Responses to reviewers

Reviewer comments are in in ***black italic type***. Author responses are labelled with [R] and authors actions with [A]. Line numbers in the responses correspond to the **revised manuscript with track-changes**. Modifications to the manuscript are in blue.

Reviewer 2

This paper studies the primary and secondary emissions of buses with a variety of different modern fuels, using a combination of gaseous, PM and CIMS measurements. This is potentially important as people switch from traditional fossil fuels to more sustainable fuels and buses often lead the way on this, mandated by local authorities.

Generally, ACP's remit would normally be concerned with atmospheric processes and implications rather than emissions profiling, however given the chemistry associated with the secondary production, I would see this an in-scope. That said, the paper is very much focused on the results rather than the atmospheric implications. But the data that is presented seems to have been collected and treated in an appropriate manner. It should be noted that the use of OFRs is not established as a perfect simulation for atmospheric processes (some of the shortcomings are referred to in the paper), but still should be taken as an indication that secondary aerosols are worthy of concern. The manuscript is generally well written, although it does rely too much on acronyms and symbols, making the paper unclear in places. I recommend publication after minor corrections.

[R0] We greatly value the reviewer's insightful feedback and constructive suggestions.

[A0] We have revised our manuscript to more clearly articulate the implications of secondary particle formation on urban air quality and the complexities of regulating such emissions across different fuel types and engine technologies. Our study highlights the potential significance of non-fuel-dependent sources like lubrication oils and fuel additives, which considerably influence secondary particle formation. Additionally, we have broadened our discussion to include a possible semi-quantitative reference for comparing SOA formation potential across diverse studies. This enhanced discussion is now detailed after line 512 in our manuscript: 'Despite more than an order of magnitude difference in $EF_{PM:Fresh}$ among buses operated with various fuel types, we observed smaller variations in $EF_{PM:Aged}$, suggesting that secondary particle formation is likely influenced by substantial non-fuel-dependent precursor sources such as lubrication oils and/or fuel additives. Recognizing these sources is crucial for refining regulations on hydrocarbon emissions, which could notably enhance SOA control. The median ratios of aged to fresh particle mass emission factors,

listed in ascending order, were for diesel (4.0), HVO (6.7), HVO_{HEV} (10.5), RME (10.8), and CNG buses (84), highlighting the significant yet often overlooked contributions of aged/photochemically processed emissions to urban air quality. Furthermore, Zhao et al. (2017) revealed a strongly nonlinear relationship between SOA formation from vehicle exhaust and the ratio of non-methane organic gas to NO_x ($NMOG:NO_x$). For instance, increasing the $NMOG:NO_x$ from 4 to 10 $ppbC/ppbNO_x$ increased the SOA yield from dilute gasoline vehicle exhaust by a factor of 8, underscoring the importance of integrated emission control policies for NO_x and organic gases for better manage SOA formation. While implementing regulations for secondary particle formation presents significant challenges, these are crucial for a thorough understanding of their impact on regional air quality and health. Our approach to measuring the maximum SOA formation potential—peaking at a photochemical age of approximately 5 equivalent days of atmospheric OH exposure—provides a possible semi-quantitative reference for comparing SOA formation potential across different studies. We acknowledge the limitations of this approach for direct regulatory application and emphasize the need for more precise and comprehensive research to develop a methodologically robust framework that stakeholders can agree upon for systematically assessing the impacts of vehicle on air quality and informing regulatory strategies.'

1. ***The paper's title and overview would give the impression that this is a more comprehensive measurement set than it is, but it must be stressed that the acetate-CIMS method is very selective towards polar molecules such as organic acids. I would suggest modifying the title to something like "... primary and secondary emissions of particulate matter and polar molecules ..." or similar to better reflect the content of the paper. Also, the part dealing with the CIMS measurements (3.2) seems based around what the CIMS is capable of seeing, rather than what is important for the atmosphere. It would help the paper to remain in-scope if the discussion could be based around the importance of the subset of molecules observed in atmospheric chemistry, rather than merely observing what was seen by the CIMS.***

[R1] We value the insightful feedback from the reviewer and acknowledge the need to more clearly address the selective nature of the acetate-CIMS method towards polar molecules such as organic acids.

[A1] To better convey the scope and selective detection capabilities of our measurement set, we have revised the title to 'Online characterization of primary and secondary emissions of particulate matter and acidic molecules from a modern fleet of city buses.' This revision aims to clarify the focus on specific types of emissions analyzed in the study. Additionally, we have refined the abstract to highlight the selective ionization characteristics of the acetate reagent ion used in our CIMS setup. The updated sentences, now inserted after Line 25, read: "Online chemical characterization of gaseous and particulate emissions from

these buses was conducted using a chemical ionization mass spectrometry (CIMS) with acetate as the reagent ion, coupled with a filter inlet for gases and aerosols (FIGAERO). Acetate reagent ion chemistry selectively ionizes acidic compounds, including organic and inorganic acids, as well as nitrated and sulfated organics."

Further, in Section 3.2—Chemical characterization using CIMS—we focus on the acidic compounds identifiable by acetate-CIMS, which hold significant atmospheric relevance. To emphasize the importance of studying these acids, we have added the following text in the introduction after Line 138:'Primary emissions can also be oxidized to higher-volatility products through fragmentation reactions, potentially producing carboxylic acids (Friedman et al., 2017). Engine exhaust is a recognized primary source of organic and inorganic acids in urban environments (Kawamura et al., 1985; Kawamura and Kaplan, 1987; Kirchstetter et al., 1996; Wentzell et al., 2013; Friedman et al., 2017). Monocarboxylic acids are produced by both diesel and spark-ignited engines (Zervas et al., 2001a; Crisp et al., 2014; Zervas et al., 2001b; Kawamura et al., 1985). Recent studies have identified gaseous dicarboxylic acids in diesel exhaust (Arnold et al., 2012), compounds likely linked to the nucleation and growth of particles (Pirjola et al., 2015; Zhang et al., 2004). Additionally, inorganic acids such as nitric (HNO_3) and nitrous (HONO) acids, along with isocyanic acid (HNCO)—implicated in serious health issues like atherosclerosis, cataracts, and rheumatoid arthritis through carbamylation reactions—have been identified in both diesel and gasoline exhausts (Wang et al., 2007; Roberts et al., 2011; Wentzell et al., 2013; Brady et al., 2014; Link et al., 2016; Li et al., 2021). However, the secondary production of organic acid from engine exhaust remains poorly characterized; and it may significantly contribute to the overall organic acid budget and help explain discrepancies between models and measurements (Millet et al., 2015; Yuan et al., 2015; Paulot et al., 2011). Furthermore, the impacts of evolving fuel and engine technologies on emissions have not been comprehensively assessed. Recent advancements in analytical techniques now enable simultaneous, high-resolution online measurements of both gas and particle phase acidic species. This is facilitated by high-resolution time-of-flight chemical ionization mass spectrometry (HR-ToF-CIMS) using acetate as the reagent ion, coupled with a filter inlet for gases and aerosols (FIGAERO) (Le Breton et al., 2019; Friedman et al., 2017; Lopez-Hilfiker et al., 2014).'

2. ***Presentation, wise, I found parts of the paper over-reliant on acronyms and symbols, particularly in the figure captions, where I found myself having to jump back and forward several times to understand what was being talked about. It would make the manuscript much clearer if the descriptions could be given verbally more.***

[R2] [A2] Thank you for highlighting this concern. We have revised the manuscript to enhance clarity by expanding the detailed textual descriptions and reducing reliance on acronyms and symbols in figure captions and text. This should improve readability and accessibility throughout the manuscript.

3. ***Section 3.3.2: It is worth noting that many of the gaseous emissions measured can also directly form secondary particulate matter in the atmosphere in the presence of water vapour and a base (e.g. ammonia), so these could also contribute to the overall secondary PM yield (in theory).***

[R3] [A3] We acknowledge the potential of gaseous emissions to directly contribute to the secondary particulate matter (PM) yield in the atmosphere. To address this important aspect, we have expanded our discussion in Section 3.2.2 to include the potential of carboxylic acids, measured in our study, to participate in secondary PM formation when interacting with water vapor and ammonia in the atmosphere.

We have added the following discussion after Line 456, 'It is important to note that many of these carboxylic acids can directly participate in secondary PM formation in the atmosphere in the presence of water vapor and a base such as ammonia (Chen et al., 2020; Huang et al., 2018; Hao et al., 2020). This process may significantly contribute to the overall secondary PM yield, reflecting a more complex interplay between gaseous emissions and particulate matter under atmospheric conditions.'

4. ***Line 401: The phrase " nitrogen-containing compounds were significantly reduced" is an unfortunate choice of words, because it is not clear whether "reduced" is in the magnitude or chemical sense. Please rephrase.***

[R4] We appreciate the reviewer's attention to detail and the potential for ambiguity in our phrasing.

[A4] To eliminate ambiguity, we have revised the phrase to specifically address the context of emission levels. The revised sentence in the manuscript now reads: "Notably, the emission levels of nitrogen-containing compounds were significantly lowered in Euro VI buses, equipped with advanced after-treatment systems that include EGR and DPF technologies in addition to SCR-only techniques." This modification appears in Line 401 and ensures clarity that we are discussing a decrease in emissions rather than a chemical reduction process.

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