of all channels from the SMPS data. CS = condensation sink. Mtp*ozone = HOM proxy product monoterpenes and ozone [ppb*ppb].*

For all date time events $SO_2$ and $NO_2$ are significantly correlated with a Pearson correlation of 0.78, suggesting a common source for both pollutants. The closest source of combustion products is the Appin Road located north of the sampling site. Given that the sampling site is away from other possible sources of $SO_2$ and $NO_2$ and the relatively low wind speeds during most of the campaign (see Figure S8), combustion

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from mobile sources is considered the most likely source of both compounds but there might be some influence of more distant coal-fired power stations. Another factor to contribute to this theory is that the $SO_2$ levels were higher during the day when most of the commuting takes place and leading to a higher vehicle density on the roads. The intermittent $SO_2$ and $NO_2$ peaks suggest the influence of mobile sources with poor emission control onboard. The effects of vehicles with poor emission control technologies on ambient concentrations of $SO_2$, $NO_x$, AVOCs and PM has been seen in different studies (Kari et al., 2019; Phillips et al., 2019; Smit et al., 2019) and the legislation controlling fuel standards and emissions is relatively lax in New South Wales (Paton-Walsh et al., 2019).

The atmospheric availability of monoterpenes to react and produce ULVOC or ELVOC with higher condensation potential to existing $SO_4$ aerosol is as important as the $SO_2$ presence and reaction, as seen in most of the events. Isoprene oxidation products also have a role in condensing on pre-existing nucleated aerosol. This has been previously reported by (Stangl et al., 2019), where chamber experiments showed that $SO_2$ presence can significantly enhance SOA formation from isoprene and monoterpene oxidation by ozone. Xu et al (2021b) reported that water and $SO_2$ availability will change the role of $SO_2$ in the particle formation process. With high $SO_2$ mole fractions, the $SO_2$ reaction path will favour reaction to peroxides instead of stable Criegee intermediates, thereby enhancing particle growth, particularly at relative humidity of greater than 45%; a condition present during most of the COALA-2020 campaign. This suggests that under high $SO_2$~~,~~ ~~The event on March 10th shows how $SO_2$ pollution occurred around 10:00 when isoprene mole fractions are about 0.5 ppb promoting NPF. This event shows how even when VOCs available if there is no $SO_2$ in the atmosphere (13:00) the particle formation will substantially decrease, as shown in the $CN_3$ concentration (see Figure S7).~~

~~A similar result to $SO_2$ NPF events is observed when the cross correlation is applied with $NO_2$ data as shown in Figure 11. (Wang et al., 2019) reported an enhanced effect of $SO_2$ oxidation to $SO_3^{2-}$ in the presence of $NO_2$ and $H_2O$. The resulting acidic aerosols can easily act as nuclei for VOC condensation explaining the correlations of $SO_2$ and $NO_2$ with the particle formation events (Wang et al., 2020a). These studies were made under urban-like conditions with high concentrations of $SO_2$ and $NO_x$ to produce this effect. The atmospheric chemistry community is still debating the role of this reaction on $SO_2$ related aerosol formation, with recent experiments showing that the enhancement effect is not as large as originally proposed (Au Yang et al., 2018; Wang et al., 2020b). There are other reaction pathways that can lead to $SO_3^{2-}$ formation such as $SO_2$ oxidation through the $OH$ path (Long et al., 2017; Margitan, 1984) or photo-oxidation of $SO_2$ (Wang et al., 2020b). Nonetheless, measurements and experiments in rural atmospheric conditions provide insights into these phenomena a because of the multiple reactions happening depending on the atmospheric conditions at a given time.~~

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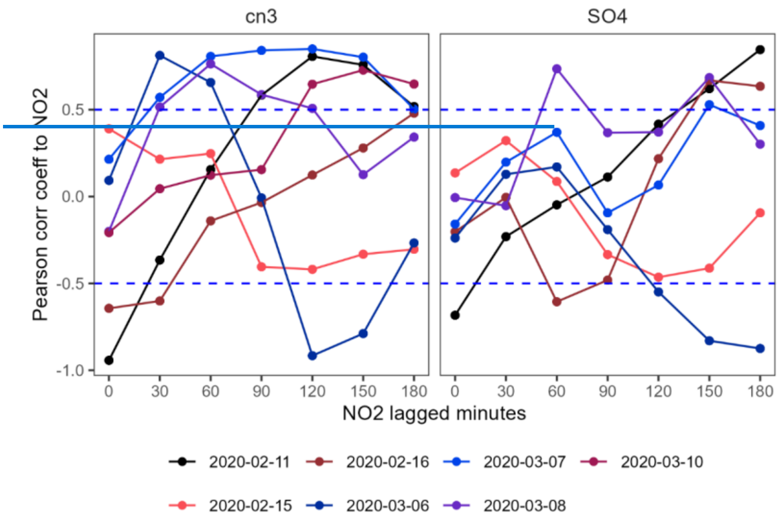

~~*Figure 5: Pearson correlation values obtained from the cross correlation between* $NO_2$ *and* $CN_3$ *and* $SO_4$ *mass. The dashed lines represent the 0.5 threshold as a reference to identify significant correlations. Events on Feb 10th and March 11th did not fit into this category and were removed from the plot.*~~

~~$SO_2$ and $NO_2$ are significantly correlated during most of the day-time events~~isoprene and monoterpene availability, and high relative humidity conditions, particle formation and eventual growth is likely to occur.

Such an effect was observed in some of the events, for example the event on February 16th (Fig S3). This event saw high relative humidity throughout the event (well above the 45% threshold suggested by Xu et al.) as well as elevated gas-phase SO2. Unfortunately VOC data wasn't available during this event, however the consistent diurnal profile of VOCs observed throughout the remaining dataset (Figure S5)can be extrapolated to this day, suggesting enhanced monoterpene and isoprene availability. Together, these prerequisites were met, and likely led to the observed aerosol growth event.

The conditions promoting sulphate formation in the event of Feb 16th are also present in multiple events. ~~with a Pearson correlation of 0.78, suggesting a common source for both pollutants. The closest source of combustion products is the Appin Road located north of the sampling site. Given that the sampling site is away from other possible sources of $SO_2$ and $NO_2$ and the relatively low wind speeds during most of the campaign (see S8), combustion from mobile sources is considered the most likely source of both compounds. Another factor to contribute to this theory is that the $SO_2$ levels were higher during the day when most of the commuting takes place and leading to a higher vehicle density on the roads. The intermittent $SO_2/NO_2$ peaks suggest the influence of mobile sources with poor emission control onboard The effects of vehicles with poor emission control technologies on ambient concentrations of $SO_2$, $NO_x$, AVOCs and PM has been seen in different studies (Kari et al., 2019; Phillips et al., 2019; Smit et al., 2019) and the legislation controlling fuel standards and emissions is relatively lax in New South Wales (Paton-Walsh et al., 2019).~~

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~~The availability of VOCs to react and produce oxygenated volatile compounds that might condense over the $SO_4^{2-}$ seeds formed from $SO_2$ pollution impacting the site, is as important as the $SO_2$ presence and reaction. This has been previously reported by (Stangl et al., 2019), where chamber experiments showed that $SO_2$ presence can significantly enhance SOA formation from isoprene and monoterpene oxidation by ozone. (Xu et al., 2021) reported that water and $SO_2$ availability will change the role of $SO_2$ in the particle formation process. With high $SO_2$ mole fractions, the $SO_2$ reaction path will favour reaction to peroxides instead of stable Criegee intermediates, thereby enhancing particle growth, when the relative humidity is higher than 45%; a condition present during most of the COALA-2020 campaign. This suggests that under high $SO_2$, VOC and relative humidity conditions, the particle formation and growth will occur. Such an effect was observed in some of the events, for example the event on February 16th (Figure S4). There was a continuous source of $SO_2$ impacting the site during this event in the period between 07:00 to 22:00. During the first half of the event (up to 14:00) organic aerosol mass fraction is almost as high as the sulphate mass, however after 14:00 there is an increase in the sulphate mass, which becomes the largest mass proportion of this event. The sulphate fraction is practically a mirrored version of the $NO_2$ and $SO_2$ lagged by an hour. The highest fraction of sulphates during this period can be explained by the previously mentioned effect of relative humidity, and VOCs.~~

As the night approaches, BVOC emissions decrease with temperature, leaving all existing VOCs to oxidize. This provides the initiation for further oxidation of OVOCs into more oxidized species, which are more likely to condense on existing particles. In addition, with the temperature decreasing the relative humidity increases, making this the ideal condition for particle growth, particularly sulphates. However, once the VOCs are mostly consumed (~~by~~assumed from diurnal cycles from the campaign to be around 22:00, see figure S5), there are insufficient VOCs to ~~generate~~promote growth. This relationship is presented in Figure 7, where relative humidity and sulphate mass are positively correlated during the afternoon hours in the events which had multiple $SO_2$ peaks enhancing sulphate formation and particle growth.

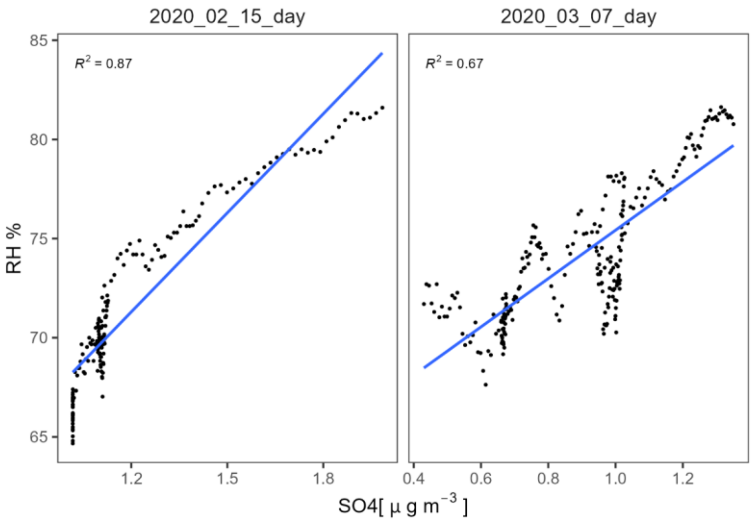

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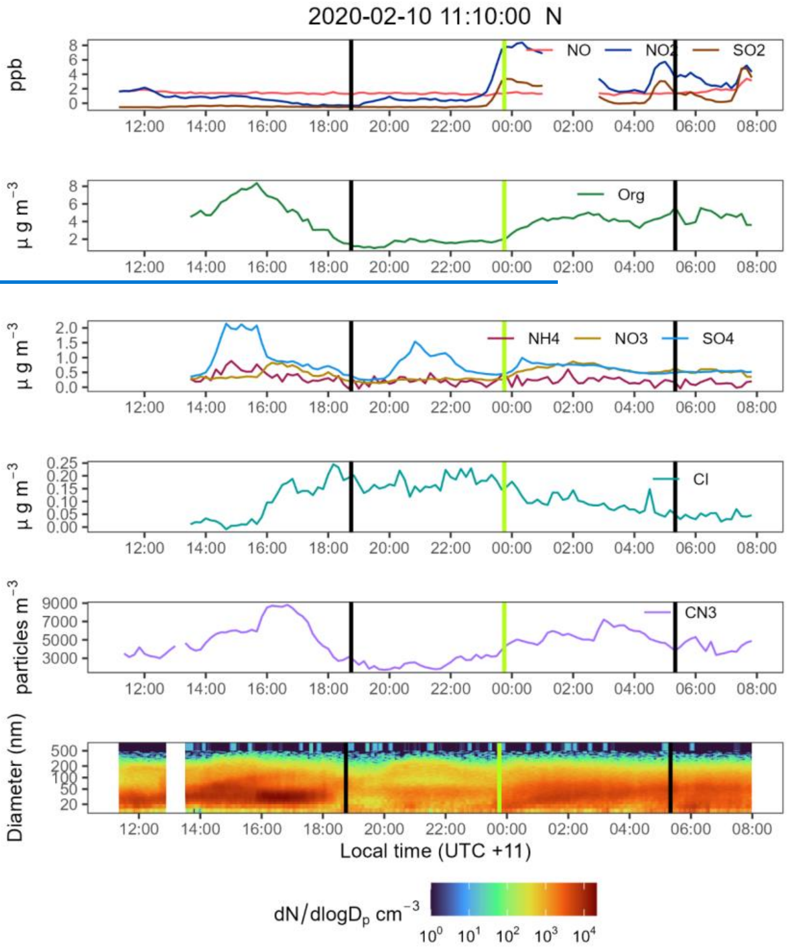
*Figure 7: Scatter plot of the events on Feb 15th and March 7th comparing total sulphate mass against relative humidity in the afternoon hours (14:00 to 17:00).*

~~The opposite conditions can also influence particle formation. When there is little $SO_2$ or $NO_2$ in the atmosphere but there are high enough VOC concentrations, there can be slow nucleation over time. Slow growth was observed during the February 10th event (Figure 7) and may be related to the condensation of monoterpenes oxidation products. Lab studies have shown that this process might take longer than other particle formation processes because methacrolein (MACR) needs to be oxidized to produce aerosols (Kroll et al., 2006; Ng et al., 2006). Other processes such as autoxidation of monoterpenes could explain these events. Recently (Nie et al., 2023)) showed that low NO concentrations can enhance highly oxygenated molecules (HOMs) formation by favouring alkoxy radicals formation that are prone to autoxidise in pristine atmosphere or low-NO regimes.~~



When there is negligible $SO_2$ in the atmosphere but there are high enough VOC concentrations, there can be particle growth when dimers $C_{15}$, produced by further OH oxidation of isoprene products, condensate over smaller particles (Heinritzi et al., 2020). Growth was observed during the first event on February 10th (see daytime data in Figure 8) and may be related to the condensation of these dimers. The average concentration of isoprene during the campaign in the morning is higher than 1 ppb, enough to initiate the reactions leading to LVOCs favouring growth of preexisting particles.

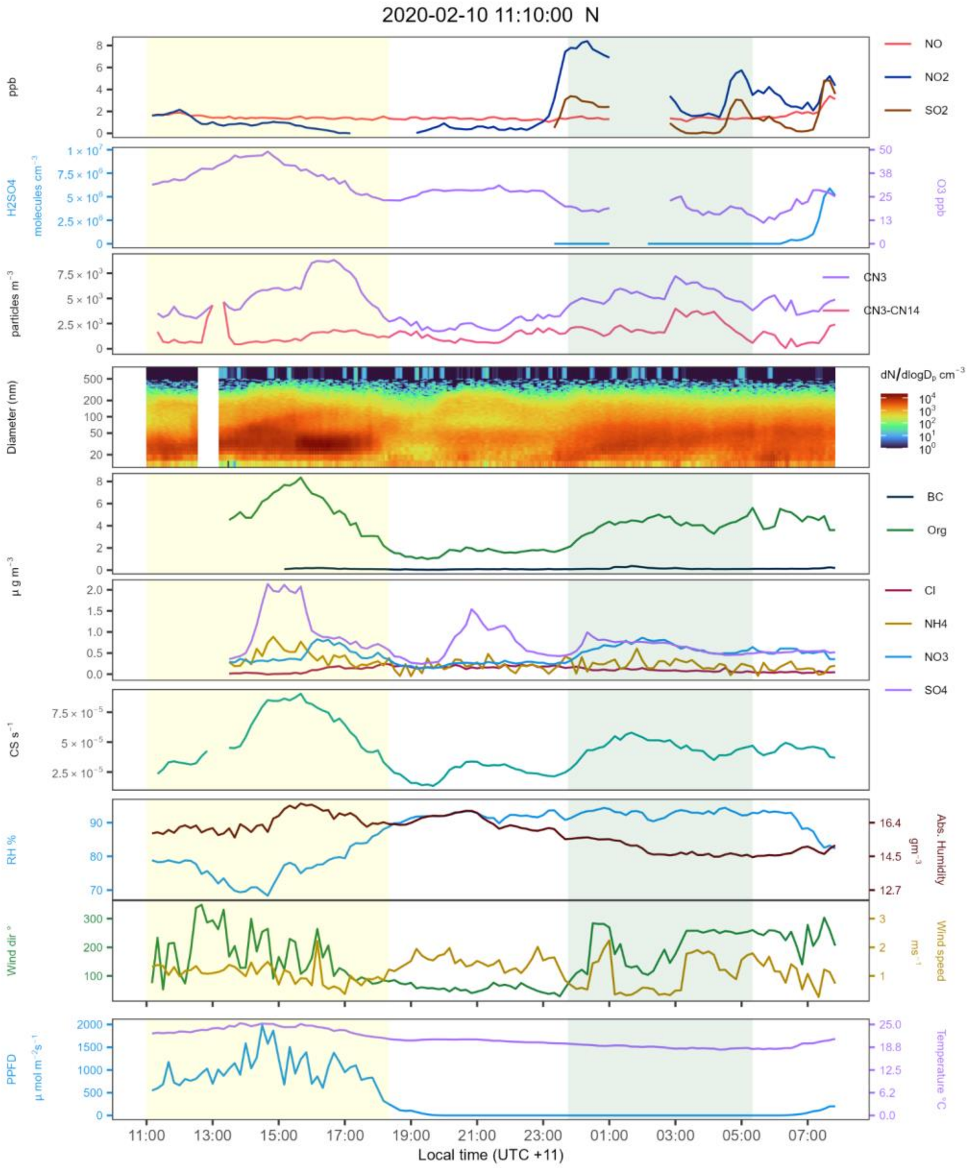


*Figure 8: Time series ~~of~~for all selected variables during the NPF event during 2020-02-10. NO = Nitric oxide, NO2 = Nitrogen dioxide, SO2 = Sulphur dioxide, H2SO4 = Sulphuric acid, O3 = Ozone, CN3 = Condensation Nuclei >3nm, CN3-CN14 = difference of CN3 minus the sum of*

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*all channels from the SMPS data. BC = Black carbon. Org = Organic mass fraction, NH4 = Ammonium mass fraction, NO3 = Nitrates mass fraction, SO4 = Sulphates mass fraction, Cl = Chloride mass fraction, ~~CN3 = Condensation Nuclei >3nm.~~ CS = condensation sink. PFFD = Photosynthetic Photon Flux Density VOCs mole fractions were not available during this specific event. Note how there does not seem to be any significant* $SO_2$ *or* $NO_2$ *pollution prior to the NPF start. At the same time of the particle growth there are enhancements in the organic, sulphate and ammonium mass fraction. There are two events in this plot. One in the morning with an unknown start and ending around 18:00, and the other at night. ~~The first black line represents the NPF approximated ending time of a morning event.~~ The light green ~~vertical line~~area marks the ~~NPF approximated starting time of~~night event, and the yellow highlight refers to the ~~nighttime~~daytime event. ~~The black line represents the NPF approximated ending time.~~*

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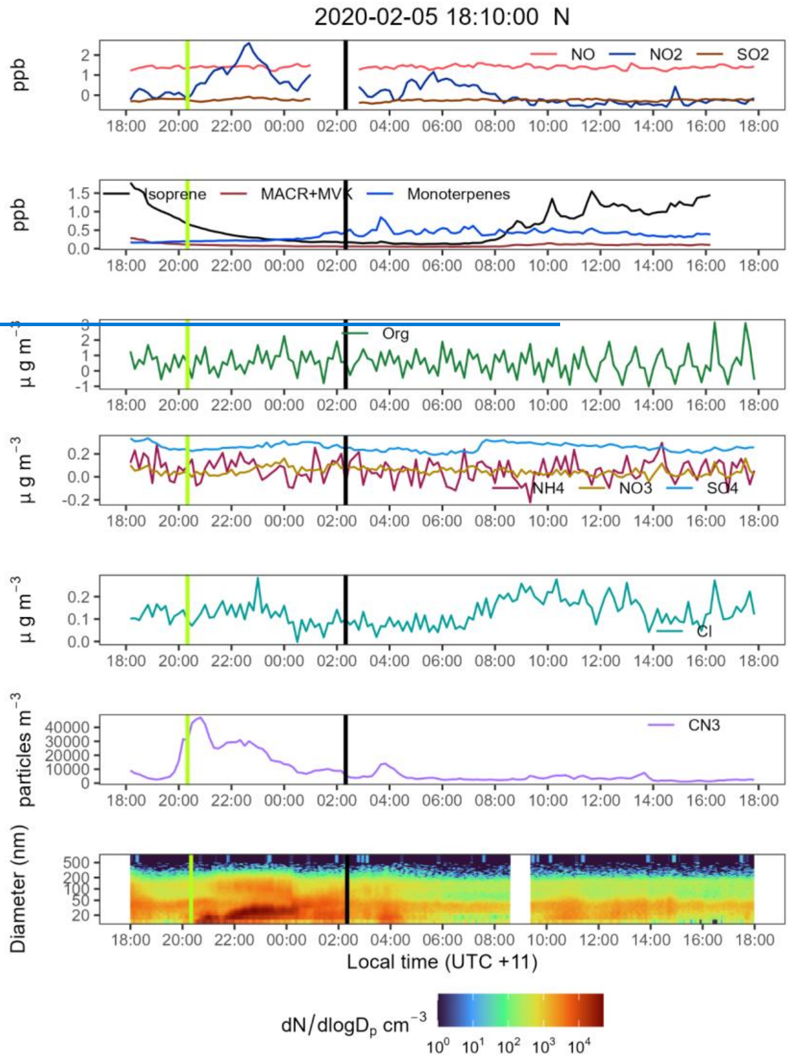
~~Like isoprene, the availability of monoterpene in the morning may determine how fast a NPF event can occur after~~ ~~$SO_2$~~ ~~reaches the site. Monoterpenes are quickly oxidized by OH with relative short lifetimes compared to isoprene (Atkinson, 2000; Atkinson and Arey, 2003). Oxidized monoterpenes through the OH pathway favour OVOCs that eventually condense faster than isoprene oxidation products (Heinritzi et al., 2020; Link et al., 2021). With these events starting in the morning ~8:00 to 9:00, there will be enough monoterpenes available for a fast oxidation once the OH starts to build up in the atmosphere, and these OVOCs are easily condensed on already formed seeds or under acidic conditions.~~

~~The availability of monoterpene and~~ ~~$SO_2$~~ ~~together may act as a catalyzer for faster particle formation compared to events with no monoterpenes, or events that start later in the day (noon) due to the absence of~~ ~~$SO_2$~~ ~~at the site. In the absence of monoterpenes but presence isoprene the particle formation may be of smaller magnitude and the formation may occur at a slower rate. Isoprene oxidises mainly through the OH path to more stable compounds; usually MACR and MVK are used as tracers to determine which path and under what conditions isoprene is oxidised. MACR is oxidised to heavier OVOCs that eventually condense. Given that the PTR-ToF-MS does not separate these two compounds it is not possible to identify when changes between ratios of MACR to MVK are significant in the NPF events on the current dataset. In general, when there are not enough VOCs in the atmosphere the nucleation and growth will be slow or might not happen at all.~~

The availability of monoterpenes increases the likelihood of NPF before or after $SO_2$ is available in the atmosphere. Although monoterpenes are quickly oxidized by OH resulting in relatively short lifetimes compared to isoprene (Atkinson, 2000; Atkinson and Arey, 2003), the ozone levels observed during the campaign are enough to promote ozonolysis and nucleation when there is no OH competing.. Australia experiences an isoprene dominated atmosphere (Emmerson et al., 2016; Ramirez-Gamboa et al., 2021) so the chemical balance in the atmosphere can rapidly change, particularly in the hotter seasons when more isoprene is emitted. Isoprene oxidises mainly through the OH pathway to more stable compounds; usually MACR and MVK are used as tracers to determine which path and under what conditions isoprene is oxidised. MACR is oxidised to heavier OVOCs that eventually condense and promote SOA formation in the larger sizes but these compounds also suppress NPF (Heinritzi et al., 2020; Link et al., 2021) as previously discussed in the event in Figure 5.

### 3.5 Night-time NPF Events

The main ~~factor~~factors influencing the night-time events ~~appears to be~~are ozone and $N$~~$O_2$~~$O_x$ pollution ~~in the atmosphere during the night~~, however the data available for this study does not provide enough information to make a more definitive statement. Unfortunately, the $NO_x$ instrument available in this study was not ideal for this type of measurement ~~given that~~for several reasons:  it is not designed to be ~~accurate at~~sensitive to the low $NO_x$ levels observed in rural areas; it is not capable of separating $NO_x$ from $NO_y$; and it was set up to calibrate in the night hours between 1:00 and 2:00 every day. Nonetheless, during the night-time events the particle size distribution data and the $CN_3$ ~~captured~~data showed particle formation and growth from nucleation to Aitken ~~mode~~modes when there were considerable increases of $NO_2$~~, but the~~ and simultaneous decreases in ozone. However, PM$_1$ aerosol mass from the ACSM showed a minimal increase at the same time (e.g. event during night of Feb 5th shown in Figure 9). This suggest that there are conditions to initiate the particle formation process but the conditions to increase the size/mass of the particles are not present at these times.



The night time nucleation observed in Figure 8 is related to an airmass change and might be the result of a combined effect of monoterpene ozonolysis and subsequent OH production after Crieege intermediates decay (Lester and Klippenstein, 2018). Once the OH is available it can produce $H_2SO_4$ and enhance the nucleation process. In this case, the increases in organic and sulphate mass shortly after the ozone depletion and the increase in CS indicate a growth in existing particles that is visible in the larger sizes in both particle numbers and mass. $CN_3$-$CN_{14}$ data suggest that there was some nucleation sporadically happening after the event started, but these particles were rapidly coagulated together with pre-existing larger particles.

The event on Feb 5th may indicate a combination of different factors at play. First, the monoterpenes and ozone levels could be triggering nucleation as observed during the daytime events, but there is a slight increase in monoterpene concentrations potentially driven by slower wind speeds and less mixing volume at night due to the reduced boundary layer height. Secondly, isoprene is observed to be steadily decreasing during this period. There are no enhancements of MACR+MVK so we could speculate that isoprene may be oxidised by the nitrate radical pathway. This is supported by the slight increase in the Nitrates fraction observed with the ACSM around midnight. Later that day around 4:00 am there is a second burst of small particles that follow the same pattern of monoterpenes/ozone. The monoterpene ozonolysis is also seeing in other night events (see Fig S8-S10).

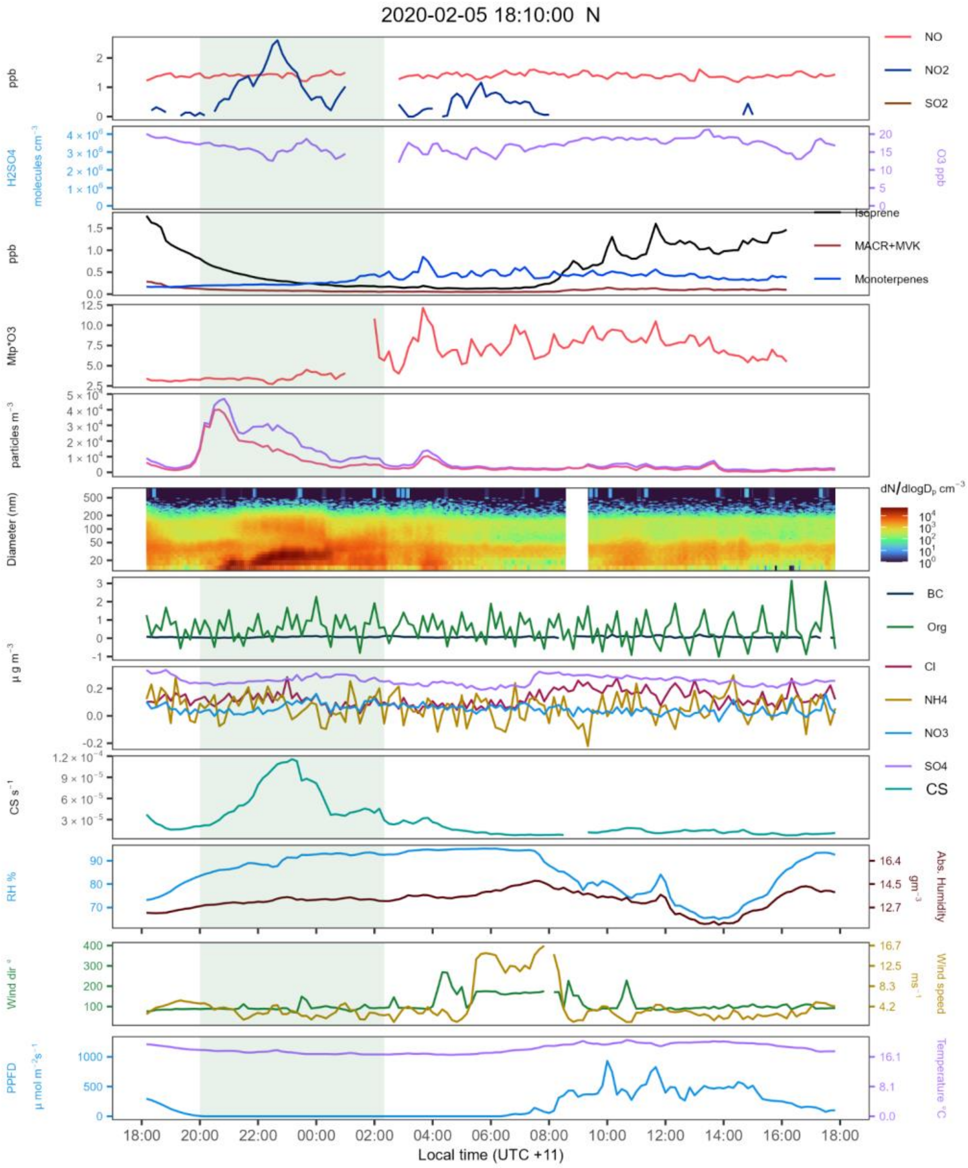


*Figure 9: Time series ~~of~~for all selected variables during the NPF event during 2020-02-05. NO = Nitric oxide, NO2 = Nitrogen dioxide, SO2 = Sulphur dioxide, H2SO4 = Sulphuric acid, O3 = Ozone, MACR+MVK = isoprene ox. products methacrolein and methyl-vinyl-ketone, CN3 =*

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*Condensation Nuclei >3nm, CN3-CN14 = difference of CN3 minus the sum of all channels from the SMPS data. BC = Black carbon. Org = Organic mass fraction, NH4 = Ammonium mass fraction, NO3 = Nitrates mass fraction, SO4 = Sulphates mass fraction, Cl = Chloride mass fraction~~, CN3 = Condensation Nuclei >3nm.~~. CS = condensation sink. Mtp*ozone = HOM proxy product monoterpenes and ozone [ppb*ppb]. Note how the particle number goes below 10000 after the growth reached Aitken mode (0:00). There is not a substantial increase in the aerosol mass when the particle number and geometrical particle diameter increase. The light green ~~vertical line~~area marks the NPF ~~approximated starting time of~~and growth period mentioned in the ~~nighttime event. The black line represents the NPF approximated ending time.~~analysis.*

~~Another factor possibly influencing the NPF events at night may include the early night VOC accumulation in the residual planetary boundary layer. This might enhance particle formation for short periods of time, inducing nucleation and clusters, but not growth (due to the lack of VOCs once the available mass has reacted or condensed over existing particle seeds). This might explain the increase in particle number and density, but the relatively low mass observed during the night of Feb 23 compared to day-time events (see Figure 9).~~

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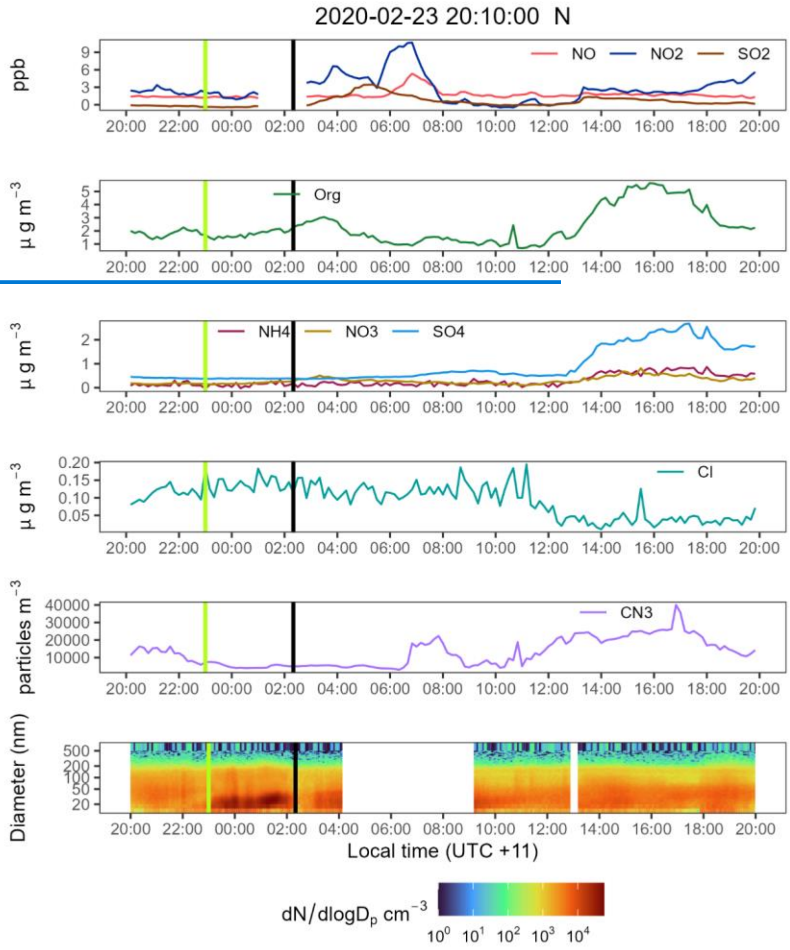
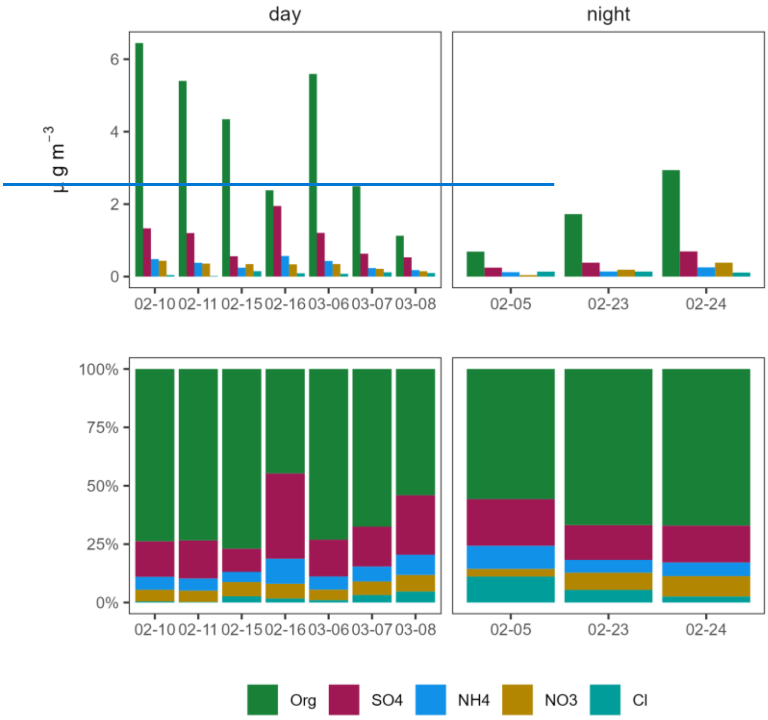


~~*Figure 9: Time series of all selected variables during the NPF event during 2020-02-23. NO = Nitric oxide, NO2 = Nitrogen dioxide, SO2 = Sulphur dioxide, Org = Organic mass fraction, NH4 = Ammonium mass fraction, NO3 = Nitrates mass fraction, SO4 = Sulphates mass fraction, Cl = Chloride mass fraction, CN3 = Condensation Nuclei >3nm. The light green vertical line marks the NPF approximated starting time of the nighttime event. The black line represents the NPF approximated ending time. There is a slight increase in the organic fraction while the event takes place. The organic fraction increases later that morning but there is not particle size distribution data to compare that period.*~~

### 3.6 Aerosol fraction: Day vs Night 666



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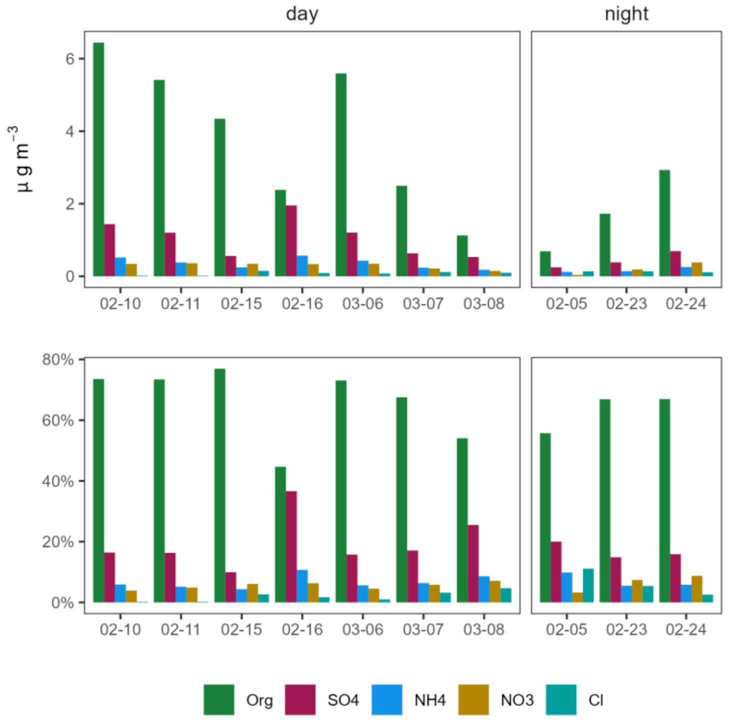

*Figure 10: Average mass for each chemical group and event on the top panels. The bottom panel presents the percentage contribution to the mass of each of those fractions based on the average value presented above. Org = Organics; SO4 = sulphates; NH4 = ammonium; NO3 = nitrates and Cl = chlorides.*

Figure 10 shows the mass fraction of the $PM_1$ aerosol mass as measured in the ACSM. Most of the daytime events show a similar mass fraction distribution. The organic fraction is the largest mass fraction followed by sulphates, ammonium, nitrates, and chlorides. We observed higher sulphate mass fractions in days with higher $SO_2$ availability ~~like~~such as the events on Feb 16th and March 8th, where the average sulphate mass fraction was larger or similar to the organic fraction (see Figure 10). These two events also display the highest proportion of ammonium during daytime events. The overall mass during night-time is much lower than during daytime, likely related to the lower concentrations of VOCs available during the night~~.~~, resulting in growth not reaching sizes where it was detectable by the ACSM. Even with less total mass during the night, the contribution of each fraction is similar to the daytime events. The most notable difference between the mass fractions during day and nighttime NPF events is the higher fraction of chlorides during night-time ~~events likely driven by a greater relative contribution from sea salt to the aerosol mass.~~ attributed to a decrease in the aerosol formation capacity of the atmosphere at night that reduces the total organic, sulphate, nitrate and ammonia mass but does not impact chlorides as much.

~~Something to highlight is the higher fraction of ammonium compared to nitrates through all the events. Regions with low $NO_x$ have been previously characterized with higher ammonium fractions compared to nitrates (Du et al., 2015; Liu et al., 2022; Petit et al., 2015; Takami et al., 2005; Topping et al., 2004), whilst regions with higher $NO_x$ concentrations favour nitrate formation (Hu et al., 2015; Parworth et al., 2015; Poulain et al., 2020; Schlag et al., 2016). The local difference in relative mass composition is evident when comparing this study with the aerosol mass fractions observed in an urban site in Sydney (Keywood et al., 2016) in which high nitrate fractions were observed during most of the campaign.~~

## ~~4. Summary and Conclusions~~

~~Here we present aerosol concentration and composition data, VOCs and air pollutant concentrations collected during part of the COALA-2020 campaign including data from 5th Feb to 17th March at a rural site south of Sydney Australia.~~Something to highlight is the higher fraction of ammonium compared to nitrates through most of the events. Regions with low $NO_x$ have been previously characterized with higher ammonium fractions compared to nitrates (Du et al., 2015; Liu et al., 2022; Petit et al., 2015; Takami et al., 2005; Topping et al., 2004), whilst regions with higher $NO_x$ concentrations favour nitrate formation (Hu et al., 2015; Parworth et al., 2015; Poulain et al., 2020; Schlag et al., 2016). The urban vs rural difference in relative mass composition is evident when comparing this study with the aerosol mass fractions observed in an urban site in Sydney (Keywood et al., 2016) in which high nitrate fractions were observed during most of the campaign.

## 4. Summary and Conclusions

Here we present aerosol concentration and composition data, VOCs and air pollutant concentrations collected during part of the COALA-2020 campaign including data from 5th Feb to 17th March at a rural site south of Sydney, Australia. This period followed the Black Summer fires after heavy rainfall cleared the smoke, offering insights into atmospheric processes under clean ~~or pristine~~background conditions.

The atmosphere during the sampling period was classified as highly reactive with ~~some~~ particle formation ~~taking place~~identified on more than 50% of the sampling days~~ with~~. Like previous studies, daytime NPF events ~~were correlated~~coincided with the arrival of anthropogenic plumes at the site, suggesting their role in initiating particle formation. The positive ~~correlation~~relationship between isoprene concentrations and both PM$_1$ organic aerosol mass and CN$_3$~~ with isoprene concentrations~~ suggests a direct relationship between biogenic emissions and organic aerosol formation.

The change between gas to aerosol phase was indirectly analysed through the evaluation of the conditions leading to NPF events. This analysis showed how SO$_2$~~ and NO$_x$~~ plumes impacting the site drove NPF. The particle growth rate was dependent on available VOCs in the atmosphere and OH availability, also enhanced during periods with higher relative humidity and multiple intrusions of SO$_2$ and NO$_x$ plumes producing particles ~~bigger~~larger than 100 $nm$.

~~Night-time events were correlated to $NO_2$, but the enviromental conditions changed between the few identified events limiting the ability to draw definitive conclusions.~~

Night-time events were attributed mainly to oxidation with ozone, and some potential growth through the isoprene/nitrate radical oxidation pathway. Although most of the night-time events showed the influence of monoterpene ozonolysis on NPF events, our data was limited and we acknowledge that other factors may have influenced nighttime NPF.

The COALA-2020 campaign highlights the significant role of biogenic emissions, particularly ~~isoprene,~~monoterpenes driving NPF and isoprene enhancing particle growth in Southeast Australia. These findings contribute to a better understanding of local atmospheric chemistry and its potential impact on regional air quality and climate. However, longer-term observations are necessary to capture the full picture of seasonal variations and non-fire related extreme events.

**Supplementary Materials:**

**Author Contributions:**

The experiment design was made by Clare Paton-Walsh (Murphy) and Melita Keywood.

The data collection was done by Jack Simmons, Travis Naylor, Paton-Walsh (Murphy), Asher Mouat, Melita Keywood, Ruhi Humpries, Malcolm Possell and Jhonathan Ramirez-Gamboa.

The data processing to convert mass spectra to concentration of VOCs was done by Asher Mouat under the direction and supervision of Jennifer Kaiser.

The data analysis was done by Jhonathan Ramirez-Gamboa

The paper was written by Jhonathan Ramirez-Gamboa and Clare Paton-Walsh (Murphy).

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**Data Availability Statement:**

Data is available at PANGEA via the following links:

- ~~VOCs: https://doi.org/10.1594/PANGAEA.927277Aerosol~~VOCs: https://doi.org/10.1594/PANGAEA.927277
- Aerosol size distributions: https://doi.org/10.1594/PANGAEA.928853
- Condensations nuclei > 3 nm in diameter: https://doi.org/10.1594/PANGAEA.925555
- Cloud condensation nuclei: https://doi.org/10.1594/PANGAEA.928925
- Green-house gases: https://doi.org/10.1594/PANGAEA.927313
- Air Quality data: https://doi.org/10.1594/PANGAEA.929001
- Meteorological data: ~~https://doi.org/10.1594/PANGAEA.928929~~https://doi.org/10.1594/PANGAEA.928929
- ACSM data: https://doi.org/10.1594/PANGAEA.973272

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**Conflicts of Interest:**

The authors declare no conflicts of interest.

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