We gratefully acknowledge the reviewers for their valuable feedback and suggestions, which have been instrumental in refining this paper. Their original comments are provided below in black, with our corresponding responses in green.

Referee #1

I appreciate the addition of the Monoterpenes*O3 trace in the figures, however, here a unit is missing on the axis labels.

Thanks for the comment we have added units [ppb*ppb] where pertinent

L 15+16: doubling of „play an important role“ + what is meant by the second part of the sentence? Typically it is more the other way round that gas phase concentrations affect the aerosol levels. But are you talking about chemistry in/on the particle?

Fixed the typo. Now it reads: “…and by affecting trace gases through chemical reactions occurring in and on aerosol particles.”

Line 368. The wording of point 3 is not clear and a bit confusing

This discussion was rephrased as:

“During the COALA-2020 campaign, many events, such as the one on February 16th (Figure S3), exhibited elevated gas-phase SO2. The availability of monoterpene to form highly condensable ULVOC/ELVOC is crucial in the observed events. While the oxidation products of isoprene can also condense on pre-existing particles (Stangl et al., 2019), the dominant pathways and their efficiency are likely driven by monoterpenes. Although VOC data was not available for February 16th, the consistent diurnal profile of VOCs observed throughout the remaining dataset (Figure S5) suggests enhanced monoterpene and isoprene availability during the daytime. Under these conditions of available BVOCs, particle growth was frequently observed, suggesting a contribution from condensed organic material. As the night approaches and BVOC emissions decrease with temperature, the remaining OVOCs can undergo further oxidation, forming less volatile species that are more prone to condensation on existing particles. However, the limited availability of VOCs after their consumption (estimated around 22:00 based on diurnal cycles in Figure S5) likely limits further growth.“

Line 606: “Although monoterpenes are quickly oxidized by OH resulting in relatively short lifetimes compared to isoprene (Atkinson, 2000; Atkinson and Arey, 2003)”. The reaction rate constant (IUPAC preferred values) of alpha pinene + OH is roughly half that of isoprene + OH for, so at any given OH level, the isoprene lifetime would be half the alpha pinene lifetime with respect to OH. This sentence is however giving the impressions that monoterpenes react faster with OH than isoprene. Can you rephrase it or be more precise here?

This discussion has been significantly revised and now reads as follows:

“Australia experiences an isoprene-dominated atmosphere (Emmerson et al., 2016; Ramirez-Gamboa et al., 2021), and the chemical balance in the atmosphere can rapidly change, particularly in the hotter seasons when more isoprene is emitted. While SOA formation on pre-existing particles can involve molecules with relatively high saturation vapor pressures, new particle formation critically depends on molecules with extremely low saturation vapor pressures due to the Kelvin effect (Tröstl et al., 2016). Heinritzi et al. (2020) showed that reducing C_{20} formation (α-pinene oxidation in isoprene presence) to favor C_{15} formation reduces nucleation rates. However, it is also important to highlight that C_{15}, C_{10}, and even C_5 oxidation products from isoprene oxidation can contribute to SOA mass on existing particles. Therefore, in Australia's isoprene-dominated environment, higher isoprene to monoterpene ratios could lead to a greater production of C_5 and C_{15} products that contribute to particle growth on

existing aerosols (and SOA mass), while simultaneously hindering new particle formation by reducing the formation of C_{20} dimers from monoterpenes."

Line 638: It is unclear what is meant with "slight increase" in monoterpenes and at which time exactly are you looking here. Additionally, it is not really clear what you think might happen here. You mention that isoprene is decreasing but from there you do not take it further. One possibility would be that the suppression effect that isoprene is having on pure biogenic nucleation, is decreasing as well as isoprene is going down and at some tipping point the same or slightly increasing monoterpenes (in the time from 18:00 to 20:00) can lead to the onset of pure biogenic nucleation. If we look at the results from Simon et al (2020) we find that roughly 300 ppt of alpha pinene (similar to what you report) should lead to a pure biogenic nucleation rate of around 2-3 #cm-3s-1 for your reported temperature, so you could compare this estimate with your measured rate and see if they are in the same ballpark or some additional vapor needs to be involved. If your measured rate is lower, it could imply remaining isoprene suppression, if it is higher it could mean additional vapors like sulphuric acid playing a role.

This discussion has been significantly revised and now reads as follows:

"When VOC data are available, monoterpene concentrations were moderate and increased steadily during the event (5th Feb and 9th March). Isoprene was high at the start of the event on 5th Feb, (see Figure 8) however the sudden decrease in isoprene concentration likely coincides with sunset on that day. When aerosol composition data was available (10th Feb) aerosol organic, nitrate and sulphate concentrations increase during the event. When ozone data were available, concentrations decreased slightly during the course of the event.

The frequency of nocturnal events observed in this study is lower than observed previously at a nearby location (Tumbarumba a eucalypt forest site located 300 km to the SE of Cataract (Suni et al., 2009)), where in the summer of 2006, nocturnal NPF events were observed on 32% of the analysed nights and occurred 2.5 times more frequently than daytime events. Simulating the NPF at Tumbarumba, Ortega et al (2012) was able to reproduce the observations from Tumbarumba by ozonolysis of 13 -carene to initiate nucleation and a-pinene to grow particle diameters. Ozonolysis of limonene was found to contribute to both nucleation and aerosol growth. The lower frequency observed in our study may be linked to the apparent initiations of nucleation by NO_2, which nocturnally can react with O_3 to form nitrate radicals. Li et al. (2024), suggest even trace amounts of NO_3 radicals suppress the NPF."

Referee #2:

Major:

The authors should explain in detail how their sulfuric acid is derived. This information has not been given in the technical section despite they referred to Dada et al. This is an important factor in the discussion as different proxies certainly give different results. A brief discussion about why the authors chose Dada et al should also be given (e.g., are the site conditions similar?).

We have clarified this in the revised manuscript with the following text:

"We estimated the H_2SO_4 proxy using the rural model developed by Dada et al (2020). This model was chosen from among the options because the environmental conditions under which it was derived are the most similar to those of our sampling site. The equation used to estimate H_2SO_4 proxy was

$$[H_2SO_4]_{\{rural\}}= -\frac{CS}{2*(2x10^{-9})}+[\left(\frac{CS}{2*(2x10^{-9})}\right)^2+\frac{[SO_2]}{(2x10^{-9})}*(9*10^{-9}*GlobRad]^{\frac{1}{2}},$$

Where CS is the condensation sink, SO_2 is the concentration of SO_2, GlobRad is the global radiation obtained from the Photosynthetic Photon Flux Density (PPFD) values as GlobRad = 0.327*PPFD."

The authors discuss isoprene and monoterpene contribution to particle growth without chemical ionization measurements. They claim isoprene contributes more which needs evidence. This paper fails to link previous quantitative information with their current paper and more work needs to be done on discussions throughout this paper.

We appreciate the reviewer's concern about the lack of chemical ionization measurements and the previous emphasis on isoprene. We have addressed this by rewording the discussion to focus more directly on our observations and have reduced the asserted contribution of isoprene NPF role based on the provided references.

For the section 3.5, the night-time event is interesting, as I already mentioned. But the discussions provided are currently not convincing enough. If monoterpene is the cause of the NPF (including proving OH and sCI for SO2), then why the mid-night in Figure 6 did not observe the same NPF event since the monoterpenes are even higher there? Additionally, since the CS has increased substantially, I'm surprised the ACSM did not see significant increase of different elements. The sulfate decreased and the organic is decreased. There are only minor changes in the ammonium, chloride and a bit later nitrate. So first of all, why ACSM measurements did not observe a significant change and 2) why these elements increase instead of sulfate and organics? This might be leaving to a more robust discussion. Also, the authors should consider the possibility of a transported event instead of a local NPF for this night time event as evidence of local NPF is rather lacking.

We appreciate the reviewer's insightful comments on the night-time NPF event. Upon further investigation, we have identified one event that was likely due to a shift in wind direction and have removed it from our analysis. The remaining discussion of night-time events has been modified to be more observation-based, and we highlight the potential involvement of NO2 chemistry. Regarding the ACSM data, the lack of fully concurrent measurements across all events limits our ability to provide a comprehensive explanation for the observed trends. However, we find it interesting that the nighttime NPF frequency in our study are significantly lower compared to previous studies in the vicinity, which could be related to nitrate suppression observed during our campaign.

The night time section now reads as:

"We observed three nighttime events during COALA. Unfortunately, none of these events coincided with all data sets being collected which limits our ability to discuss the reactions driving the nighttime events. Consistent between all nighttime events is an increase in particles (CN_3), elevated NO_2, and an increasing condensation sink. Unfortunately, the NO_x instrument available in this study was not ideal for this type of measurement for several reasons: it is not designed to be 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 data showed particle formation and growth from nucleation to Aitken modes when there were considerable increases of NO_2 and simultaneous decreases in ozone.

When VOC data are available, monoterpene concentrations were moderate and increased steadily during the event (5th Feb and 9th March). Isoprene was high at the start of the event on 5th Feb, (see Figure 8) however the sudden decrease in isoprene concentration likely coincides with sunset on that day. When aerosol composition data was available (10th Feb) aerosol organic, nitrate and sulphate concentrations increase during the event. When ozone data were available, concentrations decreased slightly during the course of the event.

The frequency of nocturnal events observed in this study is lower than observed previously at a nearby location (Tumbarumba a eucalypt forest site located 300 km to the SE of Cataract (Suni et al., 2009)), where in the summer of 2006, nocturnal NPF events were observed on 32% of the analysed nights and occurred 2.5 times more frequently than daytime events. Simulating the NPF at Tumbarumba, Ortega et al (2012) was able to reproduce the observations from Tumbarumba by ozonolysis of 13 -carene to initiate nucleation and a-pinene to grow particle diameters. Ozonolysis of limonene was found to contribute to both nucleation and aerosol growth. The lower frequency observed in our study may be linked to the apparent initiations of nucleation by NO_2, which nocturnally can react with O_3 to form nitrate radicals. Li et al. (2024), suggest even trace amounts of NO_3 radicals suppress the NPF."

Minor:

L18: It is hard to argue that vapor condensation and growth are truly distinct processes. Perhaps it would be better to simply refer to them as "nucleation and growth."

Changed as suggested

L19-20: This is gas-phase oxidation and not heterogeneous processes...

Removed the heterogeneous process attribution

L27-28: OH is not just influenced by relative humidity and there are many other factors controlling its concentration. Please remove the brackets.
Removed the brackets

L31: why wildfires are mentioned? It needs context before introducing it.

We have removed the wildfires mention as it wasn't contributing to the overall message of the paper.

L41: The chemical composition, size and concentrations "of aerosols"

Fixed

L49: define PBL

Defined

L54: it does not need to be humid (which is not clearly defined in the first place). Just remove the "in a humid place".

Removed

L66: what is "p.201"?

Caused by a bug in the reference manager. IT has being addressed.

L66-67: give a ref for ELVOC and ULVOC. Additionally, their definition is not limited to 298K.

Fixed. It reads as: *"HOMs can be characterised as ultra-low VOCs (ULVOC) or extremely low VOCs (ELVOC) depending upon the saturation concentration (Bianchi et al., 2019; Peräkylä et al., 2020)."*

L68-71: rewrite.

Whole paragraph was rewritten as: *" 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). HOMs can be characterised as ultra-low VOCs (ULVOC) or extremely low VOCs (ELVOC) depending upon the saturation concentration (Bianchi et al., 2019; Peräkylä et al., 2020).*

Oxidation of monoterpenes is a significant pathway for SOA formation, yielding higher amounts of low-volatility molecules like ULVOCs and ELVOCs compared to isoprene oxidation (Friedman and Farmer, 2018; Lee et al., 2023; Luo et al., 2024; Riva et al., 2019; Zhang et al., 2018). HOMs are key precursors for new particle formation. However, the atmospheric production of HOMs can be limited by competing reactions and the presence of other VOCs. For instance, as a general principle, once a VOC molecule oxidizes, it becomes more complex and forms larger Oxygenated VOCs (OVOCs) that are less likely to undergo further oxidation, especially in the presence of other VOCs with higher reactivity towards OH or O_3 *(Kiendler-Scharr et al., 2009). An example of this limitation is the suppression of monoterpene-derived HOM formation by isoprene oxidation products. These products can interfere with the formation of* C_{20} *dimers from monoterpene oxidation, leading to a reduced yield of HOMs and favoring the formation of weaker nucleating species* C_{15} *(Dada et al., 2023; Heinritzi et al., 2020; Liu et al., 2016a). This suppression effect is dynamic, varying non-linearly with local atmospheric composition (e.g., isoprene and monoterpene concentrations, oxidant availability) and atmospheric conditions (e.g., temperature, humidity, stability), which ultimately determine the dominant SOA formation pathways (e.g. Song et al., 2019). "*

L71: Heiritzi et al. did not suggest isoprene oxidation products (C5) contribute to particle growth above 3 nm. Please check the paper again and rephrase.

Modified as shown in the previous comment.

L72-74: This sentence is a bit confusing. Nighttime NO3 oxidation is dominant and it needs not be compared with OH unless there is a strong OH source identified.

Modified as shown before.

L78: "Isoprene, monoterpenes, OH, nitrate radical and ozone availability"

Fixed the typo

L80: comma before "so"

Added a comma.

L83: C20 dimers "from monoterpene oxidation"

Fixed.

L115: a period before "On February" and a comma after.

Fixed.

L120: correct 5 February 5th.

Fixed.

L202: the subscription of vapours should be unified throughout the manuscript.

Fixed throughout the manuscript

L205: aerosol sulphate should be (SO4(2-)) and not SO4. Since this paper discusses gas phase radicals as well as particle phase compounds, it is advised to stick to coherent and annotations for these two categories throughout the manuscript, including captions such as Figure 2 etc.

We have changed SO4 to SO42- in both discussion and most captions.

L207-218: these discussions should be connected with an overview figure showing all the data. It can be presented in the SI for example. Since the cases are quite limited, it is a good idea to present a table giving a summary of all the events and what data each event has. So it would be easier to identify the events with the most complete data sets.

We have added Table 2 as a graphical way to briefly state what data is available on each event

L235-236: why Figure3 is mentioned before Figure2?

It wasn't. Figure 2 was introduced in line 201.

L247: why it increased? Could you give some discussions based on your data?

Added some discussions as follows: " …The first part of the regression shows slower growth rate. After the 6th hour of slow growth, the rate increases substantially, attributed to an increase of H_2SO_4 around this time. Shortly after this accelerated growth, there is a wind change from northerly to southerly (Figure S4). Following the southerly wind shift, a lower condensation sink and higher relative humidity likely contributed to the Gdp increase via enhanced condensation and water uptake. Declining tracer levels SO_2 and NO_x indicate that local particle growth mechanisms were likely dominant over the influence of a new air mass up to the 7th hour when increases in NO_x and SO_2 are observed. "

L252-255: rewrite

Rephrased as: "… These reaction pathways might include 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 may initiate 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. …"

L299: missing a period

Fixed.

L301: Kirkby et al should be referred to for the monoterpene nucleation1.

Added Kirby et al (2023) as a reference here.

L302-303: could the authors give reasons why they believe the isoprene is contributing more to particle growth in their studies? I believe their instruments and methodology are not sufficient to derive such conclusion without detailed chemical modelling.

As suggested, we have rewritten much of the analysis in light of the references provided by the referee. The attribution to isoprene has been removed in most cases and it's only attributed to the growth phase (post NPF) under specific conditions.

L303-304: once again, how does the authors establish the connection of isoprene oxidation at the boundary layer with ELVOC without chemical information measured? The concentration of ELVOC by isoprene should be rather limited at this temperature. The authors should provide evidence to this. In fact, monoterpene concentration is also expected to increase by the same mechanism.

As stated in the previous comment, the discussion has been changed to reflect the literature.

L307: 1 ppb of monoterpene is substantial! The authors should check relevant papers such as Kirkby et al. and Lehtipalo et al.1,3 for quantitative assessment. This they should base their discussions on quantitative information provided in previous chamber experiments to further derive their conclusion. This is another piece of information that goes against their conclusion of significant isoprene contribution.

As stated in the previous comment, the discussion has been changed to reflect the literature.

L321: HOMS proxy or HOM proxy as written earlier? Again, HOMS or HOMs? Anyway, please be consistent with your writing and editing. Also note that throughout the manuscript, the subscriptions for H2SO4 etc has not been consistently applied. Please edit these details carefully.

Fixed throughout the text

L319-322: rewrite

Rephrased as: *"This is the first step in the reaction chain to produce* C_{15} *dimers. This observation aligns with the HOM proxy (monoterpenes*ozone): higher proxy values corresponded to periods of higher particle numbers, while a decrease in the HOM proxy coincided with a decrease in particle numbers and an increase in MACR + MVK products, suggesting a shift towards more isoprene-influenced atmospheric chemistry. Concurrently, increases in the organic and sulfate fractions, along with the condensation sink, indicate a shift towards conditions favoring the growth of existing larger particles through condensation and coagulation, rather than nucleation events."*

L343-344: again, please provide evidence of significant contribution of isoprene oxidation products in terms of previous laboratory experiments.

Rephrased to reflect the literature as: "The event on March 10 (see **Error! Reference source not found.**) 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."

L367-378: the discussions here are very poor. The choice of the referred paper is also rather problematic. The authors should check the conditions used in that experiments and whether that is really representative for the conditions in their site. For example, the experiments used SO2 concentration of over 100 ppb and the conclusion about sCI and peroxides is rather odd. The main sink of SO2 should either by OH or sCI.

We have removed all the discussion around SO2 and humidity given that the conditions during the campaign are too different from the experiments and the results of those are only applicable under haze formation conditions.

L391-393: this is really a strong indication that the authors did not read Heinritzi paper at al.. The C15 is a product of monoterpene C10 and isoprene C5 and just from isoprene oxidation.. In fact, the Heinritzi paper clearly suggested that C15 is less able than monoterpene C20 in both nucleation and growth which the authors should take into account throughout the manuscript.

This was included in the SO2 humidity discussion that was removed from the manuscript.

L408: duplication period.

fixed

L413 on: In my previous comment on that the statement "MACR is oxidised to heavier OVOCs that eventually condense." is wrong, the authors used Heinritzi et al. 2020 as the support of their statement which was totally non relevant to the discussion. The problem is that MACR is a four carbon species which is not believed to be the major precursor of condensable isoprene molecules (C5 species). I refer the authors to Wennberg et al.4 for some basic knowledge of isoprene oxidation mechanisms.

This discussion was changed to reflect current literature and Australian conditions as follows: " Australia experiences an isoprene-dominated atmosphere (Emmerson et al., 2016; Ramirez-Gamboa et al., 2021), and the chemical balance in the atmosphere can rapidly change, particularly in the hotter seasons when more isoprene is emitted. While SOA formation on pre-existing particles can involve molecules with relatively high saturation vapor pressures, new particle formation critically depends on molecules with extremely low saturation vapor pressures due to the Kelvin effect (Tröstl et al., 2016). Heinritzi et al. (2020) showed that reducing C_{20} formation (α-pinene oxidation in isoprene presence) to favor C_{15} formation reduces nucleation rates. However, it is also important to highlight that C_{15}, C_{10}, and even C_5 oxidation products from isoprene oxidation can contribute to SOA mass on existing particles. Therefore, in Australia's isoprene-dominated environment, higher isoprene to monoterpene ratios could lead to a greater production of C_5 and C_{15} products that contribute to particle growth on existing aerosols (and SOA mass), while simultaneously hindering new particle formation by reducing the formation of C_{20} dimers from monoterpenes. "

Figure 9 is missing a legend for particles.

Fixed

L440-441: isoprene oxidation by nitrate pathway also produces MVK and MACR4. Could this discussion be more quantitative. Additionally, from the figure the decrease of isoprene seems not relevant to the NOx increase. So why the authors believe that isoprene has a role here?

This discussion has been significantly revised and now reads as follows:

"When VOC data are available, monoterpene concentrations were moderate and increased steadily during the event (5th Feb and 9th March). Isoprene was high at the start of the event on 5th Feb, (see Figure 8) however the sudden decrease in isoprene concentration likely coincides with sunset on that day. When aerosol composition data was available (10th Feb) aerosol organic, nitrate and sulphate concentrations increase during the event. When ozone data were available, concentrations decreased slightly during the course of the event.

The frequency of nocturnal events observed in this study is lower than observed previously at a nearby location (Tumbarumba a eucalypt forest site located 300 km to the SE of Cataract (Suni et al., 2009)), where in the summer of 2006, nocturnal NPF events were observed on 32% of the analysed nights and occurred 2.5 times more frequently than daytime events. Simulating the NPF at Tumbarumba, Ortega et al (2012) was able to reproduce the observations from Tumbarumba by ozonolysis of 13 -

carene to initiate nucleation and a-pinene to grow particle diameters. Ozonolysis of limonene was found to contribute to both nucleation and aerosol growth. The lower frequency observed in our study may be linked to the apparent initiations of nucleation by NO_2, which nocturnally can react with O_3 to form nitrate radicals. Li et al. (2024), suggest even trace amounts of NO_3 radicals suppress the NPF."