

Responses to reviewers

Reviewer comments are 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 1

The paper reports on measurements of particulate and gaseous compounds in primary emissions and secondary mass formation in the exhaust plumes of transit buses that utilize different fuels and after-treatment systems. The primary focus of this study to explore the potential for secondary pollutant formation using an oxidative flow reactor and to conduct a detailed chemical characterization of both gas and particle phase compounds.

The study is interesting and presents comprehensive data on primary emissions of buses and composition of aged exhaust. With regards to the novelty of methods the study should be published in Atmospheric Chemistry and Physics. However, the employed methodologies for exhaust sampling and determining particle mass emission factors of fresh and aged emissions are difficult to evaluate based on the provided information. The paper lacks an explanation of the regulatory purpose of secondary particle mass (Delta-PM) and how such a regulation can be implemented across engines and fuels given the wide variation of oxidation conditions in the oxidative flow reactor.

[R0] We appreciate the reviewer's valuable feedback and constructive suggestions.

[A0] To address concerns regarding the methodologies used in our study, we have improved the manuscript with additional details on exhaust sampling and the calculation of emission factors for various pollutants for each bus. After line 175, we have added: ‘Roadside measurements were conducted at a designated urban bus stop, featuring a bus-only lane, in Gothenburg, Sweden. (Supporting information (SI), Figure S1). Extractive sampling of individual bus plumes in real traffic was used to characterize emissions, adhering to the method outlined by Hallquist et al. (2013). [Air was continuously drawn through a cord-reinforced flexible conductive hose to the instruments housed within a nearby container.](#) Additional details of the experimental conditions are available in our prior publication by Liu et al. (2019a).’

And after line 219: ‘The EFs of constituents per kilogram of fuel burnt were calculated by relating the concentration change of a specific compound in the diluted exhaust plume to the change in CO₂ concentration. CO₂ served as a tracer for exhaust gas dilution, relative to background

concentration (Hallquist et al., 2013; Janhäll and Hallquist, 2005; Watne et al., 2018; Hak et al., 2009). Assumptions were made for complete combustion and carbon contents of 86.1, 77.3, 70.5, and 69.2% for DSL, RME, HVO, and CNG, respectively, were assumed (Edwards et al., 2004). Further methodological details are elaborated in Liu et al. (2019a). A more comprehensive description of the EF calculations is provided in the Supporting Information.'

We have added in the Supporting Information the detailed methodology for calculating the emission factors (EFs) of gaseous and particulate emissions for individual buses:

‘Calculation of emission factors (EFs)

The EFs are calculated as the quantity of pollutant emitted per kilogram of fuel combusted, employing the carbon balance method adapted from established methodologies in our prior work and other studies in the field (Ban-Weiss et al., 2009; Hak et al., 2009; Hallquist et al., 2013; Zhou et al., 2020):

$$EF_{pollutant} = \left(\frac{\int_{t_1}^{t_2} ([pollutant]_t - [pollutant]_{t_1}) dt}{\int_{t_1}^{t_2} ([CO_2]_t - [CO_2]_{t_1}) dt} \right) \times EF_{CO_2}, \quad (1)$$

where $EF_{pollutant}$ denotes the emission factor for the specific pollutant. The time interval from t_1 to t_2 is critical for capturing the emission dynamics from individual buses. This interval starts just before the sharp rise in pollutant concentration (t_1) and ends as levels stabilize and blend with ambient conditions (t_2), as illustrated in Figure S4, similar to methods we have described previously (Zhou et al., 2020; Zhou et al., 2021). This approach ensures the robustness of peak integration, given that contributions beyond t_2 typically oscillate around zero. The start and end times, t_1 and t_2 , for each pollutant peak are independently determined to account for the differing response times of the measuring instruments to the exhaust plume. The resultant concentration changes of the pollutant and CO_2 , recorded between t_1 and t_2 , are integral to this calculation. For EF_{CO_2} , specific values are assigned based on the type of fuel used, consistent with values reported in earlier studies: 3156 g kg⁻¹ for DSL, 2834 g kg⁻¹ for RME, 3107 g kg⁻¹ for HVO and 2536 g kg⁻¹ for CNG (Edwards et al., 2004).'

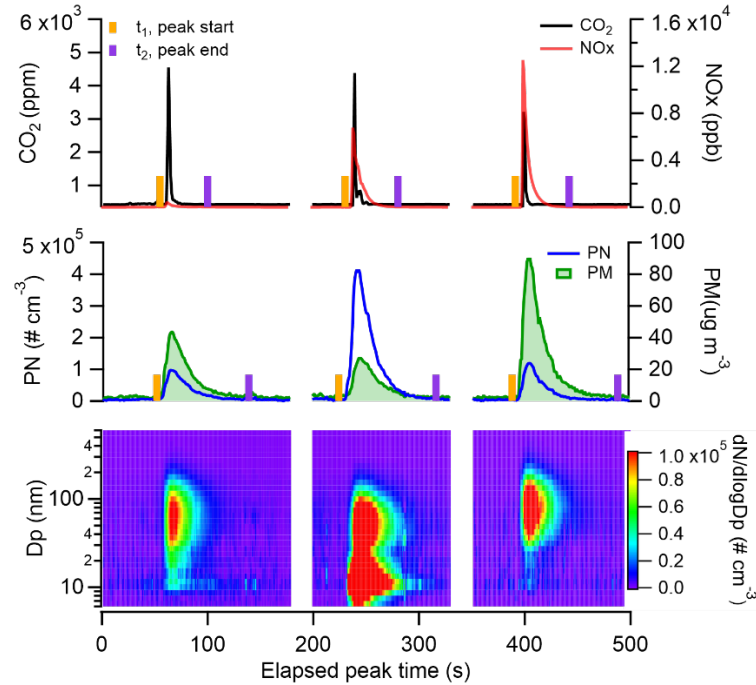


Figure S4. Representative concentration profiles of CO₂, NO_x, particle number (PN), particle mass (PM), and particle number size distribution measured from three individual buses.

A regulatory framework for secondary particle mass (Δ PM) would serve a crucial role in addressing the significant yet often overlooked contributions of aged/photochemically processed emissions to PM in urban air quality. Δ PM captures the additional PM formed after emissions have undergone atmospheric aging processes, reflecting their potential environmental impact more accurately than fresh emissions alone.

Implementing Δ PM regulations across various engine types and fuel compositions is indeed challenging, given that the contribution of on-road vehicles to atmospheric SOA is influenced by multiple factors, including precursor concentrations and atmospheric chemistry (such as SOA yield and OH_{exp}). Our study observed smaller variations in EF_{PM:Aged} compared to EF_{PM:Fresh} across different fuel types, likely due to significant non-fuel-dependent precursor sources such as lubrication oils and/or fuel additives. This highlights the necessity of thoroughly understanding all potential precursor emissions—including those from fuels, lubrication oils, and fuel additives—to enhance current regulations on hydrocarbon emissions. Such improvements could substantially benefit the control of SOA formation. Furthermore, the study by Zhao et al. (2017) demonstrated a strongly nonlinear relationship between SOA formation from vehicle exhaust and the ratio of non-methane organic gas to NO_x (NMOG:NO_x), significantly affecting peroxy radicals. For example, increasing the NMOG:NO_x from 4 to 10ppbC/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 control SOA formation. These findings advocate for a detailed understanding and regulatory consideration to manage SOA formation more effectively. 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.

In response to these findings, we have included the following discussion in our manuscript after line 512: ‘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.) Introduction (P3, line 77-82): Mention that dicarboxylic acids have been found in the primary emissions of diesel vehicles (Arnold et al., 2012) and that they are possible candidates for nucleation of particles in diesel exhaust, please refer to Pirjola et al. (2015).

[R1] Thanks for the suggestion.

[A1] We have revised the introduction to include pertinent references that highlight the relevance of dicarboxylic acids in diesel emissions. The revised text now reads: ‘Primary emissions can 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., 2001b; Crisp et al., 2014; Zervas et al., 2001a; 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).’

2.) Introduction (P3, line 85-92): Suggest a separate paragraph on oxidation flow reactors. Their use in connection with point sampling at street locations should be explained in more detail. For example, the cited study by Kuittinen et al. (2021) uses the OFR to assess secondary aerosol production during standard driving cycles and real-world driving cycles. The combination with point sampling seems to be relatively new and the in-plume measurement at a single point is not well characterized compared to the measurement in driving cycles where the diluted exhaust is directly introduced into an oxidation flow reactor.

[R2] Thank you for the valuable suggestion.

[A2] We have expanded our manuscript to clarify the distinctions among various emission measurement methods, including roadside point sampling, chassis dynamometer measurements with different driving cycles, on-road vehicle chasing, and on-board measurements with portable emission measurement systems (PEMS). After line 76, we have added: ‘Accurately determining vehicle emission factors (EFs) is crucial for devising and implementing effective air quality policies (Fitzmaurice and Cohen, 2022). Methods such as chassis dynamometer tests, on-board measurements with portable emission measurement systems (PEMS), and on-road vehicle chasing experiments have been employed to assess emissions from various types of vehicles (Kwak et al., 2014; Jezek et al., 2015; Pirjola et al., 2016). Chassis dynamometer tests offer high repeatability over standard drive cycles but may not reflect real-world driving conditions or fleet maintenance levels. There are also challenges in accurately replicating real-world dilution effects (Vogt et al., 2003; Kuittinen et al., 2021). On-board measurements with PEMS provide data under a wide range of operating conditions, yet like dynamometers, they may not realistically mimic ambient dilution processes (Wang et al., 2020; Giechaskiel et al., 2015). On-road vehicle chasing experiments involve following individual vehicles with a mobile laboratory to capture the exhaust plumes, providing insights

into realistic dilution processes from the tailpipe to ambient air, though these experiments often require a test track to ensure traffic safety (Wang et al., 2020; Tong et al., 2022). All three methods are limited by small sample sizes, which constrain understanding of the real emission characteristics of vehicle fleets. Alternatively, roadside or near-road measurements provide the ability to monitor emissions from a large number of vehicles under actual driving conditions within a short timeframe (Hallquist et al., 2013; Liu et al., 2019a; Watne et al., 2018), which is particularly important for assessing exposure risks to pedestrians and bus passengers. However, this method is limited by its inability to monitor specific engines or operational conditions, such as varying engine speeds and loads. Integrating results from diverse methodologies would ideally yield a comprehensive understanding of emissions from vehicle transport systems. In a prior study, we conducted roadside point measurements and reported EFs for general air pollutants such as PM, NO_x, CO, and THC from individual buses during stop-and-go operations at a bus stop in Gothenburg, Sweden (Liu et al., 2019a). Our findings showed that hybrid buses, when using their combustion engines to accelerate from a standstill at bus stops, tended to emit higher particle numbers (PN) than traditional DSL buses, likely due to their relatively smaller engines.'

Furthermore, to directly address your point about the application of OFRs, we have included a separate paragraph in the introduction detailing their use in combination with point sampling at street locations after Line 120: 'Expanding on our prior findings, it is important to acknowledge that primary emissions are not the only way in which engine emissions impact air quality. Emissions from engine exhaust can contribute to secondary particles through oxidation of gas-phase species, primarily via functionalization reactions, yielding lower-volatility products (Hallquist et al., 2009; Kroll et al., 2009). Laboratory studies have demonstrated that secondary organic aerosols (SOA) produced from diluted vehicle exhaust frequently exceed the levels of primary organic aerosols (POA) in less than one day of atmospheric equivalent aging (Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014; Liu et al., 2015; Chirico et al., 2010). Oxidation flow reactors (OFRs) enable the simulation of several days of atmospheric aging in a few minutes, with minimized wall effects compared to traditional smog chamber experiments (Palm et al., 2016; Bruns et al., 2015). OFRs have been extensively employed to assess the SOA formation potential of ambient air and emissions from diverse sources, including motor exhausts (Simonen et al., 2017; Kuittinen et al., 2021; Bruns et al., 2015; Tkacik et al., 2014; Watne et al., 2018; Liu et al., 2019b; Yao et al., 2022; Zhou et al., 2021). In real-world traffic scenarios, the rapid response capabilities and convenient deployment of OFRs, coupled with roadside point measurements, provide a robust method for evaluating emissions from a significant number of vehicles. This approach effectively captures the considerable variability among individual vehicles within a fleet, offering a comprehensive view of emissions under actual driving conditions (Watne et al., 2018; Zhou et al., 2021; Liao et al., 2021; Ghadimi et al., 2023), although it may

not encompass as extensive a range of engine operations as setups that integrate OFRs with chassis dynamometer tests (Kuittinen et al., 2021).’

We have also revised the description after Line 164 as follows: ‘In this study, we employed the OFR Gothenburg Potential Aerosol Mass Reactor (Go:PAM) along with roadside point measurements to capture emissions from a diverse array of fuel types and engine technologies in in-use transit buses. We present findings on the photochemical aging of emissions from a modern fleet operating on diesel (DSL) and the latest generation of alternative fuels, including compressed natural gas (CNG), rapeseed methyl ester (RME), and hydrotreated vegetable oil (HVO). Our study aims to compare the secondary production of PM from individual buses in real traffic scenarios to their primary PM emissions, examining the impact of fuel type, engine technology, and photochemical age. Furthermore, both fresh and aged emissions of gas and particle phases are characterized using HR-ToF-CIMS, providing a comprehensive understanding of the emissions profile and their environmental implications.’

3.) Methods (P4, line 104-106) It remains uncertain how well the sampling represents concentrations in the bus plume. Does the sampling integrate over the horizontal and vertical expansion of the plume? Please discuss how temperature, wind speed and direction affected the emission factor of fresh PM.

[R3] We apologize for any confusion caused.

[A3] To calculate the emission factors, we determined particle and gaseous emissions from individual vehicles by measuring changes in concentration, reflecting the integrated concentration over the entire pollutant peak, in the diluted exhaust plume relative to pre-passage levels and changes in CO₂ concentration. For more details, please refer to [R0]. This method does not require absolute concentration measurements as the ratio to CO₂ is assumed constant during dilution (Hak et al., 2009; Hallquist et al., 2013), effectively compensating for varying degrees of dilution. Thus, factors such as wind speed and direction do not affect the emission factors of fresh PM.

Our campaign was conducted in the winter from March 2nd to 12th, 2016, in Gothenburg, Sweden, where average daytime temperatures ranged from 2 to 5°C, with an overall average of 3.9°C. These conditions are unlikely to affect the comparative analysis of EFs for different buses within this study. However, caution is advised when directly comparing these results to data obtained under significantly higher ambient temperatures. Wang et al. (2017) observed that fleet average particle number EFs were lower in summer than in winter, likely due to enhanced nucleation or condensation of gaseous organics at lower temperatures, as opposed to summer conditions that tend to favor particle evaporation. The impact of temperature on

vehicle emissions is most pronounced during the initial cold start phase, where vehicles and their catalytic converters, still cold, lead to inefficient combustion and potentially operate under fuel-rich conditions (Nam et al., 2010). On the other hand, Ristimäki et al. (2005) found that soot mode particles are relatively unaffected by ambient temperatures post-engine warm-up. Additionally, Book et al. (2015) examined temperature effects on particulate emissions from DPF-equipped diesel trucks operating on conventional diesel and biodiesel fuels, finding that particle number and mass emission factors showed varying trends depending on the driving cycles, and concluded that temperature effects were inconclusive. In light of this, the following has been added to the manuscript after line 175: ‘Roadside measurements were conducted at a designated urban bus stop, featuring a bus-only lane, in Gothenburg, Sweden. (Supporting information (SI), Figure S1). The sampling occurred from March 2nd to 12th, 2016, with the average temperature during this period recorded at approximately 3.9°C.’ and after line 531, ‘It is important to note that the ambient temperature during this study was relatively low, which does not affect the EF comparison across different buses but should be aware of when comparing these results to studies conducted at significantly higher temperatures. Wang et al. (2017) noted lower particle number EFs in summer compared to winter, potentially due to increased nucleation or condensation at cooler temperatures. Temperature impacts on emissions are significant during cold starts when combustion is inefficient (Nam et al., 2010). Post-warm-up, soot mode particles show little temperature sensitivity (Ristimäki et al., 2005). Book et al. (2015) found inconsistent trends in particle emissions from DPF-equipped diesel trucks across various temperatures and driving cycles, suggesting that more research is needed to understand the temperature effects on emissions from different bus types under varied operational conditions.’

4.) The aged PM from different measurements seems to be hardly comparable because of a wide range of different OH exposure in the chamber. Were there any controls made for ageing PM to ensure that no desorption from the wall or losses on the walls affects it? Lubrication oils might substantially contribute to aged PM, which do not depend on the type of fuel.

[R4] [A4] In our study, the transmission efficiency for particles with mobility diameters (d_m) larger than 25 nm was over 90% in the Go:PAM, as characterized using nebulized ammonium sulfate particles (Watne et al., 2018). We accounted for potential losses by correcting with size-dependent transmission efficiency, as detailed at line 237: ‘particle wall losses in the Go:PAM were corrected using size-dependent transmission efficiency (Watne et al., 2018).’

We agree that lubrication oils could significantly contribute to aged PM, independently of the fuel type used. Consequently, we have incorporated additional discussions into our manuscript to address this, indicated after line 273: ‘The variance in median $EF_{PM:aged}$ among different fuel types was less pronounced

compared to $EF_{PM:Fresh}$, suggesting the presence of significant non-fuel-dependent precursor sources, such as lubrication oils and/or fuel additives (Watne et al., 2018; Le Breton et al., 2019).’

5.) Page 7, line 209-210: The explanation for the less pronounced dependence of $EF_{PM:aged}$ on OH_{exp} for other buses is unclear. Potential large differences in emissions and dilution effects are already reflected in the fresh PM, how can that affect the dependence of aged PM on OH_{exp} ?

[R5] We apologize for any confusion caused.

[A5] To clarify the points raised, we have revised the paragraph in line 292 as follows: ‘Figure 2 shows the bus average $EF_{PM:Fresh}$ vs the corresponding $EF_{PM:aged}$ for individual bus passages, where the average $EF_{PM:aged}$ for each bus is indicated by a solid horizontal line. This analysis focuses on Euro V/EEV buses to ensure a sufficient number of buses in the comparison, while buses from other Euro classes were not included due to their limited numbers. The median ratio of $EF_{PM:aged}$ to $EF_{PM:Fresh}$ was highest for CNG buses (84), followed by RME (10.8), HVO_{HEV} (10.5), HVO (6.7) and DSL(4.0) buses. Buses equipped with DPFs, such as DSL Euro III and HVO_{HEV} Euro VI (not included in Figure 2), exhibited a median ratio exceeding 50. $EF_{PM:aged}$ exhibited notable variation between passages of the same bus, likely attributable to emission variability between passages and different dilution levels for plumes prior to sampling into the Go:PAM. This is illustrated in Figure 2b, where $EF_{PM:Fresh}$ and $EF_{PM:aged}$ are presented as a function of the dilution level, indicated by the integrated CO_2 area. Generally, a higher integrated CO_2 area suggests a more concentrated plume, leading to increased external OH and O_3 reactivity, which in turn reduces the concentration of OH radicals available in the Go:PAM for precursor oxidation (Emanuelsson et al., 2013; Watne et al., 2018). Some buses displayed primary emissions too dilute for detection (markers located to the left in Figure 2b) but still exhibited non-negligible $EF_{PM:aged}$ after oxidation. To further examine the effects of simulated atmospheric oxidation in the Go:PAM, an estimated minimum OH_{exp} was calculated for each plume by incorporating the OH reactivities of CO and HC and the titration of O_3 with NO, following methodologies from Watne et al. (2018) and Zhou et al. (2021). For all plumes, OH_{exp} varied between 1.1×10^9 to 4.6×10^{11} molecules cm^{-3} s. The $EF_{PM:aged}$ for some buses, for example, the DSL and HVO located to the right in Figure 2c, increased with increasing OH_{exp} . However, due to potential large differences in the chemical composition of emissions across different passages of the same bus, where some species are more prone to forming secondary particle mass even at lower OH_{exp} , the OH_{exp} dependent $EF_{PM:aged}$ for other buses was less pronounced.’

6.) Figure 3: The grouping of Delta-PM according OH_{exp} in Fig. 3 should be explained. Where all buses measured at five different OH_{exp} in the Go:PAM or do the groups represent different vehicle and fuel types? What is the explanation of the lower dPM at 1-5 OH days in the tunnel study by Tkacik et al., 2014?

[R6] We apologize for any confusion caused.

[A6] The box plot in Figure 3 summarizes ΔPM as a function of OH exposure (OH_{exp}), incorporating various bus types from Go:PAM measurements in this study. The composition of the buses includes 40% DSL, 12.2% CNG, 20% RME, 20.8% HVO, and 7% HVO_{HEV}. The results were grouped according to different ranges of OH_{exp} , covering from 1.1×10^9 to 4.6×10^{11} molecules cm^{-3} s. To clarify, we have revised line 339 as follows: ‘Figure 3 illustrates ΔPM as a function of OH_{exp} for the bus fleet in this study, which includes 40% DSL, 12.2% CNG, 20% RME, 20.8% HVO, and 7% HVO_{HEV}. The results were grouped based on OH_{exp} , spanning a range from 1.1×10^9 to 4.6×10^{11} molecules cm^{-3} s.’

The secondary PM formation reported in Tkacik et al. (2014) involved a fleet predominantly composed of light-duty gasoline vehicles (at least 80%), which likely yields lower ΔPM than observed in our study. We have included additional comparative data after line 362: ‘The ΔPM in this study was comparable to 855 mg kg-fuel^{-1} for a mixed fleet consisting of 44.1% gasoline, 41.3% diesel, and 14.6% LPG vehicles measured at an urban roadside in Hong Kong (Liu et al., 2019b). It was slightly higher than the ΔPM measured from a Euro VI dominated (more than 70%) heavy-duty truck fleet at an urban roadside in Gothenburg (Zhou et al., 2021), and from a fleet with over 80% light-duty gasoline vehicles in a Pittsburgh tunnel study (Tkacik et al., 2014).’

7.) Table 2: a sulfur-containing compound with sum formula CH_4SO_3 is among the top 10 emission factors of fresh gaseous emissions. Is this methanesulfonic acid, $\text{CH}_4\text{O}_3\text{S}$? If yes, then elaborate more on it because it is usually known as a tracer of secondary biogenic organics in marine environments.

[R6] [A6] Corrêa and Arbilla (2008) have noted that mercaptans are emitted in diesel and biodiesel exhaust, which are particularly reactive under high NO_x concentrations. In such environments, NO_x may catalyze the transformation of mercaptans into products including methanesulfonic acid. Additionally, diesel fuel and lubricants commonly contain sulfur-containing organic compounds that, upon combustion, can potentially form various sulfuric derivatives. The presence of catalytic converters in diesel engines might further facilitate chemical reactions leading to unexpected byproducts, as the high temperatures and catalytic surfaces within these systems could modify the transformation pathways of sulfur compounds. In our study, we identified CH_4SO_3 , potentially methanesulfonic acid, in the emissions from DSL and RME buses. Given the complexity of these reactions and the conditions within diesel exhaust systems, a detailed pathway for the formation of CH_4SO_3 remains to be fully elucidated. To address this, we have incorporated the following text after line 424: ‘ CH_4SO_3 , potentially identified as methanesulfonic acid, was detected in the emissions from DSL and RME buses. Previous studies, such as those by Corrêa and Arbilla (2008), have shown that mercaptans, emitted from diesel and biodiesel exhausts, can transform under high NO_x

conditions into products including methanesulfonic acid. The presence of sulfur-containing organic compounds in diesel fuel and lubricants, and their potential transformation upon combustion into various sulfuric derivatives, alongside the catalytic activity of engine converters, could also contribute to such findings. However, the detailed formation pathway of CH_4SO_3 in our study remains unknown."

8.) Conclusion/ atmospheric implications (P17, line 389-392): It is obvious that the omission of the secondary formation of particulate matter in engine exhaust in current legislation is problematic for understanding the potential impacts of mobile sources. However, it is unclear how the secondary PM from mobile sources should be implemented in regulations, given that dPM measurements depend on a variety of environmental factors that cannot be controlled, such as OH_{exp} and dilution. The authors should present recommendations how to standardize the comparison of dPM measured at different OH_{exp}.

[R8] Thank you for your insightful suggestions. For a more detailed response, please refer to [R0].

[A8] We have included the following discussion in our manuscript after line 512: ‘Despite more than an order of magnitude difference in $\text{EF}_{\text{PM:Fresh}}$ among buses operated with various fuel types, we observed smaller variations in $\text{EF}_{\text{PM:Aged}}$, 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/ppb NO_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.’

9.) Conclusion/ atmospheric implications (P17, line 396-400): Please elaborate more on the atmospheric implications of HNCO from city buses, e.g. chemical reactions in the atmosphere, relevance of urea-SCR exhaust systems in different buses and bus fleets, and expected concentration in street environments. For example, relate the results of this study on bus emissions of isocyanic acid to the study by Jathar et al. (2017) who investigate diesel engines as an atmospheric source of isocyanic acid in urban areas.

[R9] [A9] Thank you for your suggestions. In our original manuscript, we provided a comparison of HNCO EF with findings from Jathar et al. (2017) and other studies on line 414. We noted, ‘Isocyanic acid, likely an intermediate product of the thermal degradation of urea in SCR systems without sufficient hydrolysis (Bernhard et al., 2012), was detected in emissions from all bus types, with ^{Md}EFs of 0.08-14.74 mg kg-fuel⁻¹. These values are slightly lower than those from a non-road diesel engine (31-56 mg kg-fuel⁻¹) reported by Jathar et al. (2017), but align well with SCR-equipped diesel vehicles tested by Suarez-Bertoa and Astorga (2016) (1.3-9.7 mg kg-fuel⁻¹) and a diesel engine with a diesel oxidation catalyst (DOC) (Wentzell et al., 2013) (0.21-3.96 mg kg-fuel⁻¹). Among all Euro V/EEV buses, HVO_{HEV} buses showed the highest emissions of HNCO, potentially attributed to cold engine conditions since the combustion engine does not operate continuously.’

Furthermore, we have expanded our discussion on the atmospheric implications of HNCO emissions and incorporated the following revisions after line 544 in our manuscript: ‘Furthermore, there is a risk that some abatement systems might generate unintended compounds, such as HNCO from the thermal degradation of urea in SCR systems without sufficient hydrolysis. Additionally, Jathar et al. (2017) observed substantial direct emissions of HNCO from diesel engines and estimated that ambient concentrations in Los Angeles could vary widely, ranging from 20 to 107 ppt depending on different parameterizations of diesel engine emissions. The persistence of HNCO in the atmosphere, particularly under dry conditions, poses significant health risks. It has been linked to severe outcomes including respiratory and cardiovascular disorders, atherosclerosis, cataracts, and rheumatoid arthritis (Leslie et al., 2019; Roberts et al., 2011).’

References

- Arnold, F., Pirjola, L., Ronkko, T., Reichl, U., Schlager, H., Lahde, T., Heikkila, J., and Keskinen, J.: First online measurements of sulfuric acid gas in modern heavy-duty diesel engine exhaust: implications for nanoparticle formation, *Environmental science & technology*, 46, 11227-11234, 2012.
- Ban-Weiss, G. A., Lunden, M. M., Kirchstetter, T. W., and Harley, R. A.: Measurement of black carbon and particle number emission factors from individual heavy-duty trucks, *Environmental science & technology*, 43, 1419-1424, 2009.
- Bernhard, A. M., Peitz, D., Elsener, M., Wokaun, A., and Kröcher, O.: Hydrolysis and thermolysis of urea and its decomposition byproducts biuret, cyanuric acid and melamine over anatase TiO₂, *Applied Catalysis B: Environmental*, 115, 129-137, 2012.
- Book, E. K., Snow, R., Long, T., Fang, T., and Baldauf, R.: Temperature effects on particulate emissions from DPF-equipped diesel trucks operating on conventional and biodiesel fuels, *Journal of the Air & Waste Management Association*, 65, 751-758, 2015.
- Bruns, E., El Haddad, I., Keller, A., Klein, F., Kumar, N., Pieber, S., Corbin, J., Slowik, J., Brune, W., and Baltensperger, U.: Inter-comparison of laboratory smog chamber and flow reactor systems on organic aerosol yield and composition, *Atmospheric Measurement Techniques*, 8, 2315-2332, 2015.
- Chirico, R., DeCarlo, P., Heringa, M., Tritscher, T., Richter, R., Prévôt, A., Dommen, J., Weingartner, E., Wehrle, G., and Gysel, M.: Impact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments, *Atmospheric Chemistry & Physics*, 10, 11545-11563, 2010.
- Corrêa, S. M., and Arbilla, G.: Mercaptans emissions in diesel and biodiesel exhaust, *Atmospheric Environment*, 42, 6721-6725, 2008.
- Crisp, T. A., Brady, J. M., Cappa, C. D., Collier, S., Forestieri, S. D., Kleeman, M. J., Kuwayama, T., Lerner, B. M., Williams, E. J., and Zhang, Q.: On the primary emission of formic acid from light duty gasoline vehicles and ocean-going vessels, *Atmospheric Environment*, 98, 426-433, 2014.
- Edwards, R., Mahieu, V., Griesemann, J.-C., Larivé, J.-F., and Rickeard, D. J.: Well-to-wheels analysis of future automotive fuels and powertrains in the European context, *SAE Technical Paper0148-7191*, 2004.
- Emanuelsson, E. U., Hallquist, M., Kristensen, K., Glasius, M., Bohn, B., Fuchs, H., Kammer, B., Kiendler-Scharr, A., Nehr, S., and Rubach, F.: Formation of anthropogenic secondary organic aerosol (SOA) and its influence on biogenic SOA properties, *Atmospheric Chemistry and Physics*, 13, 2837-2855, 2013.
- Fitzmaurice, H. L., and Cohen, R. C.: A method for using stationary networks to observe long-term trends of on-road emission factors of primary aerosol from heavy-duty vehicles, *Atmospheric Chemistry and Physics*, 22, 15403-15411, 2022.
- Friedman, B., Link, M. F., Fulgham, S. R., Brophy, P., Galang, A., Brune, W. H., Jathar, S. H., and Farmer, D. K.: Primary and Secondary Sources of Gas-Phase Organic Acids from Diesel Exhaust, *Environ Sci Technol*, 51, 10872-10880, 10.1021/acs.est.7b01169, 2017.
- Ghadimi, S., Zhu, H., Durbin, T. D., Cocker III, D. R., and Karavalakis, G.: Exceedances of Secondary Aerosol Formation from In-Use Natural Gas Heavy-Duty Vehicles Compared to Diesel Heavy-Duty Vehicles, *Environmental Science & Technology*, 57, 19979-19989, 2023.
- Giechaskiel, B., Riccobono, F., Vlachos, T., Mendoza-Villafuerte, P., Suarez-Bertoa, R., Fontaras, G., Bonnel, P., and Weiss, M.: Vehicle emission factors of solid nanoparticles in the laboratory and on the road using portable emission measurement systems (PEMS), *Frontiers in Environmental Science*, 3, 82, 2015.
- Gordon, T. D., Presto, A. A., Nguyen, N. T., Robertson, W. H., Na, K., Sahay, K. N., Zhang, M., Maddox, C., Rieger, P., Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Secondary organic aerosol production from diesel vehicle exhaust: impact of aftertreatment, fuel chemistry and driving cycle, *Atmospheric Chemistry and Physics*, 14, 4643-4659, 10.5194/acp-14-4643-2014, 2014.
- Hak, C. S., Hallquist, M., Ljungstrom, E., Svane, M., and Pettersson, J. B. C.: A new approach to in-situ determination of roadside particle emission factors of individual vehicles under conventional driving conditions, *Atmospheric Environment*, 43, 2481-2488, 10.1016/j.atmosenv.2009.01.041, 2009.

Hallquist, A. M., Jerksjö, M., Fallgren, H., Westerlund, J., and Sjödin, A.: Particle and gaseous emissions from individual diesel and CNG buses, *Atmospheric Chemistry and Physics*, 13, 5337-5350, 10.5194/acp-13-5337-2013, 2013.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N., George, C., and Goldstein, A.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmospheric chemistry and physics*, 9, 5155-5236, 2009.

Janhäll, S., and Hallquist, M.: A novel method for determination of size-resolved, submicrometer particle traffic emission factors, *Environmental Science & Technology*, 39, 7609-7615, <http://doi.org/10.1021/es048208y>, 2005.

Jathar, S. H., Heppding, C., Link, M. F., Farmer, D. K., Akherati, A., Kleeman, M. J., de Gouw, J. A., Veres, P. R., and Roberts, J. M.: Investigating diesel engines as an atmospheric source of isocyanic acid in urban areas, *Atmospheric Chemistry and Physics*, 17, 8959-8970, 10.5194/acp-17-8959-2017, 2017.

Jezek, I., Drinovec, L., Ferrero, L., Carriero, M., and Mocnik, G.: Determination of car on-road black carbon and particle number emission factors and comparison between mobile and stationary measurements, *Atmospheric Measurement Techniques*, 8, 43-55, 10.5194/amt-8-43-2015, 2015.

Kawamura, K., Ng, L. L., and Kaplan, I. R.: Determination of organic acids (C1-C10) in the atmosphere, motor exhausts, and engine oils, *Environmental science & technology*, 19, 1082-1086, 1985.

Kawamura, K., and Kaplan, I. R.: Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environmental science & technology*, 21, 105-110, 1987.

Kirchstetter, T. W., Harley, R. A., and Littlejohn, D.: Measurement of nitrous acid in motor vehicle exhaust, *Environmental science & technology*, 30, 2843-2849, 1996.

Kroll, J. H., Smith, J. D., Che, D. L., Kessler, S. H., Worsnop, D. R., and Wilson, K. R.: Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol, *Physical Chemistry Chemical Physics*, 11, 8005-8014, 2009.

Kuittinen, N., McCaffery, C., Peng, W., Zimmerman, S., Roth, P., Simonen, P., Karjalainen, P., Keskinen, J., Cocker, D. R., and Durbin, T. D.: Effects of driving conditions on secondary aerosol formation from a GDI vehicle using an oxidation flow reactor, *Environmental Pollution*, 282, 117069, 2021.

Kwak, J. H., Kim, H. S., Lee, J. H., and Lee, S. H.: On-Road Chasing Measurement of Exhaust Particle Emissions from Diesel, Cng Lpg and Dme-Fueled Vehicles Using a Mobile Emission Laboratory, *International Journal of Automotive Technology*, 15, 543-551, <http://doi.org/10.1007/s12239-014-0057-z>, 2014.

Le Breton, M., Psichoudaki, M., Hallquist, M., Watne, Å., Lutz, A., and Hallquist, Å.: Application of a FIGAERO ToF CIMS for on-line characterization of real-world fresh and aged particle emissions from buses, *Aerosol Science and Technology*, 53, 244-259, 2019.

Leslie, M. D., Ridoli, M., Murphy, J. G., and Borduas-Dedekind, N.: Isocyanic acid (HNCO) and its fate in the atmosphere: a review, *Environmental Science: Processes & Impacts*, 21, 793-808, 2019.

Liao, K., Chen, Q., Liu, Y., Li, Y. J., Lambe, A. T., Zhu, T., Huang, R.-J., Zheng, Y., Cheng, X., and Miao, R.: Secondary organic aerosol formation of fleet vehicle emissions in China: Potential seasonality of spatial distributions, *Environmental Science & Technology*, 55, 7276-7286, 2021.

Liu, Q., Hallquist, Å. M., Fallgren, H., Jerksjö, M., Jutterström, S., Salberg, H., Hallquist, M., Le Breton, M., Pei, X., and Pathak, R. K.: Roadside assessment of a modern city bus fleet: Gaseous and particle emissions, *Atmospheric Environment: X*, 3, 100044, 2019a.

Liu, T., Wang, X., Deng, W., Hu, Q., Ding, X., Zhang, Y., He, Q., Zhang, Z., Lu, S., Bi, X., Chen, J., and Yu, J.: Secondary organic aerosol formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber, *Atmospheric Chemistry and Physics*, 15, 9049-9062, 10.5194/acp-15-9049-2015, 2015.

Liu, T., Zhou, L., Liu, Q., Lee, B. P., Yao, D., Lu, H., Lyu, X., Guo, H., and Chan, C. K.: Secondary Organic Aerosol Formation from Urban Roadside Air in Hong Kong, *Environ Sci Technol*, 53, 3001-3009, 10.1021/acs.est.8b06587, 2019b.

Nam, E., Kishan, S., Baldauf, R. W., Fulper, C. R., Sabisch, M., and Warila, J.: Temperature effects on particulate matter emissions from light-duty, gasoline-powered motor vehicles, *Environmental science & technology*, 44, 4672-4677, 2010.

Nordin, E. Z., Eriksson, A. C., Roldin, P., Nilsson, P. T., Carlsson, J. E., Kajos, M. K., Hellen, H., Wittbom, C., Rissler, J., Londahl, J., Swietlicki, E., Svenningsson, B., Bohgard, M., Kulmala, M., Hallquist, M., and Pagels, J. H.: Secondary organic aerosol formation from idling gasoline passenger vehicle emissions investigated in a smog chamber, *Atmospheric Chemistry and Physics*, 13, 6101-6116, 10.5194/acp-13-6101-2013, 2013.

Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J. F., and Cross, E. S.: In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor, *Atmospheric Chemistry and Physics*, 16, 2943-2970, 2016.

Pirjola, L., Karl, M., Rönkkö, T., and Arnold, F.: Model studies of volatile diesel exhaust particle formation: are organic vapours involved in nucleation and growth?, *Atmospheric Chemistry and Physics*, 15, 10435-10452, 2015.

Pirjola, L., Dittrich, A., Niemi, J. V., Saarikoski, S., Timonen, H., Kuuluvainen, H., Jarvinen, A., Kousa, A., Ronkko, T., and Hillamo, R.: Physical and Chemical Characterization of Real-World Particle Number and Mass Emissions from City Buses in Finland, *Environ Sci Technol*, 50, 294-304, <http://doi.org/10.1021/acs.est.5b04105>, 2016.

Platt, S. M., El Haddad, I., Zardini, A. A., Clairotte, M., Astorga, C., Wolf, R., Slowik, J. G., Temime-Roussel, B., Marchand, N., Jezek, I., Drinovec, L., Mocnik, G., Mohler, O., Richter, R., Barmet, P., Bianchi, F., Baltensperger, U., and Prevot, A. S. H.: Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, *Atmospheric Chemistry and Physics*, 13, 9141-9158, 10.5194/acp-13-9141-2013, 2013.

Ristimäki, J., Keskinen, J., Virtanen, A., Maricq, M., and Aakko, P.: Cold temperature PM emissions measurement: Method evaluation and application to light duty vehicles, *Environmental science & technology*, 39, 9424-9430, 2005.

Roberts, J. M., Veres, P. R., Cochran, A. K., Warneke, C., Burling, I. R., Yokelson, R. J., Lerner, B., Gilman, J. B., Kuster, W. C., and Fall, R.: Isocyanic acid in the atmosphere and its possible link to smoke-related health effects, *Proceedings of the National Academy of Sciences*, 108, 8966-8971, 2011.

Simonen, P., Saukko, E., Karjalainen, P., Timonen, H., Bloss, M., Aakko-Saksa, P., Rönkkö, T., Keskinen, J., and Dal Maso, M.: A new oxidation flow reactor for measuring secondary aerosol formation of rapidly changing emission sources, *Atmospheric Measurement Techniques*, 10, 1519-1537, 2017.

Suarez-Bertoa, R., and Astorga, C.: Isocyanic acid and ammonia in vehicle emissions, *Transportation Research Part D: Transport and Environment*, 49, 259-270, 2016.

Tkacik, D. S., Lambe, A. T., Jathar, S., Li, X., Presto, A. A., Zhao, Y. L., Blake, D., Meinardi, S., Jayne, J. T., Croteau, P. L., and Robinson, A. L.: Secondary Organic Aerosol Formation from in-Use Motor Vehicle Emissions Using a Potential Aerosol Mass Reactor, *Environmental Science & Technology*, 48, 11235-11242, 10.1021/es502239v, 2014.

Tong, Z., Li, Y., Lin, Q., Wang, H., Zhang, S., Wu, Y., and Zhang, K. M.: Uncertainty investigation of plume-chasing method for measuring on-road NOx emission factors of heavy-duty diesel vehicles, *Journal of hazardous materials*, 424, 127372, 2022.

Vogt, R., Scheer, V., Casati, R., and Benter, T.: On-road measurement of particle emission in the exhaust plume of a diesel passenger car, *Environmental science & technology*, 37, 4070-4076, 2003.

Wang, H., Wu, Y., Zhang, K. M., Zhang, S., Baldauf, R. W., Snow, R., Deshmukh, P., Zheng, X., He, L., and Hao, J.: Evaluating mobile monitoring of on-road emission factors by comparing concurrent PEMS measurements, *Science of the Total Environment*, 736, 139507, 2020.

Wang, J. M., Jeong, C.-H., Zimmerman, N., Healy, R. M., Hilker, N., and Evans, G. J.: Real-world emission of particles from vehicles: volatility and the effects of ambient temperature, *Environmental Science & Technology*, 51, 4081-4090, 2017.

Watne, A. K., Psychoudaki, M., Ljungstrom, E., Le Breton, M., Hallquist, M., Jerksjo, M., Fallgren, H., Jutterstrom, S., and Hallquist, A. M.: Fresh and Oxidized Emissions from In-Use Transit Buses Running

on Diesel, Biodiesel, and CNG, *Environ Sci Technol*, 52, 7720-7728, <https://doi.org/10.1021/acs.est.8b01394>, 2018.

Wentzell, J. J., Liggio, J., Li, S. M., Vlasenko, A., Staebler, R., Lu, G., Poitras, M. J., Chan, T., and Brook, J. R.: Measurements of gas phase acids in diesel exhaust: a relevant source of HNCO?, *Environ Sci Technol*, 47, 7663-7671, 10.1021/es401127j, 2013.

Yao, D., Guo, H., Lyu, X., Lu, H., and Huo, Y.: Secondary organic aerosol formation at an urban background site on the coastline of South China: Precursors and aging processes, *Environmental Pollution*, 309, 119778, 2022.

Zervas, E., Montagne, X., and Lahaye, J.: C1– C5 organic acid emissions from an SI engine: Influence of fuel and air/fuel equivalence ratio, *Environmental science & technology*, 35, 2746-2751, 2001a.

Zervas, E., Montagne, X., and Lahaye, J.: Emission of specific pollutants from a compression ignition engine. Influence of fuel hydrotreatment and fuel/air equivalence ratio, *Atmospheric Environment*, 35, 1301-1306, 2001b.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J.: Atmospheric new particle formation enhanced by organic acids, *Science*, 304, 1487-1490, 2004.

Zhao, Y., Saleh, R., Saliba, G., Presto, A. A., Gordon, T. D., Drozd, G. T., Goldstein, A. H., Donahue, N. M., and Robinson, A. L.: Reducing secondary organic aerosol formation from gasoline vehicle exhaust, *Proceedings of the National Academy of Sciences*, 114, 6984-6989, 2017.

Zhou, L., Hallquist, Å. M., Hallquist, M., Salvador, C. M., Gaita, S. M., Sjödin, Å., Jerksjö, M., Salberg, H., Wängberg, I., and Mellqvist, J.: A transition of atmospheric emissions of particles and gases from on-road heavy-duty trucks, *Atmospheric Chemistry and Physics*, 20, 1701-1722, 2020.

Zhou, L., Salvador, C. M., Priestley, M., Hallquist, M., Liu, Q., Chan, C. K., and Hallquist, Å. M.: Emissions and secondary formation of air pollutants from modern heavy-duty trucks in real-world traffic—chemical characteristics using on-line mass spectrometry, *Environmental Science & Technology*, 55, 14515-14525, 2021.