

1 Online characterization of primary and secondary emissions of 2 particulate matter and acidic molecules from a modern fleet of city 3 buses

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19

20 **Abstract.** The potential impact of transitioning from conventional fossil fuel to a non-fossil fuel vehicle fleet was investigated
21 by measuring primary emissions via extractive sampling of bus plumes and assessing secondary mass formation using a
22 Gothenburg Potential Aerosol Mass (Go:PAM) reactor from 76 in-use transit buses. Online chemical characterization of
23 gaseous and particulate emissions from these buses was conducted using a chemical ionization mass spectrometry (CIMS)
24 with acetate as the reagent ion, coupled with a filter inlet for gases and aerosols (FIGAERO). Acetate reagent ion chemistry
25 selectively ionizes acidic compounds, including organic and inorganic acids, as well as nitrated and sulfated organics. A
26 significant reduction (48-98%) in fresh particle emissions was observed in buses utilizing compressed natural gas (CNG),
27 biodiesels like rapeseed methyl ester (RME) and hydrotreated vegetable oil (HVO), as well as hybrid-electric HVO (HVO_{HEV}),
28 compared to diesel (DSL) buses. However, secondary particle formation from photooxidation of emissions was substantial
29 across all fuel types. The median ratio of particle mass emission factors of aged to fresh emissions increased in the following
30 order: DSL buses at 4.0, HVO buses at 6.7, HVO_{HEV} buses at 10.5, RME buses at 10.8, and CNG buses at 84. Of the compounds
31 that can be identified by CIMS, fresh gaseous emissions from all Euro V/EEV buses, regardless of fuel type, were dominated
32 by nitrogen-containing compounds such as nitrous acid (HONO), nitric acid (HNO₃), and isocyanic acid (HNCO), alongside
33 small monoacids (C₁-C₃). Notably, the emission of nitrogen-containing compounds was notably lower in Euro VI buses
34 equipped with more advanced emission control technologies. Secondary gaseous organic acids correlated strongly with

35 gaseous HNO₃ signals (R²= 0.85-0.99) in Go:PAM, but their moderate to weak correlations with post-photooxidation
36 secondary particle mass suggest they are not reliable tracers for secondary organic aerosol formation from bus exhaust. Our
37 study highlights that non-regulated compounds and secondary pollutant formation, not currently addressed in legislation, are
38 crucial considerations in the evaluation of environmental impacts of future fuel and engine technology shifts.

39 **1. Introduction**

40 Air pollution remains a critical global issue, posing significant threats to both human health and the environment. Despite
41 substantial progress in reducing emissions from major sources like industry, energy production, households, transportation,
42 and agriculture, the worldwide achievement of air quality targets continues to be a daunting challenge. Notably, the road
43 transport sector, particularly in urban environments, significantly contributes to the emissions of nitrogen oxides (NO_x) and
44 particulate matter (PM), impacting the health of individuals in densely populated regions. In tandem with these concerns,
45 efforts to combat climate change have spurred an increase in the adoption of renewable energy sources within the transportation
46 sector. Biodiesel has risen as the most prevalent renewable fuel, followed by biogas and ED95 ethanol (Guerreiro et al., 2014).
47 Moreover, numerous cities are progressively integrating hybrid-electric and electric vehicles into their public transport fleets,
48 aiming to reduce emissions.

49
50 Emissions from vehicles, especially buses, exhibit considerable variability. They are influenced by fuel type, engine design,
51 operational conditions, emission after-treatment technologies and maintenance (Pirjola et al., 2016; Zhao et al., 2018; Watne
52 et al., 2018; Liu et al., 2019a; Zhou et al., 2020). While diesel (DSL) buses are common, there is an increasing trend towards
53 the use of alternative fuels such as compressed natural gas (CNG), rapeseed methyl ester (RME), and hydrotreated vegetable
54 oil (HVO). These alternative fuels offer several benefits, including reduced PM emissions, particularly soot, and lower levels
55 of carbon monoxide (CO) and total hydrocarbons (THC) (Pflaum et al., 2010; Hassaneen et al., 2012; Liu et al., 2019a).
56 However, the efficacy of RME and HVO in diminishing NO_x emissions can be inconsistent (Pirjola et al., 2016; Liu et al.,
57 2019a); and CNG buses exhibit considerable variability in particle number (PN) emissions (Watne et al., 2018). In Sweden,
58 approximately 23% of the fuel mix of the transport sector in 2020 comprised renewable fuels, with HVO accounting for over
59 half of this proportion (Vourliotakis and Platsakis, 2022; Energimyndigheten, 2021). Emission control strategies, such as
60 aftertreatment systems including diesel particulate filters (DPFs) and selective catalytic reduction (SCR) systems, have been
61 implemented to mitigate pollutant emissions from vehicles. These systems have shown significant efficacy in reducing PM
62 and NO_x emissions respectively, though their performance can vary under different operational conditions.

63
64 Accurately determining vehicle emission factors (EFs) is crucial for devising and implementing effective air quality
65 policies (Fitzmaurice and Cohen, 2022). Methods such as chassis dynamometer tests, on-board measurements with portable
66 emission measurement systems (PEMS), and on-road vehicle chasing experiments have been employed to assess emissions

67 from various types of vehicles (Kwak et al., 2014; Jezek et al., 2015; Pirjola et al., 2016). Chassis dynamometer tests offer
68 high repeatability over standard drive cycles but may not reflect real-world driving conditions or fleet maintenance levels.
69 There are also challenges in accurately replicating real-world dilution effects (Vogt et al., 2003; Kuittinen et al., 2021). On-
70 board measurements with PEMS provide data under a wide range of operating conditions, yet like dynamometers, they may
71 not realistically mimic ambient dilution processes (Giechaskiel et al., 2015; Wang et al., 2020). On-road vehicle chasing
72 experiments involve following individual vehicles with a mobile laboratory to capture the exhaust plumes, providing insights
73 into realistic dilution processes from the tailpipe to ambient air, though these experiments often require a test track to ensure
74 traffic safety (Wang et al., 2020; Tong et al., 2022). All three methods are limited by small sample sizes, which constrain
75 understanding of the real emission characteristics of vehicle fleets. Alternatively, roadside or near-road measurements provide
76 the ability to monitor emissions from a large number of vehicles under actual driving conditions within a short
77 timeframe (Hallquist et al., 2013; Watne et al., 2018; Liu et al., 2019a), which is particularly important for assessing exposure
78 risks to pedestrians and bus passengers. However, this method is limited by its inability to monitor specific engines or
79 operational conditions, such as varying engine speeds and loads. Integrating results from diverse methodologies would ideally
80 yield a comprehensive understanding of emissions from vehicle transport systems.

81

82 In a prior study, we conducted roadside point measurements and reported EFs for general air pollutants such as PM, NO_x, CO,
83 and THC from individual buses during stop-and-go operations at a bus stop in Gothenburg, Sweden (Liu et al., 2019a). Our
84 findings showed that hybrid buses, when using their combustion engines to accelerate from a standstill at bus stops, tended to
85 emit higher particle numbers (PN) than traditional DSL buses, likely due to their relatively smaller engines. Expanding on our
86 prior findings, it is important to acknowledge that primary emissions are not the only way in which engine emissions impact
87 air quality. Emissions from engine exhaust can contribute to secondary particles through oxidation of gas-phase species,
88 primarily via functionalization reactions, yielding lower-volatility products (Hallquist et al., 2009; Kroll et al., 2009).
89 Laboratory studies have demonstrated that secondary organic aerosols (SOA) produced from diluted vehicle exhaust frequently
90 exceed the levels of primary organic aerosols (POA) in less than one day of atmospheric equivalent aging (Chirico et al., 2010;
91 Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014b; Liu et al., 2015). Oxidation flow reactors (OFRs) enable the
92 simulation of several days of atmospheric aging in a few minutes, with minimized wall effects compared to traditional smog
93 chamber experiments (Palm et al., 2016; Bruns et al., 2015). OFRs have been extensively employed to assess the SOA
94 formation potential of ambient air and emissions from diverse sources, including motor exhausts (Tkacik et al., 2014; Bruns
95 et al., 2015; Simonen et al., 2017; Watne et al., 2018; Liu et al., 2019b; Kuittinen et al., 2021; Zhou et al., 2021; Liao et al.,
96 2021a; Yao et al., 2022). In real-world traffic scenarios, the rapid response capabilities and convenient deployment of OFRs,
97 coupled with roadside point measurements, provide a robust method for evaluating emissions from a significant number of
98 vehicles. This approach effectively captures the considerable variability among individual vehicles within a fleet, offering a
99 comprehensive view of emissions under actual driving conditions (Watne et al., 2018; Zhou et al., 2021), although it may not

100 encompass as extensive a range of engine operations as setups that integrate OFRs with chassis dynamometer tests (Kuittinen
101 et al., 2021).

102

103 Primary emissions can also be oxidized to higher-volatility products through fragmentation reactions, potentially producing
104 carboxylic acids (Friedman et al., 2017). Engine exhaust is a recognized primary source of organic and inorganic acids in urban
105 environments (Kawamura et al., 1985; Kawamura and Kaplan, 1987; Kirchstetter et al., 1996; Wentzell et al., 2013; Friedman
106 et al., 2017). Monocarboxylic acids are produced by both diesel and spark-ignited engines (Zervas et al., 2001b; Crisp et al.,
107 2014; Zervas et al., 2001a; Kawamura et al., 1985). Recent studies have identified gaseous dicarboxylic acids in diesel
108 exhaust (Arnold et al., 2012), compounds likely linked to the nucleation and growth of particles (Zhang et al., 2004; Pirjola et
109 al., 2015). Additionally, inorganic acids such as nitric (HNO_3) and nitrous (HONO) acids, along with isocyanic acid (HNCO)—
110 implicated in serious health issues like atherosclerosis, cataracts, and rheumatoid arthritis through carbamylation reactions—
111 have been identified in both diesel and gasoline exhausts (Wang et al., 2007; Roberts et al., 2011; Wentzell et al., 2013; Brady
112 et al., 2014; Link et al., 2016; Li et al., 2021). However, the secondary production of organic acid from engine exhaust remains
113 poorly characterized; and it may significantly contribute to the overall organic acid budget and help explain discrepancies
114 between models and measurements (Paulot et al., 2011; Millet et al., 2015; Yuan et al., 2015). Furthermore, the impacts of
115 evolving fuel and engine technologies on emissions have not been comprehensively assessed. Recent advancements in
116 analytical techniques now enable simultaneous, high-resolution online measurements of both gas and particle phase acidic
117 species. This is facilitated by high-resolution time-of-flight chemical ionization mass spectrometry (HR-ToF-CIMS) using
118 acetate as the reagent ion, coupled with a filter inlet for gases and aerosols (FIGAERO) (Le Breton et al., 2019; Friedman et
119 al., 2017; Lopez-Hilfiker et al., 2014).

120

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

129

130 **2. Methods**

131 **2.1 Emission measurements**

132 Roadside measurements were conducted at a designated urban bus stop, featuring a bus-only lane, in Gothenburg, Sweden.
133 (Supporting information (SI), Figure S1). The sampling occurred from March 2nd to 12th, 2016, with the average temperature
134 during this period recorded at approximately 3.9°C. Extractive sampling of individual bus plumes in real traffic was used to
135 characterize emissions, adhering to the method outlined by Hallquist et al. (2013). Air was continuously drawn through a cord-
136 reinforced flexible conductive hose to the instruments housed within a nearby container. Additional details of the experimental
137 conditions are available in our prior publication by Liu et al. (2019a). The primary focus of this study was to utilize the OFR
138 Go:PAM and the HR-ToF-CIMS to explore the potential for secondary pollutant formation and to conduct a detailed chemical
139 characterization of both gas and particle phase compounds. An experimental schematic of the roadside sampling is shown in
140 Figure S2. Briefly, the emissions from passing bus plumes were characterized as they accelerated from standstill at the bus
141 stop. A camera was positioned at the roadside to capture bus plate numbers, facilitating bus identification and enabling the
142 collection of specific information on each bus, including fuel type, engine technology, and exhaust after-treatment systems.
143 The effective identification of emissions from individual buses was achieved by employing CO₂ as a tracer, as delineated by
144 Hak et al. (2009). The concentration of CO₂ was measured with a non-dispersive infrared gas analyzer (LI-840A, time
145 resolution 1 Hz). NO and NO_x were measured with two separate chemiluminescent analyzers (Thermo Scientific™ Model 42i
146 NO-NO₂-NO_x Analyzer). In addition, specific gaseous compounds like CO, NO, and THC, were measured using a remote
147 sensing device (AccuScan RSD 3000, Environmental System Products Inc.). Particle emissions were characterized using a
148 high time resolution engine exhaust particle sizer spectrometer (EEPS, Model 3090 TSI Inc., time resolution 10 Hz) across a
149 size range of 5.6-560 nm. Due to the lack of detailed knowledge about the chemical composition of the emitted particles,
150 particle mass calculations were based on the assumption of spherical particles of unit density.

151

152 The HR-ToF-CIMS coupled with a FIGAERO was used to derive chemical information of both gas and particle phase species.
153 A detailed description of the configuration of the instrument can be found elsewhere (Aljawhary et al., 2013; Lopez-Hilfiker
154 et al., 2014; Le Breton et al., 2018; Le Breton et al., 2019). Acetate, employed as the reagent ion, was generated using an acetic
155 anhydride permeation source through a ²¹⁰Po ion source (²¹⁰Po inline ionizer, NRD inc, Static Solutions Limited). In the ion-
156 molecular reaction (IMR) chamber, the gaseous sampling flow interacted with the reagent ions, leading to the ionization of
157 target molecules. The dual inlets of the FIGAERO enable simultaneous gas phase sampling directly into the IMR and particle
158 sample collection on a PTFE filter for the duration of the plume via a separate inlet. The duration of the target plume for
159 particle collection was indicated by particle number (PN) concentration measured by the EEPS. Once the PN concentration
160 reduced to undistinguishable at background levels, the filter was automatically positioned to allow the collected particles to be
161 evaporated into the IMR. The nitrogen flow over the filter was incrementally heated from room temperature to 200°C within
162 5 minutes and then maintained at this maximum temperature for 8 minutes, ensuring complete desorption of mass from the
163 filter, followed by analysis via HR-ToF-CIMS. Perfluoropentanoic acid (PFPA), a reliable high mass calibrant, was injected
164 into the CIMS inlet during the sampling period (Le Breton et al., 2019). Mass spectra were calibrated using known masses
165 (m/z), accurate within 4 ppm: O₂⁻, CNO⁻, C₃H₅O₃⁻, C₂F₃O₃⁻, C₅F₉O₂⁻, C₁₀F₁₈O₄⁻, covering a range of 32-526 m/z (more details

166 can be found in SI). The data were acquired at 1 s time resolution. To estimate absolute EFs, a conversion of the CIMS signal
167 to concentration using a sensitivity factor is necessary. Based on the method of Lopez-Hilfiker et al. (2015), the maximum
168 sensitivity was determined to be 20 Hz ppt⁻¹, which falls within previously reported ranges (Mohr et al., 2017). Using this
169 maximum sensitivity provides a lower-limit estimate of EFs for all oxygenated volatile organic compounds (Zhou et al., 2021).
170 The assumption on sensitivity did not affect the comparative analysis of EFs with respect to different fuel types.

171

172 The EFs of constituents per kilogram of fuel burnt were calculated by relating the concentration change of a specific compound
173 in the diluted exhaust plume to the change in CO₂ concentration. CO₂ served as a tracer for exhaust gas dilution, relative to
174 background concentration (Janhäll and Hallquist, 2005; Hak et al., 2009; Hallquist et al., 2013; Watne et al., 2018).
175 Assumptions were made for complete combustion and carbon contents of 86.1, 77.3, 70.5, and 69.2% for DSL, RME, HVO,
176 and CNG, respectively, were assumed (Edwards et al., 2004). Further methodological details are elaborated in Liu et al.
177 (2019a). A more comprehensive description of the EF calculations is provided in the Supporting Information.

178

179 **2.2 Oxidation flow reactor setup**

180 The OFR Go:PAM was utilized for photochemical aging of emissions from individual buses to investigate the potential for
181 secondary pollutant formation. The comprehensive description and operational protocols of the Go:PAM have been detailed
182 previously (Watne et al., 2018; Zhou et al., 2021). Briefly, the Go:PAM is a 6.1 L continuous-flow quartz glass flow reactor
183 with input flows such that the median residence time is approximately 37s. The reactor is equipped with two Philips TUV 30
184 W fluorescent lamps ($\lambda=254$ nm) and enclosed by reflective and polished aluminium mirrors to ensure a homogeneous photon
185 field. The UV lamps generate OH radicals through the photolysis of O₃ in the presence of water vapor. The relative humidity
186 (RH) within the reactor was around 60 - 80%. The O₃ concentration inside the Go:PAM was measured using an ozone monitor
187 (2B technology, model 205 dual beam ozone monitor) at around 880 ppb prior to the introduction of vehicle exhaust. Particle
188 wall losses in the Go:PAM were corrected using size-dependent transmission efficiency (Watne et al., 2018). The OH exposure
189 (OH_{exp}) inside the Go:PAM was calibrated offline using sulfur dioxide (SO₂), following methodologies established in previous
190 studies (Lambe et al., 2011; Kang et al., 2007), with additional details provided in the SI. During on-road measurements, the
191 OH_{exp} may be significantly influenced by the OH reactivity (i.e., CO and HC) and titration of O₃ by NO in the plumes, which
192 varied between vehicles. Thus, the OH reactivity was estimated for each bus passage using the maximum NO_x, CO and HC
193 concentrations in the Go:PAM, along with corresponding water and ozone levels (Watne et al., 2018; Zhou et al., 2021).
194 Employing the maximum concentrations of these OH- or O₃-consuming species represents a minimum estimate of OH_{exp} in
195 our calculations. The flow-design incorporated in the Go:PAM enables investigation of transient phenomena, such as passing
196 plumes. It also works at relatively low ozone concentrations (less than 1 ppm), limiting reactions of other potential oxidants
197 such as O₃, NO₃, or O¹D (Zhou et al., 2021).

198

199 3. Results and discussion

200 3.1 Fresh and aged PM emissions from buses

201 The aged PM emissions ($EF_{PM:aged}$) of 133 plumes from a diverse set of buses, including 16 diesel (DSL), 11 compressed
202 natural gas (CNG), 20 rapeseed methyl ester (RME), 20 hydrotreated vegetable oil (HVO) and 9 hybrid-electric HVO
203 (HVO_{HEV}) buses, were investigated using Go:PAM. The corresponding average fresh PM emissions ($EF_{PM:Fresh}$) for these 76
204 buses were measured during several sequential days (Figure S2). These buses were a subset of the 234 buses described in our
205 previous study (Liu et al., 2019a), and represent data corresponding to available Go:PAM measurements. A comprehensive
206 discussion on the full data set for fresh condition is available in Liu et al. (2019a). Figure 1 shows the average $EF_{PM:Fresh}$ and
207 $EF_{PM:aged}$ with respect to fuel type. Among the buses, Euro V DSL models had the highest median $EF_{PM:Fresh}$, $MdEF_{PM:Fresh}$
208 (represented by the horizontal yellow lines), of 208 mg kg-fuel⁻¹, followed by HVO_{HEV} , RME and HVO buses with $MdEF_{PM:Fresh}$
209 of 109, 74 and 62 mg kg-fuel⁻¹ respectively. CNG buses and HVO_{HEV} buses equipped with a DPF under Euro VI standards
210 exhibited the lowest $MdEF_{PM:Fresh}$, with over half of these buses exhibiting $EF_{PM:Fresh}$ below the detection limit (<4.3 mg kg-fuel⁻¹).
211 Except for HVO_{HEV} buses with a DPF, which was limited to a small tested number, all other bus types in this subset had
212 $MdEF_{PM:Fresh}$ comparable to those of the full data set in Liu et al. (2019a), within $\pm 30\%$ and following the same rank order. The
213 average EFs of fresh and aged particle emissions and general gaseous pollutants for individual buses are given in Table 1.

214

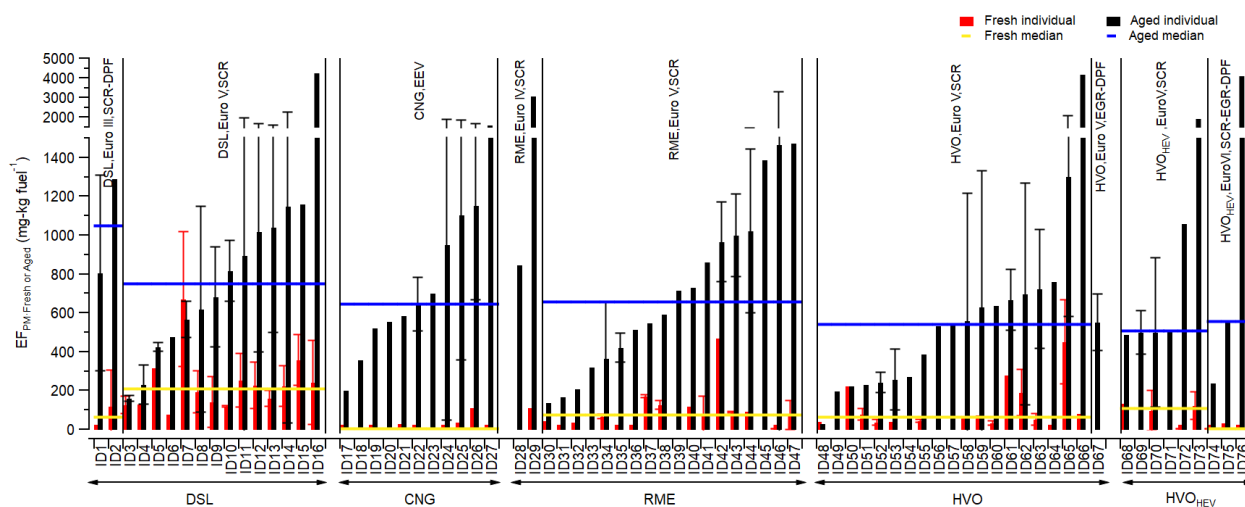
215 After photooxidation in Go:PAM, particle mass increased markedly, with half of the individual buses showing average
216 $EF_{PM:aged}$ more than eight times their average $EF_{PM:Fresh}$. For all Euro V/EEV buses, the median $EF_{PM:aged}$, $MdEF_{PM:aged}$
217 (represented by the horizontal blue lines), was highest for DSL buses of 749 mg kg-fuel⁻¹ followed by a descending order of
218 RME (655) > CNG (645) > HVO (543) > HVO_{HEV} (509). Despite low $EF_{PM:Fresh}$, CNG buses produced substantial secondary
219 particle mass. The DPF, proven effective in earlier studies (Martinet et al., 2017; Preble et al., 2015; May et al., 2014),
220 efficiently reduced primary particle emissions from DSL Euro III and HVO_{HEV} Euro VI buses. However, these bus types, even
221 with DPFs, exhibited higher $EF_{PM:aged}$ than those using the same fuels but without DPFs (Euro V), albeit the number of tested
222 buses with DPFs was limited. The variance in median $EF_{PM:aged}$ among different fuel types was less pronounced compared to
223 $EF_{PM:Fresh}$, suggesting the presence of significant non-fuel-dependent precursor sources, such as lubrication oils and/or fuel
224 additives (Watne et al., 2018; Le Breton et al., 2019).

225

226 Figure 2 shows the bus average $EF_{PM:Fresh}$ vs the corresponding $EF_{PM:aged}$ for individual bus passages, where the average
227 $EF_{PM:aged}$ for each bus is indicated by a solid horizontal line. This analysis focuses on Euro V/EEV buses to ensure a sufficient
228 number of buses in the comparison, while buses from other Euro classes were not included due to their limited numbers. The
229 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)
230 and DSL(4.0) buses. Buses equipped with DPFs, such as DSL Euro III and HVO_{HEV} Euro VI (not included in Figure 2),
231 exhibited a median ratio exceeding 50. $EF_{PM:aged}$ exhibited notable variation between passages of the same bus, likely

232 attributable to emission variability between passages and different dilution levels for plumes prior to sampling into the
 233 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,
 234 indicated by the integrated CO_2 area. Generally, a higher integrated CO_2 area suggests a more concentrated plume, leading to
 235 increased external OH and O_3 reactivity, which in turn reduces the concentration of OH radicals available in the Go:PAM for
 236 precursor oxidation (Emanuelsson et al., 2013; Watne et al., 2018). Some buses displayed primary emissions too dilute for
 237 detection (markers located to the left in Figure 2b) but still exhibited non-negligible $EF_{PM:aged}$ after oxidation. To further
 238 examine the effects of simulated atmospheric oxidation in the Go:PAM, an estimated minimum OH_{exp} was calculated for each
 239 plume by incorporating the OH reactivities of CO and HC and the titration of O_3 with NO, following methodologies from
 240 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
 241 $EF_{PM:aged}$ for some buses, for example, the DSL and HVO located to the right in Figure 2c, increased with increasing OH_{exp} .
 242 However, due to potential large differences in the chemical composition of emissions across different passages of the same
 243 bus, where some species are more prone to forming secondary particle mass even at lower OH_{exp} , the OH_{exp} dependent $EF_{PM:aged}$
 244 for other buses was less pronounced.

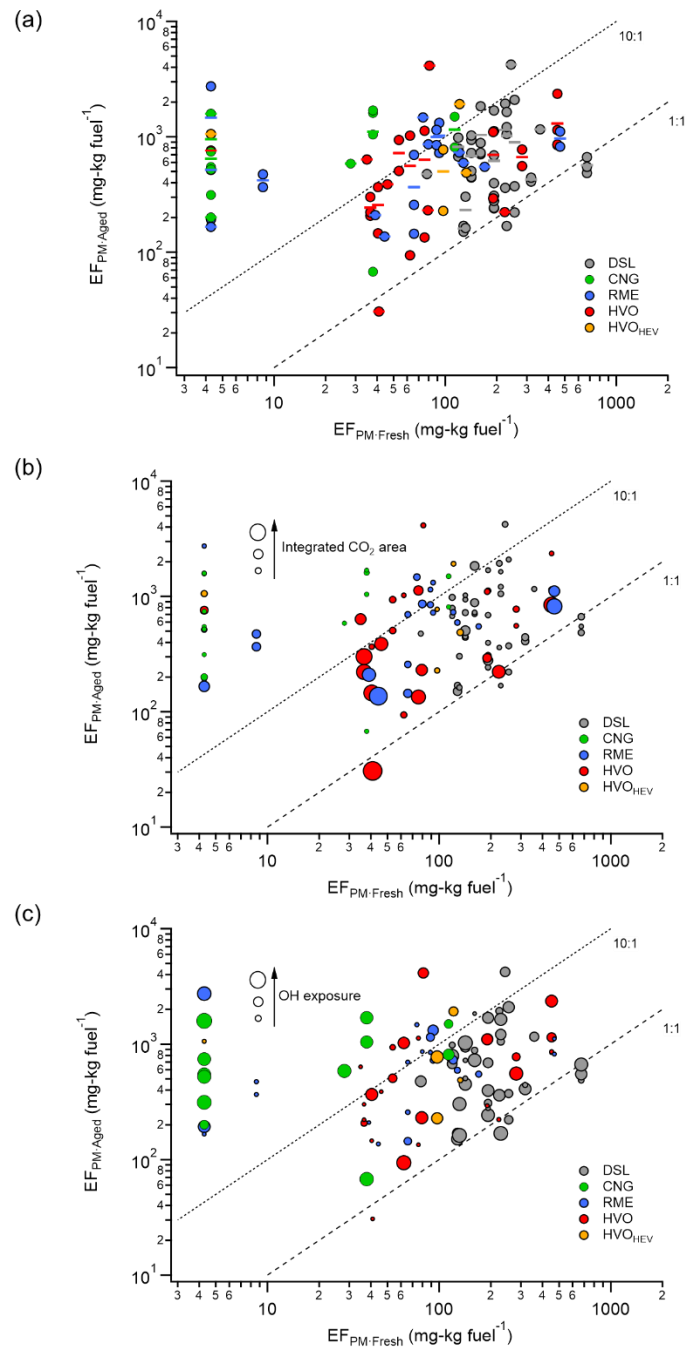
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246

247 Figure 1. $EF_{PM:Fresh}$ (red bar) and $EF_{PM:aged}$ (black bar) with respect to fuel class: DSL (diesel, ID₁-ID₁₆), CNG (compressed
 248 natural gas, ID₁₇-ID₂₇), RME (rapeseed methyl ester, ID₂₈-ID₄₇), HVO (rapeseed methyl ester, ID₄₈-ID₆₇) and HVO_{HEV} (hybrid-
 249 electric HVO, ID₆₈-ID₇₆) buses. Median values for $EF_{PM:Fresh}$ ($^{Md}EF_{PM:Fresh}$) and $EF_{PM:aged}$ ($^{Md}EF_{PM:aged}$) are indicated by
 250 horizontal yellow and blue lines, respectively. The information on engine technology and exhaust after-treatment systems is
 251 also shown. Given errors represent the standard deviation (1σ).

252



253

254

255 Figure 2. $EF_{PM:aged}$ vs average $EF_{PM:Fresh}$ for all the studied bus passages (Euro V) with respect to fuel type (a) and as a function
 256 of integrated CO₂ area (b) and OH exposure (OH_{exp}) (c). The dashed lines denote the 10:1 and 1:1 $EF_{PM:aged}$: $EF_{PM:Fresh}$ ratios,
 257 and the solid lines in (a) represent bus averages. One may note that the buses with $EF_{PM:Fresh}$ values below detection limit were

258 set to 4.3 mg kg-fuel⁻¹. Abbreviations: DSL (diesel), CNG (compressed natural gas), RME (rapeseed methyl ester), HVO
 259 (hydrotreated vegetable oil), HVO_{HEV} (hybrid-electric HVO).

260

261 Table 1. Average particle and gaseous EFs of individual buses for fresh emissions and average EF_{PM} for aged emissions^a.

Bus ID	Fuel ^c	Euro standard	Exhaust after-treatment system ^d	EF _{PM:Fresh} (mg kg ⁻¹ _{fuel})	EF _{PN:Fresh} (10 ¹⁴ # kg ⁻¹ _{fuel})	EF _{CO} (g kg ⁻¹ _{fuel})	EF _{THC} (g kg ⁻¹ _{fuel})	EF _{NOx} (g kg ⁻¹ _{fuel})	EF _{PM:Aged} (mg kg ⁻¹ _{fuel})
1	DSL	III	SCR, DPF	4.3	0.41	3.9±11	1.5±2.9	10±3.2	810±510
2	DSL	III	SCR, DPF	120±190	34±61	2.7±7	1.7±3.7	11±5	1300
3	DSL	V	SCR	130±45	3.3±1.3	17±18	0.35±1.3	3.9±3.7	160±13
4	DSL	V	SCR	130	3.6	20±22	1.5±3.6	4.7±7.2	230±100
5	DSL	V	SCR	320	5.9	20±28	2±3.5	9.7±7	430±23
6	DSL	V	SCR	78	1.6	20±21	2.7±5.6	13±12	480
7	DSL	V	SCR	670±350	10±6.8	42±44	2.3±3.7	6.8±5	570±92
8	DSL	V	SCR	190±110	6.5±3	14±21	0.75±1.7	12±5.1	620±530
9	DSL	V	SCR	140±130	4.3±2.6	9.8±14	1±1.5	15±13	680±260
10	DSL	V	SCR	120±4.7	3.2±0.66	16±18	2.5±4.7	12±6.9	820±160
11	DSL	V	SCR	250±140	4.7±2.7	16±23	0.8±1.4	12±8.9	900±1000
12	DSL	V	SCR	230±120	5.1±1.5	16±26	2.6±4.6	12±9.9	1000±620
13	DSL	V	SCR	160±41	3.5±0.97	27±27	1.4±2.7	17±9.8	1000±540
14	DSL	V	SCR	220±110	5.2±1.3	12±17	2.6±4.1	11±7.4	1100±1100
15	DSL	V	SCR	360±130	6.8±4.2	21±25	1.2±3.3	5.7±4.4	1200
16	DSL	V	SCR	240±220	22±11	5.5±7.5	0.74±1.6	6.8±5.6	4200
17	CNG	EEV	-	4.3±0	0.41±0	n.a.	n.a.	4.8±1.7	200
18	CNG	EEV	-	n.a.	n.a.	n.a.	n.a.	11±4.9	360
19	CNG	EEV	-	4.3±0	0.41±0	n.a.	n.a.	4±3.8	520
20	CNG	EEV	-	n.a.	n.a.	n.a.	n.a.	15±17	560
21	CNG	EEV	-	28	1.3	n.a.	n.a.	2.2±0.93	590
22	CNG	EEV	-	4.3	0.41	n.a.	n.a.	1.8±1	650±140
23	CNG	EEV	-	n.a.	n.a.	n.a.	n.a.	3.2±0.53	700
24	CNG	EEV	-	4.3	0.41	n.a.	n.a.	6.9±1.4	950±900
25	CNG	EEV	-	38	11	n.a.	n.a.	7.3±5.3	1100±750
26	CNG	EEV	-	110	200	n.a.	n.a.	8.2±4.2	1200±480
27	CNG	EEV	-	4.3±0	0.41±0	n.a.	n.a.	6±1.8	1600
28	RME	IV	SCR	n.a.	n.a.	10±8.7	3.1±3	46±20	850
29	RME	IV	SCR	110	4.1	4.2±8.4	0.19±0.38	7.2±6.8	3000
30	RME	V	SCR	44	2.2	12±14	2.2±3.6	32±32	140
31	RME	V	SCR	4.3	0.41	7.4±7.1	0.075±0.17	13±5.1	170
32	RME	V	SCR	39	6.2	5.2±4.8	0.87±1.1	18±5.4	210
33	RME	V	SCR	n.a.	n.a.	0.24±0.54	0.24±0.39	10±3.3	320
34	RME	V	SCR	66±11	2.4±1	7±7.2	1.8±2.7	23±13	370±290
35	RME	V	SCR	8.6	0.96	4.9±3.6	0.59±0.73	20±5.1	420±75
36	RME	V	SCR	4.3	0.41	22±23	1.8±2	25±16	520
37	RME	V	SCR	170±7.7	6.4±1	34±35	0.016±0.043	19±10	550
38	RME	V	SCR	130±24	11±14	17±20	2±4	16±15	590
39	RME	V	SCR	n.a.	n.a.	1.2	0.64	21	720
40	RME	V	SCR	120	5.3	12±9.4	1.8±2.6	18±8.2	730
41	RME	V	SCR	80±95	4.2±2.9	8.8±17	0.72±0.87	25±5.7	860
42	RME	V	SCR	470	5.8	4.5±5.1	0.23±0.38	18±7.8	970±210
43	RME	V	SCR	89±2.3	2.6±0.16	5.4±9.4	0.68±1.9	28±17	1000±210
44	RME	V	SCR	92	1.6	14±19	1.8±3	23±17	1000±420
45	RME	V	SCR	n.a.	n.a.	37±26	5.8±3.6	14±6.3	1400
46	RME	V	SCR	4.3±0	0.41±0	9.6±14	0.89±1.4	28±8.4	1500±1800
47	RME	V	SCR	74±75	12±6	6.1±6.3	1.1±1.4	18±5.2	1500
48	HVO	V	SCR	41	1.5	8.4±2	0.14±0.31	10±0.4	31
49	HVO	V	SCR	n.a.	n.a.	5.8±8	0.7±0.62	13±10	200
50	HVO	V	SCR	220	6.6	8.3±9.1	0.91±0.97	13±8.6	220
51	HVO	V	SCR	79±31	2.6±0.74	7.8±5.8	0.41±0.59	12±8.2	230

52	HVO	V	SCR	37±13	1.9±0.65	4.8±5.5	0.64±0.82	20±3	240±51
53	HVO	V	SCR	40	2.5	2.1±3.4	0.0083±0.019	16±4.3	260±160
54	HVO	V	SCR	n.a.	n.a.	2.1±3	0.55±0.77	22	270
55	HVO	V	SCR	46±6.6	2.6±0.52	6.2±4.1	0.79±0.55	12±8.2	390
56	HVO	V	SCR	n.a.	n.a.	11±10	0.74±0.84	5.7	530
57	HVO	V	SCR	n.a.	n.a.	14±17	0.79±1.2	11±2.6	540
58	HVO	V	SCR	62	4.1	6.8±6.7	0.22±0.31	11±6.3	560±660
59	HVO	V	SCR	76	5.3	2.3±2	0.24±0.47	19±3.4	630±700
60	HVO	V	SCR	35±11	1.5±0.19	3.3±5	0.45±0.86	9.2±9	640
61	HVO	V	SCR	280	14	9.9±16	0.55±0.73	11±3.6	670±160
62	HVO	V	SCR	190±120	68±86	1.1±1.9	0.3±0.49	9.3±4.9	700±570
63	HVO	V	SCR	54±30	4.6±2.2	3.5±4.6	0.49±0.48	14±3.5	720±310
64	HVO	V	SCR	4.3	0.41	2.2±3.8	0.33±0.73	12±4.8	760
65	HVO	V	SCR	450±220	18±18	1.4±1.6	0.28±0.37	12±2.6	1300±720
66	HVO	V	SCR	81	11	0.88±0.93	0.28±0.25	13±6.5	4100
67	HVO	V	EGR, DPF	n.a.	n.a.	4.6±5.9	0.64±1.2	11±8.1	550±150
68	HVO _{HEV}	V	SCR	130	52	12±19	0.97±1.4	20±15	490
69	HVO _{HEV}	V	SCR	n.a.	n.a.	4.1±8.4	0.5±1.3	18±3.3	500±110
70	HVO _{HEV}	V	SCR	97±100	25±18	3.8±6.8	1.1±1.8	17±5.7	500±390
71	HVO _{HEV}	V	SCR	n.a.	n.a.	7.6±9.9	2.9±2.4	12±2.1	520
72	HVO _{HEV}	V	SCR	4.3±0	0.41±0	3.7±5.8	1±2.4	20±10	1100
73	HVO _{HEV}	V	SCR	120±72	8.9±2.9	1.2±1.7	0.18±0.26	17±7	1900
74	HVO _{HEV}	VI	SCR,EGR,DPF	4.3±0	0.41±0	4.7±11	2.2±4.7	7.2±8.5	240
75	HVO _{HEV}	VI	SCR,EGR,DPF	33	29	1.2±2.4	0.22±0.49	6.7±3.3	550
76	HVO _{HEV}	VI	SCR,EGR,DPF	4.3	0.41	10±9.2	1.5±2.3	8.8±8.7	4100

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^aGiven errors represent the standard deviation (1σ).

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^bn.a., abbreviation for not available.

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^cDSL, CNG, RME, HVO and HVO_{HEV}, abbreviations for diesel, compressed natural gas, rapeseed methyl ester, hydrotreated vegetable oil, and hybrid-electric hydrotreated vegetable oil.

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^dSCR, DPF and EGR, abbreviations for selective catalytic reduction, diesel particulate filter and exhaust gas recirculation systems.

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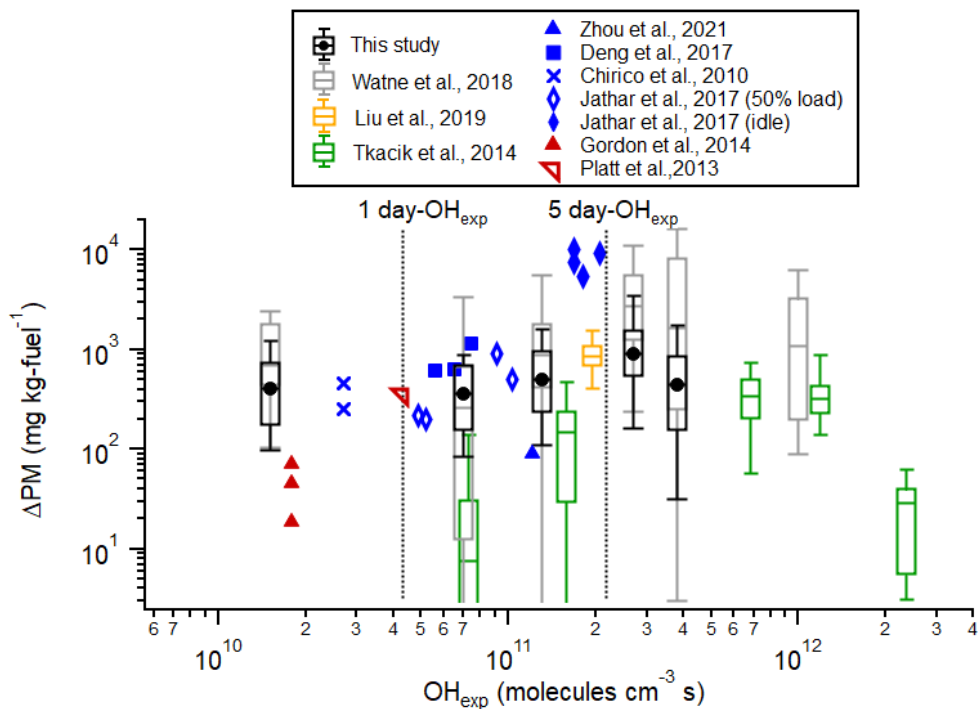
271 The secondary particle mass formed (Δ PM) was calculated as the difference between $EF_{PM,aged}$ for a plume and the average
272 $EF_{PM:Fresh}$ for the corresponding individual bus. Figure 3 illustrates Δ PM as a function of OH_{exp} for the bus fleet in this study,
273 which includes 40% DSL, 12.2% CNG, 20% RME, 20.8% HVO, and 7% HVO_{HEV}. The results were grouped based on OH_{exp} ,
274 spanning a range from 1.1×10^9 to 4.6×10^{11} molecules cm^{-3} s. The results in this study are compared with those reported from
275 a tunnel study (Tkacik et al., 2014), an urban roadside study of a mixed fleet in Hong Kong (Liu et al., 2019b), a depot study
276 on rather modern types of city buses (Watne et al., 2018) and roadside measurements of a heavy-duty truck fleet in
277 Gothenburg (Zhou et al., 2021). Laboratory OFR and chamber studies of middle-duty and heavy-duty diesel vehicles (Deng
278 et al., 2017), diesel passenger cars (Chirico et al., 2010), a diesel engine (Jathar et al., 2017a), and gasoline vehicles (Gordon
279 et al., 2014a; Platt et al., 2013) were also included for comparison.

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281 The Δ PM from vehicle emissions is influenced by factors such as vehicle and fuel types, driving modes, and OH_{exp} during
282 experiments (Gentner et al., 2017). Considering the variability of OH reactivity among vehicles and the consequently wide
283 range of OH_{exp} , this study, along with Watne et al. (2018), categorizes Δ PM trend into OH_{exp} bins. The median Δ PM was
284 approximately 400 mg kg-fuel⁻¹ at $OH_{exp} < 4.3 \times 10^{10}$ molecules cm^{-3} s (corresponding to 1 OH day, assuming an OH
285 concentration of 1×10^6 molecules cm^{-3} for 12 h per day) and was 364-495 mg kg-fuel⁻¹ at 1-5 OH days, reaching a maximum

286 of around $920 \text{ mg kg-fuel}^{-1}$ at approximately 5-6 OH days for the bus fleet in this study. This peak value of ΔPM was lower
287 than the approximately $3000 \text{ mg kg-fuel}^{-1}$ at ~5-6 OH days observed in the depot measurements by Watne et al. (2018), a
288 difference potentially due to variations in engine technology and fuel types used in the bus fleets. Notably, HVO was not used
289 in the depot study, while some buses switched from RME to HVO prior to this study. The ΔPM peaked and then decreased at
290 higher OH_{exp} , likely due to the transition from functionalization-dominated reactions and condensation at lower OH_{exp} to
291 fragmentation reactions and evaporation dominance at higher OH_{exp} (Tkacik et al., 2014; Ortega et al., 2016). The ΔPM in this
292 study was comparable to $855 \text{ mg kg-fuel}^{-1}$ for a mixed fleet consisting of 44.1% gasoline, 41.3% diesel, and 14.6% LPG
293 vehicles measured at an urban roadside in Hong Kong (Liu et al., 2019b). It was slightly higher than the ΔPM measured from
294 a Euro VI dominated (more than 70%) heavy-duty truck fleet at an urban roadside in Gothenburg (Zhou et al., 2021), and
295 from a fleet with over 80% light-duty gasoline vehicles in a Pittsburgh tunnel study (Tkacik et al., 2014). Additionally, the
296 ΔPM in this study was consistent with that for middle-duty and heavy-duty diesel vehicles (Deng et al., 2017), diesel passenger
297 cars (Chirico et al., 2010), and a diesel (or biodiesel)-fuelled engine under 50% load condition (Jathar et al., 2017a) (around
298 $190\text{-}1133 \text{ mg kg-fuel}^{-1}$). However, the diesel (or biodiesel)-fuelled engine under idle conditions can produce significantly
299 higher ΔPM (more than $5000 \text{ mg kg-fuel}^{-1}$), likely because engines at idle loads are less efficient at burning fuel, leading to
300 higher emissions of unburnt gaseous combustion products (as precursors of secondary PM) (Nordin et al., 2013; Saliba et al.,
301 2017; Jathar et al., 2017a). In contrast, experiments conducted for gasoline vehicles at relatively low photochemical ages (< 1
302 OH day) typically produced ΔPM lower than $70 \text{ mg kg-fuel}^{-1}$ (Gordon et al., 2014a), except for a Euro 5 gasoline vehicle (340
303 mg kg-fuel^{-1}) operated with a New European Driving Cycle (Platt et al., 2013).

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307 Figure 3. Secondary particle mass formed (ΔPM), calculated as $\text{EF}_{\text{PM:aged}}$ subtracted by the average $\text{EF}_{\text{PM:Fresh}}$, vs modeled OH
 308 exposure (OH_{exp}) for the bus fleet in this study and comparison with those reported for a tunnel study (Tkacik et al., 2014), a
 309 depot study (Watne et al., 2018), roadside measurements (Liu et al., 2019b; Zhou et al., 2021), middle-duty and heavy-duty
 310 diesel vehicles (Deng et al., 2017), diesel passenger cars (Chirico et al., 2010), a diesel engine (Jathar et al., 2017a), and
 311 gasoline vehicles (Gordon et al., 2014a; Platt et al., 2013). Dashed lines indicate 1- and 5-day OH_{exp} assuming an OH
 312 concentration of 1×10^6 molecules cm^{-3} 12 h per day (Watne et al., 2018). Note that ΔPM in this study, alongside those by
 313 Watne et al. (2018), Zhou et al. (2021) and Liu et al. (2019b), includes both secondary organic and inorganic aerosol, while
 314 ΔPM in research by Deng et al. (2017), Chirico et al. (2010), Jathar et al. (2017a), Gordon et al. (2014a), Platt et al. (2013)
 315 and Tkacik et al. (2014) pertains only to secondary organic aerosol mass.

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319 3.2 Chemical characterization using CIMS

320 3.2.1 Fresh gaseous emissions

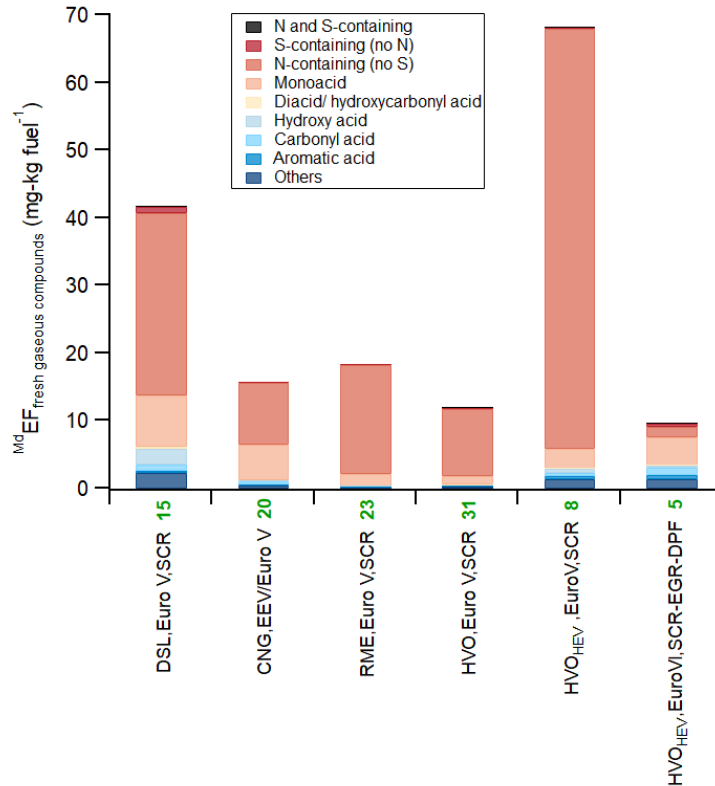
321 Figure 4 presents the median emission factors ($^{\text{M}}\text{dEFs}$) of acetate CIMS measured fresh gaseous emissions with respect to fuel
 322 type. The identities of the organic compounds detected by HR-ToF-CIMS are assigned based on knowledge of sensitivities of
 323 the ionization scheme and the expected compounds emitted from the buses. Plausible compounds are assigned from the

324 formulae, with a caveat that other isomers might contribute to the signal. These compounds were classified into nine families
325 based on their molecular characteristics as outlined by Liu et al. (2017), with additional details provided in the SI. Among all
326 Euro V/EEV buses, hybrid-electric HVO (HVO_{HEV}) buses exhibited the highest ^{Md}EF of CIMS measured fresh gaseous
327 emissions (68 mg kg-fuel⁻¹), followed by DSL (42 mg kg-fuel⁻¹), RME (18 mg kg-fuel⁻¹), and CNG (16 mg kg-fuel⁻¹), while
328 HVO had the lowest ^{Md}EF of 12 mg kg-fuel⁻¹. Nitrogen (N) -containing compounds (no sulfur) and monoacid families
329 predominantly composed these fresh gaseous emissions. Compared to Euro V HVO_{HEV} buses, HVO_{HEV} buses equipped with
330 exhaust gas recirculation (EGR) and DPF systems (Euro VI) demonstrated a significant reduction in ^{Md}EF (10 mg kg-fuel⁻¹),
331 primarily due to decreased emissions of N-containing compounds, although the ^{Md}EF of other compound families were higher.
332 In contrast, Zhou et al. (2021) reported significant reductions in both carboxylic acids and carbonyl compounds (by 94% on
333 average), and acidic nitrogen-containing organic and inorganic species (79%) when transitioning from Euro V to Euro VI
334 heavy-duty trucks. However, details on the types of exhaust after-treatment systems used in the trucks from such study are not
335 specified. Moreover, this study utilized acetate as a different reagent ion for CIMS compared to the iodide used by Zhou et al.
336 (2021). Table 2 lists the top 10 ^{Md}EFs of fresh gaseous compounds, contributing over 88% of total fresh gaseous emissions
337 measured by CIMS for most bus types, except for Euro VI HVO_{HEV} (61%). The fresh gaseous emissions from all types of Euro
338 V/EEV buses were primarily composed of nitrous acid (HONO) and nitric acid (HNO₃), with HONO being the most significant
339 acidic emission. The ^{Md}EFs of HONO and HNO₃ generally align with values reported in the literature, ranging from
340 approximately 7-250 mg kg-fuel⁻¹ for HONO (Kurtenbach et al., 2001; Wentzell et al., 2013; Liao et al., 2020; Nakashima and
341 Kondo, 2022) and around 4-14 mg kg-fuel⁻¹ for HNO₃ (Wentzell et al., 2013). Acetic acid (C₂H₄O₂), formic acid (CH₂O₂), and
342 isocyanic acid (HNCO) also exhibited relatively high ^{Md}EFs. The ^{Md}EFs of formic acid for all Euro V/EEV bus types (0.02-
343 1.97 mg kg-fuel⁻¹) were consistent with those from a light-duty gasoline fleet (0.57–0.94 mg kg-fuel⁻¹) reported by Crisp et al.
344 (2014). The ^{Md}EFs of acetic acid ranged from 1.23 to 4.84 mg kg-fuel⁻¹, falling between values for gasoline vehicles (0.78 mg
345 kg-fuel⁻¹) and diesel buses (approximately 12-23 mg kg-fuel⁻¹) (Li et al., 2021). Isocyanic acid, likely an intermediate product
346 of the thermal degradation of urea in SCR systems without sufficient hydrolysis (Bernhard et al., 2012), was detected in
347 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-
348 road diesel engine (31-56 mg kg-fuel⁻¹) reported by Jathar et al. (2017b), but align well with SCR-equipped diesel vehicles
349 tested by Suarez-Bertoa and Astorga (2016) (1.3-9.7 mg kg-fuel⁻¹) and a diesel engine with a diesel oxidation catalyst
350 (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
351 emissions of HNCO, potentially attributed to cold engine conditions since the combustion engine does not operate
352 continuously. Notably, emissions of HNCO were significantly lowered and neither HONO nor HNO₃ were identified among
353 the top 10 ^{Md}EFs for HVO_{HEV} buses equipped with EGR and DPF systems (Euro VI), suggesting that newer engine technologies
354 incorporating EGR and DPF systems likely effective in reducing emissions of NO_x (Table 1) as well as HNCO, HONO and
355 HNO₃. CH₄SO₃, potentially identified as methanesulfonic acid, was detected in the emissions from DSL and RME buses.
356 Previous studies, such as those by Corrêa and Arbilla (2008), have shown that mercaptans, emitted from diesel and biodiesel
357 exhausts, can transform under high NO_x conditions into products including methanesulfonic acid. The presence of sulfur-

358 containing organic compounds in diesel fuel and lubricants, and their potential transformation upon combustion into various
 359 sulfuric derivatives, alongside the catalytic activity of engine converters, could also contribute to such findings. However, the
 360 detailed formation pathway of CH_4SO_3 in our study remains unknown.

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364 Figure 4. $M_d E F_s$ of CIMS measured fresh gaseous emissions with respect to fuel class: DSL (diesel, 15), CNG (compressed
 365 natural gas, 20), RME (rapeseed methyl ester, 23), HVO (rapeseed methyl ester, 31) and HVO_{HEV} (hybrid-electric HVO, 13)
 366 buses. The number in bold green represents the number of buses examined.

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374 Table 2. Summary of top 10 ^{Md}EFs of fresh gaseous compounds measured using HR-ToF-CIMS of DSL, CNG, RME, HVO
 375 and HVO_{HEV} buses^a (color coded by different families shown in Figure 4).

DSL, Euro V, SCR		CNG, EEV/Euro V		RME, Euro V, SCR		HVO, Euro V, SCR		HVO _{HEV} , Euro V, SCR		HVO _{HEV} , Euro VI	
Species	^{Md} EF (mg kg _{fuel} ⁻¹)	Species	^{Md} EF (mg kg _{fuel} ⁻¹)	Species	^{Md} EF (mg kg _{fuel} ⁻¹)	Species	^{Md} EF (mg kg _{fuel} ⁻¹)	Species	^{Md} EF (mg kg _{fuel} ⁻¹)	Species	^{Md} EF (mg kg _{fuel} ⁻¹)
HONO	20.64	HONO	4.92	HONO	12.72	HONO	7.62	HONO	38.96	C ₃ H ₂ O ₂	2.42
HNO ₃	5.29	C ₂ H ₄ O ₂	4.68	HNO ₃	3.24	HNO ₃	2.20	HNCO	14.74	C ₂ H ₄ O ₂	1.23
C ₂ H ₄ O ₂	4.84	HNO ₃	3.48	C ₂ H ₄ O ₂	1.23	C ₂ H ₄ O ₂	1.23	HNO ₃	7.89	C ₂ H ₂ O ₃	0.62
CH ₂ O ₂	1.97	HNCO	0.51	CH ₂ O ₂	0.48	C ₃ H ₆ O ₃	0.14	C ₂ H ₄ O ₂	1.83	C ₈ H ₆ O ₄	0.40
C ₃ H ₆ O ₃	1.79	CH ₂ O ₂	0.30	HNCO	0.15	C ₃ H ₂ O ₂	0.09	CH ₂ O ₂	0.45	C ₆ H ₅ NO ₂	0.31
CH ₄ SO ₃	0.71	C ₂ H ₂ O ₃	0.25	C ₂ H ₂ O ₃	0.05	HNCO	0.08	C ₃ H ₆ O ₃	0.43	HNCO	0.27
HNCO	0.67	C ₃ H ₂ O ₂	0.14	C ₃ H ₈ O ₃	0.03	CH ₂ O ₂	0.02	C ₃ H ₂ O ₂	0.34	C ₃ H ₄ O ₅	0.22
C ₃ H ₄ O ₃	0.37	C ₃ H ₄ O ₂	0.06	CH ₄ SO ₃	0.02	C ₂ H ₂ O ₃	0.02	C ₉ H ₁₀ O ₃	0.16	C ₇ H ₆ O ₃	0.20
C ₂ H ₂ O ₃	0.31	C ₇ H ₆ O ₃	0.05	C ₃ H ₄ O ₂	0.02	C ₃ H ₄ O ₃	0.02	C ₈ H ₆ O ₄	0.12	C ₅ H ₈ O ₃	0.17
C ₄ H ₆ O ₄	0.22	C ₅ H ₈ O ₄	0.05	C ₆ H ₆ N ₂ O ₂	0.01	C ₄ H ₆ O ₄	0.01	C ₅ H ₈ O ₃	0.10	H ₄ N ₂ O ₂ S	0.16

376 ^aDSL, CNG, RME, HVO and HVO_{HEV}, abbreviations for diesel, compressed natural gas, rapeseed methyl ester, hydrotreated vegetable oil, and hybrid-electric
 377 hydrotreated vegetable oil.

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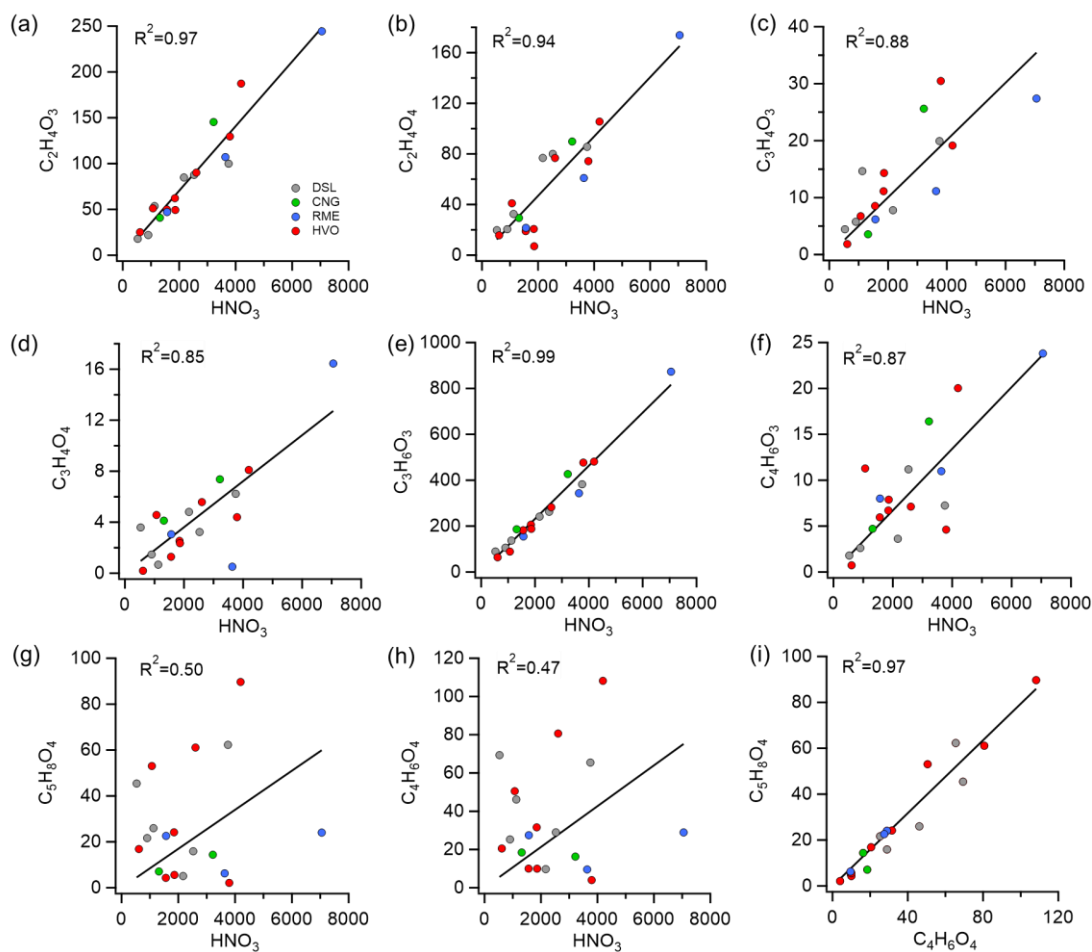
380 3.2.2 Aged gaseous emissions

381 Secondary carboxylic acids were measured following exposure of the exhaust to OH radicals. Figure 5 shows the correlations
 382 between ion counts of the most abundant gas-phase organic acids and nitric acid (HNO₃) after oxidation in the Go:PAM. HNO₃
 383 serves as an indicator of NO_x oxidation. Most acids exhibited both primary and secondary sources, except for dihydroxyacetic
 384 acid (C₂H₄O₄), which was only identified post-aging. The chemical characterization of the aged emissions was conducted on
 385 separate occasions using HR-ToF-CIMS, capturing a limited number of buses (N=19). When these buses were categorized by
 386 fuel type, the sample size for each category became smaller, constraining statistical comparison across different bus types.
 387 Nevertheless, we analyzed the relationship between various chemical species across all buses. Glycolic acid (C₂H₄O₃),
 388 dihydroxyacetic acid (C₂H₄O₄), pyruvic acid (C₃H₄O₃), malonic acid (C₃H₄O₄), lactic acid (C₃H₆O₃) and acetoacetic acid
 389 (C₄H₆O₃) showed high correlations (R²= 0.85-0.99, Fig. 5a-f) with HNO₃ signals. In contrast, glutaric acid (C₅H₈O₄) and
 390 succinic acid (C₄H₆O₄) exhibited poorer correlations with HNO₃, suggesting different formation mechanisms for these two
 391 organic acids compared to the others mentioned. Notably, these two acids showed a strong correlation with each other (R²=
 392 0.97, Fig. 5i) and both belong to the diacid/hydroxycarbonyl acid families. It is important to note that many of these carboxylic
 393 acids can directly participate in secondary PM formation in the atmosphere in the presence of water vapor and a base such as
 394 ammonia (Chen et al., 2020; Huang et al., 2018; Hao et al., 2020). This process may significantly contribute to the overall
 395 secondary PM yield, reflecting a more complex interplay between gaseous emissions and particulate matter under atmospheric
 396 conditions. While most of these small organic acids correlated well with HNO₃, their correlations with EF_{PM:aged} or ΔPM were

397 moderate to weak ($R^2 < 0.6$, Figure S5). This possibly indicates that the OH-driven formation of these carboxylic acids occurs
 398 on a different time scale compared to the production of organic aerosol (Friedman et al., 2017), at least in this Go:PAM
 399 experiment. This could also be due to different subsets of hydrocarbon precursors driving the production of organic acids and
 400 secondary particle mass. Similarly, Friedman et al. (2017) observed a lack of correlation between organic aerosol and gaseous
 401 organic acid concentrations downstream of the flow reactor from a diesel engine, indicating that organic acids may not be
 402 reliable tracers for secondary organic aerosol formation from diesel exhaust.

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406 Figure 5. Correlations between ion counts of most abundant gas-phase organic acids and HNO_3 (a-h) and correlation between
 407 glutaric acid ($\text{C}_5\text{H}_8\text{O}_4$) and succinic acid ($\text{C}_4\text{H}_6\text{O}_4$) (i) from 19 buses after oxidation in the Go:PAM. Abbreviations: DSL
 408 (diesel), CNG (compressed natural gas), RME (rapeseed methyl ester), HVO (hydrotreated vegetable oil), HVO_{HEV} (hybrid-
 409 electric HVO).

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413 **3.2.3 Particulate emissions**

414 Table 3 displays the top 10 EFs of fresh particle-phase compounds (EF_{fresh}), as characterized by the FIGAERO ToF-CIMS,
 415 alongside their respective aged EFs (EF_{aged}), for Euro V DSL and RME buses. These top 10 EF_{fresh} contributed to over 82% of
 416 the total fresh particulate emissions measured by CIMS. Fresh particulate emissions from DSL buses were predominantly
 417 composed of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). Benzene/toluene oxidation products ($C_7H_4O_7$, C_7H_8O , $C_6H_5NO_3$,
 418 C_6H_5O , $C_7H_7NO_3$) also had relatively high EF_{fresh} , aligning with the findings in Le Breton et al. (2019). Similarly, high EF_{fresh}
 419 of HNO_3 ($2.5 \text{ mg kg-fuel}^{-1}$) and H_2SO_4 ($0.61 \text{ kg-fuel}^{-1}$) were observed for the RME bus. Additionally, fatty acids, known as
 420 main components of unburned rapeseed oil (Usmanov et al., 2015), such as $C_{18}H_{34}O_2$, $C_{14}H_{28}O_2$, $C_{18}H_{36}O_2$, $C_{16}H_{32}O_2$, and
 421 $C_{16}H_{30}O_2$, significantly contributed to the identified mass loadings from the RME bus. When comparing the percentage mass
 422 observed by CIMS for both DSL and RME fuels in fresh and aged exhaust plumes, the total emission factors measured by
 423 CIMS (EF_{CIMS}) were notably lower than the total emission factors measured by the EEPS (EF_{total}). This difference is expected
 424 due to the sensitivity of the acetate ionization scheme of CIMS, which efficiently detects oxygenated volatile organic
 425 compounds, particularly carboxylic acids and inorganic acids, but has low sensitivity towards hydrocarbons and cannot detect
 426 metallic ions and soot. The CIMS measured EF_{fresh} accounted for 10.4% and 5.9% of the fresh EF_{total} measured by the EEPS
 427 for DSL and RME, respectively. In aged exhaust, EF_{CIMS} represented a higher percentage of EF_{total} (25.8% for DSL and 17.9%
 428 for RME), likely because of an increased proportion of organics with acid groups.

429

430 Table 3. Summary of top 10 EF_{fresh} of PM contributing species with respective EF_{aged} in Euro V DSL and RME emissions.

Species	DSL		Species	RME	
	EF_{fresh} ($\text{mg kg}_{\text{fuel}}^{-1}$)	EF_{aged} ($\text{mg kg}_{\text{fuel}}^{-1}$)		EF_{fresh} ($\text{mg kg}_{\text{fuel}}^{-1}$)	EF_{aged} ($\text{mg kg}_{\text{fuel}}^{-1}$)
H_2SO_4	4.8	6.8	HNO_3	2.5	45
HNO_3	3.2	50	$C_{18}H_{34}O_2$	1.2	0.81
$C_7H_4O_7$	1.8	3.8	H_2SO_4	0.61	0.68
$HNCO$	1.1	1.2	$C_{14}H_{28}O_2$	0.52	0.85
C_7H_8O	0.9	7.2	$HNCO$	0.45	0.089
$C_3H_6O_3$	0.6	23	$C_{18}H_{36}O_2$	0.32	0.046
$C_6H_5NO_3$	0.53	2.6	$C_{16}H_{32}O_2$	0.30	0.18
$C_4H_6O_5$	0.45	0.30	$C_6H_5O_2$	0.12	8.6
C_6H_5O	0.26	15.6	$C_4H_6O_4$	0.089	6.3
$C_7H_7NO_3$	0.15	4.6	$C_{16}H_{30}O_2$	0.081	0.012
EF_{total} measured by the EEPS	160.9	1289.8	EF_{total} measured by the EEPS	127.7	1320.6
EF_{CIMS}	16.8	320.1	EF_{CIMS}	7.5	237.2
$EF_{\text{CIMS}}/EF_{\text{total}}$ (%)	10.4	25.8	$EF_{\text{CIMS}}/EF_{\text{total}}$ (%)	5.9	17.9

431

432

433 4. Conclusion/ atmospheric implications

434 To address the challenges posed by increasing transportation needs, associated greenhouse gas emissions, and related climate
435 change impacts, biofuels have been promoted as a low-carbon alternative to fossil fuels. In 2020, for the 27 Member States of
436 the European Union, 93.2% of the total fuel supply for road transport was derived from fossil fuels, while 6.8% came from
437 biofuels, with Sweden having the highest biofuel share at 23.2% (Vourliotakis and Platsakis, 2022). This study investigated
438 renewable fuels like rapeseed methyl ester (RME), hydrotreated vegetable oil (HVO), and methane (when using biogas) in
439 terms of primary emissions of pollutants and their secondary formation after photochemical aging. DSL buses without a DPF
440 displayed the highest $EF_{PM:Fresh}$, whereas compressed natural gas (CNG) buses emitted the least, with a median $EF_{PM:Fresh}$ below
441 the detection limit. Despite more than an order of magnitude difference in $EF_{PM:Fresh}$ among buses operated with various fuel
442 types, we observed smaller variations in $EF_{PM:Aged}$, suggesting that secondary particle formation is likely influenced by
443 substantial non-fuel-dependent precursor sources such as lubrication oils and/or fuel additives. Recognizing these sources is
444 crucial for refining regulations on hydrocarbon emissions, which could notably enhance SOA control. The median ratios of
445 aged to fresh particle mass emission factors, listed in ascending order, were for diesel (4.0), HVO (6.7), HVO_{HEV} (10.5), RME
446 (10.8), and CNG buses (84), highlighting the significant yet often overlooked contributions of aged/photochemically processed
447 emissions to urban air quality. Furthermore, Zhao et al. (2017) revealed a strongly nonlinear relationship between SOA
448 formation from vehicle exhaust and the ratio of non-methane organic gas to NO_x (NMOG: NO_x). For instance, increasing the
449 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,
450 underscoring the importance of integrated emission control policies for NO_x and organic gases for better manage SOA
451 formation. While implementing regulations for secondary particle formation presents significant challenges, these are crucial
452 for a thorough understanding of their impact on regional air quality and health. Our approach to measuring the maximum SOA
453 formation potential—peaking at a photochemical age of approximately 5 equivalent days of atmospheric OH exposure—
454 provides a possible semi-quantitative reference for comparing SOA formation potential across different studies. We
455 acknowledge the limitations of this approach for direct regulatory application and emphasize the need for more precise and
456 comprehensive research to develop a methodologically robust framework that stakeholders can agree upon for systematically
457 assessing the impacts of vehicle on air quality and informing regulatory strategies.

458

459 It is important to note that the ambient temperature during this study was relatively low, which does not affect the EF
460 comparison across different buses but should be aware of when comparing these results to studies conducted at significantly
461 higher temperatures. Wang et al. (2017) noted lower particle number EFs in summer compared to winter, potentially due to
462 increased nucleation or condensation at cooler temperatures. Temperature impacts on emissions are significant during cold
463 starts when combustion is inefficient (Nam et al., 2010). Post-warm-up, soot mode particles show little temperature
464 sensitivity (Ristimäki et al., 2005). Book et al. (2015) found inconsistent trends in particle emissions from DPF-equipped

465 diesel trucks across various temperatures and driving cycles, suggesting that more research is needed to understand the
466 temperature effects on emissions from different bus types under varied operational conditions.

467

468 Non-regulated chemical species can also have serious negative impacts on air quality and human health. Organic and inorganic
469 acids influence the pH of precipitation and will potentially contribute to acid deposition, affecting ecosystem health.
470 Furthermore, there is a risk that some abatement systems might generate unintended compounds, such as HNCO from the
471 thermal degradation of urea in SCR systems without sufficient hydrolysis. Additionally, Jathar et al. (2017b) observed
472 substantial direct emissions of HNCO from diesel engines and estimated that ambient concentrations in Los Angeles could
473 vary widely, ranging from 20 to 107 ppt depending on different parameterizations of diesel engine emissions. The persistence
474 of HNCO in the atmosphere, particularly under dry conditions, poses significant health risks. It has been linked to severe
475 outcomes including respiratory and cardiovascular disorders, atherosclerosis, cataracts, and rheumatoid arthritis (Leslie et al.,
476 2019; Roberts et al., 2011). In our study, small monoacids (C₁-C₃) and nitrogen-containing compounds, such as nitrous acid
477 (HONO), nitric acid (HNO₃), and HNCO, dominated the fresh gaseous emissions measured by acetate-CIMS for all Euro
478 V/EEV buses regardless of fuel type, with HVO_{HEV} buses exhibiting the highest emissions. Notably, the emission levels of
479 nitrogen-containing compounds were significantly lowered in Euro VI buses, equipped with advanced after-treatment systems
480 that include EGR and DPF technologies in addition to SCR-only techniques. This indicates that transitioning to vehicles
481 equipped with more advanced emission control technologies can be beneficial, even though these technologies may not be
482 specifically designed to target emissions of HONO, HNO₃, and HNCO. Consequently, a detailed evaluation of the
483 environmental and health effects of emerging engine and after-treatment technologies is highly desirable for future
484 considerations. Overall, the extended online chemical characterization of in-use fleet emissions, utilizing advanced techniques
485 like HR-ToF-CIMS, enables the identification of unregulated pollutants, which is crucial for more informed policy decisions
486 and vehicle technology developments.

487

488 ***Data availability.***

489 The data used in this publication are available to the community and can be accessed by request to the corresponding author.

490

491 ***Author contributions.***

492 ÅMH, MLB and QL conducted the measurements. ÅMH designed the project, coordinated the measurements and together
493 with MH and CKC supervised the study. LZ, QL, MLB, CMS and ÅMH carried out the data analysis. LZ, QL, JZY, MH,
494 ÅMH and CKC prepared the manuscript. All co-authors contributed to the discussion and the interpretation of the results.

495

496 ***Competing interests.***

497 The authors declare that they have no known competing financial interests or personal relationships that could have appeared
498 to influence the work reported in this paper.

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505 **References**

- 506 Aljawhary, D., Lee, A. K. Y., and Abbatt, J. P. D.: High-resolution chemical ionization mass spectrometry (ToF-CIMS): application to study
 507 SOA composition and processing, *Atmospheric Measurement Techniques*, 6, 3211-3224, 10.5194/amt-6-3211-2013, 2013.
- 508 Arnold, F., Pirjola, L., Ronkko, T., Reichl, U., Schlager, H., Lahde, T., Heikkila, J., and Keskinen, J.: First online measurements of sulfuric
 509 acid gas in modern heavy-duty diesel engine exhaust: implications for nanoparticle formation, *Environmental science & technology*, 46,
 510 11227-11234, 2012.
- 511 Bernhard, A. M., Peitz, D., Elsener, M., Wokaun, A., and Kröcher, O.: Hydrolysis and thermolysis of urea and its decomposition byproducts
 512 biuret, cyanuric acid and melamine over anatase TiO₂, *Applied Catalysis B: Environmental*, 115, 129-137, 2012.
- 513 Book, E. K., Snow, R., Long, T., Fang, T., and Baldauf, R.: Temperature effects on particulate emissions from DPF-equipped diesel trucks
 514 operating on conventional and biodiesel fuels, *Journal of the Air & Waste Management Association*, 65, 751-758, 2015.
- 515 Brady, J. M., Crisp, T. A., Collier, S., Kuwayama, T., Forestieri, S. D., Perraud, V., Zhang, Q., Kleeman, M. J., Cappa, C. D., and Bertram,
 516 T. H.: Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles, *Environ Sci Technol*, 48, 11405-11412,
 517 10.1021/es504354p, 2014.
- 518 Bruns, E., El Haddad, I., Keller, A., Klein, F., Kumar, N., Pieber, S., Corbin, J., Slowik, J., Brune, W., and Baltensperger, U.: Inter-
 519 comparison of laboratory smog chamber and flow reactor systems on organic aerosol yield and composition, *Atmospheric Measurement*
 520 *Techniques*, 8, 2315-2332, 2015.
- 521 Chen, L., Bao, Z., Wu, X., Li, K., Han, L., Zhao, X., Zhang, X., Wang, Z., Azzi, M., and Cen, K.: The effects of humidity and ammonia on
 522 the chemical composition of secondary aerosols from toluene/NO_x photo-oxidation, *Science of The Total Environment*, 728, 138671, 2020.
- 523 Chirico, R., DeCarlo, P., Heringa, M., Tritscher, T., Richter, R., Prévôt, A., Dommen, J., Weingartner, E., Wehrle, G., and Gysel, M.: Impact
 524 of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from
 525 smog chamber experiments, *Atmospheric Chemistry & Physics*, 10, 11545-11563, 2010.
- 526 Corrêa, S. M., and Arbilla, G.: Mercaptans emissions in diesel and biodiesel exhaust, *Atmospheric Environment*, 42, 6721-6725, 2008.
- 527 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
 528 Zhang, Q.: On the primary emission of formic acid from light duty gasoline vehicles and ocean-going vessels, *Atmospheric Environment*,
 529 98, 426-433, 2014.
- 530 Deng, W., Hu, Q., Liu, T., Wang, X., Zhang, Y., Song, W., Sun, Y., Bi, X., Yu, J., Yang, W., Huang, X., Zhang, Z., Huang, Z., He, Q.,
 531 Mellouki, A., and George, C.: Primary particulate emissions and secondary organic aerosol (SOA) formation from idling diesel vehicle
 532 exhaust in China, *Sci Total Environ*, 593-594, 462-469, 10.1016/j.scitotenv.2017.03.088, 2017.
- 533 Edwards, R., Mahieu, V., Griesemann, J.-C., Larivé, J.-F., and Rickeard, D. J.: Well-to-wheels analysis of future automotive fuels and
 534 powertrains in the European context, *SAE Technical Paper0148-7191*, 2004.
- 535 Emanuelsson, E. U., Hallquist, M., Kristensen, K., Glasius, M., Bohn, B., Fuchs, H., Kammer, B., Kiendler-Scharr, A., Nehr, S., and Rubach,
 536 F.: Formation of anthropogenic secondary organic aerosol (SOA) and its influence on biogenic SOA properties, *Atmospheric Chemistry and*
 537 *Physics*, 13, 2837-2855, 2013.
- 538 *Energimyndigheten: Energy in Sweden 2021 – An Overview*, 2021.
- 539 Fitzmaurice, H. L., and Cohen, R. C.: A method for using stationary networks to observe long-term trends of on-road emission factors of
 540 primary aerosol from heavy-duty vehicles, *Atmospheric Chemistry and Physics*, 22, 15403-15411, 2022.
- 541 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
 542 Sources of Gas-Phase Organic Acids from Diesel Exhaust, *Environ Sci Technol*, 51, 10872-10880, 10.1021/acs.est.7b01169, 2017.
- 543 Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., and de Gouw,
 544 J.: Review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions, *Environmental science &*
 545 *technology*, 51, 1074-1093, 2017.

546 Ghadimi, S., Zhu, H., Durbin, T. D., Cocker III, D. R., and Karavalakis, G.: Exceedances of Secondary Aerosol Formation from In-Use
547 Natural Gas Heavy-Duty Vehicles Compared to Diesel Heavy-Duty Vehicles, *Environmental Science & Technology*, 57, 19979-19989,
548 2023.

549 Giechaskiel, B., Riccobono, F., Vlachos, T., Mendoza-Villafuerte, P., Suarez-Bertoa, R., Fontaras, G., Bonnel, P., and Weiss, M.: Vehicle
550 emission factors of solid nanoparticles in the laboratory and on the road using portable emission measurement systems (PEMS), *Frontiers in*
551 *Environmental Science*, 3, 82, 2015.

552 Gordon, T. D., Presto, A. A., May, A. A., Nguyen, N. T., Lipsky, E. M., Donahue, N. M., Gutierrez, A., Zhang, M., Maddox, C., Rieger, P.,
553 Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Secondary organic aerosol formation exceeds primary particulate
554 matter emissions for light-duty gasoline vehicles, *Atmospheric Chemistry and Physics*, 14, 4661-4678, 10.5194/acp-14-4661-2014, 2014a.

555 Gordon, T. D., Presto, A. A., Nguyen, N. T., Robertson, W. H., Na, K., Sahay, K. N., Zhang, M., Maddox, C., Rieger, P., Chattopadhyay,
556 S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Secondary organic aerosol production from diesel vehicle exhaust: impact of
557 aftertreatment, fuel chemistry and driving cycle, *Atmospheric Chemistry and Physics*, 14, 4643-4659, 10.5194/acp-14-4643-2014, 2014b.

558 Guerreiro, C. B., Foltescu, V., and De Leeuw, F.: Air quality status and trends in Europe, *Atmospheric environment*, 98, 376-384, 2014.

559 Hak, C. S., Hallquist, M., Ljungstrom, E., Svane, M., and Pettersson, J. B. C.: A new approach to in-situ determination of roadside particle
560 emission factors of individual vehicles under conventional driving conditions, *Atmospheric Environment*, 43, 2481-2488,
561 10.1016/j.atmosenv.2009.01.041, 2009.

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

564 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N., George, C., and Goldstein,
565 A.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmospheric chemistry and physics*, 9,
566 5155-5236, 2009.

567 Hao, L., Kari, E., Leskinen, A., Worsnop, D. R., and Virtanen, A.: Direct contribution of ammonia to α -pinene secondary organic
568 aerosol formation, *Atmospheric Chemistry and Physics*, 20, 14393-14405, 2020.

569 Hassaneen, A., Munack, A., Ruschel, Y., Schroeder, O., and Krahl, J.: Fuel economy and emission characteristics of Gas-to-Liquid (GTL)
570 and Rapeseed Methyl Ester (RME) as alternative fuels for diesel engines, *Fuel*, 97, 125-130, 2012.

571 Huang, M., Xu, J., Cai, S., Liu, X., Hu, C., Gu, X., Zhao, W., Fang, L., and Zhang, W.: Chemical analysis of particulate products of aged 1,
572 3, 5-trimethylbenzene secondary organic aerosol in the presence of ammonia, *Atmospheric Pollution Research*, 9, 146-155, 2018.

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

575 Jathar, S. H., Friedman, B., Galang, A. A., Link, M. F., Brophy, P., Volckens, J., Eluri, S., and Farmer, D. K.: Linking load, fuel, and
576 emission controls to photochemical production of secondary organic aerosol from a diesel engine, *Environmental science & technology*, 51,
577 1377-1386, 2017a.

578 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.:
579 Investigating diesel engines as an atmospheric source of isocyanic acid in urban areas, *Atmospheric Chemistry and Physics*, 17, 8959-8970,
580 10.5194/acp-17-8959-2017, 2017b.

581 Jezek, I., Drinovec, L., Ferrero, L., Carriero, M., and Mocnik, G.: Determination of car on-road black carbon and particle number emission
582 factors and comparison between mobile and stationary measurements, *Atmospheric Measurement Techniques*, 8, 43-55, 10.5194/amt-8-43-
583 2015, 2015.

584 Kang, E., Root, M. J., Toohey, D. W., and Brune, W. H.: Introducing the concept of Potential Aerosol Mass (PAM), *Atmospheric Chemistry*
585 *and Physics*, 7, 5727-5744, DOI 10.5194/acp-7-5727-2007, 2007.

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

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

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

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

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

597 Kurtenbach, R., Becker, K., Gomes, J., Kleffmann, J., Lörzer, J., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.:
598 Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, *Atmospheric Environment*, 35, 3385-3394, 2001.

599 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
600 and Dme-Fueled Vehicles Using a Mobile Emission Laboratory, *International Journal of Automotive Technology*, 15, 543-551,
601 <http://doi.org/10.1007/s12239-014-0057-z>, 2014.

602 Lambe, A., Ahern, A., Williams, L., Slowik, J., Wong, J., Abbatt, J., Brune, W., Ng, N., Wright, J., and Croasdale, D.: Characterization of
603 aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity
604 measurements, *Atmospheric Measurement Techniques*, 4, 445-461, 2011.

605 Le Breton, M., Wang, Y., Hallquist, Å. M., Pathak, R. K., Zheng, J., Yang, Y., Shang, D., Glasius, M., Bannan, T. J., and Liu, Q.: Online
606 gas-and particle-phase measurements of organosulfates, organosulfonates and nitrooxy organosulfates in Beijing utilizing a FIGAERO ToF-
607 CIMS, *Atmospheric Chemistry and Physics*, 18, 10355-10371, 2018.

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

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

612 Li, T., Wang, Z., Yuan, B., Ye, C., Lin, Y., Wang, S., Yuan, Z., Zheng, J., and Shao, M.: Emissions of carboxylic acids, hydrogen cyanide
613 (HCN) and isocyanic acid (HNCO) from vehicle exhaust, *Atmospheric Environment*, 247, 118218, 2021.

614 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
615 Formation of Fleet Vehicle Emissions in China: Potential Seasonality of Spatial Distributions, *Environmental Science & Technology*, 2021a.

616 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
617 formation of fleet vehicle emissions in China: Potential seasonality of spatial distributions, *Environmental Science & Technology*, 55, 7276-
618 7286, 2021b.

619 Liao, S., Zhang, J., Yu, F., Zhu, M., Liu, J., Ou, J., Dong, H., Sha, Q., Zhong, Z., and Xie, Y.: High gaseous nitrous acid (HONO) emissions
620 from light-duty diesel vehicles, *Environmental science & technology*, 55, 200-208, 2020.

621 Link, M. F., Friedman, B., Fulgham, R., Brophy, P., Galang, A., Jathar, S. H., Veres, P., Roberts, J. M., and Farmer, D. K.: Photochemical
622 processing of diesel fuel emissions as a large secondary source of isocyanic acid (HNCO), *Geophysical Research Letters*, 43, 4033-4041,
623 10.1002/2016gl068207, 2016.

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

626 Liu, S., Thompson, S. L., Stark, H., Ziemann, P. J., and Jimenez, J. L.: Gas-phase carboxylic acids in a university classroom: Abundance,
627 variability, and sources, *Environmental Science & Technology*, 51, 5454-5463, 2017.

628 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
629 formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber, *Atmospheric Chemistry and Physics*, 15,
630 9049-9062, 10.5194/acp-15-9049-2015, 2015.

631 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
632 Roadside Air in Hong Kong, *Environ Sci Technol*, 53, 3001-3009, 10.1021/acs.est.8b06587, 2019b.

633 Lopez-Hilfiker, F., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Carrasquillo, A., Daumit, K., and Hunter, J.: Phase
634 partitioning and volatility of secondary organic aerosol components formed from α -pinene ozonolysis and OH oxidation: the importance of
635 accretion products and other low volatility compounds, *Atmospheric chemistry and physics*, 15, 7765-7776, 2015.

636 Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton,
637 J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols
638 (FIGAERO), *Atmospheric Measurement Techniques*, 7, 983-1001, 10.5194/amt-7-983-2014, 2014.

639 Martinet, S., Liu, Y., Louis, C., Tassel, P., Perret, P., Chaumond, A., and Andre, M.: Euro 6 unregulated pollutant characterization and
640 statistical analysis of after-treatment device and driving-condition impact on recent passenger-car emissions, *Environmental Science &
641 Technology*, 51, 5847-5855, 2017.

642 May, A. A., Nguyen, N. T., Presto, A. A., Gordon, T. D., Lipsky, E. M., Karve, M., Gutierrez, A., Robertson, W. H., Zhang, M., Brandow,
643 C., Chang, O., Chen, S. Y., Cicero-Fernandez, P., Dinkins, L., Fuentes, M., Huang, S. M., Ling, R., Long, J., Maddox, C., Massetti, J.,
644 McCauley, E., Miguel, A., Na, K., Ong, R., Pang, Y. B., Rieger, P., Sax, T., Truong, T., Vo, T., Chattopadhyay, S., Maldonado, H., Maricq,
645 M. M., and Robinson, A. L.: Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles, *Atmospheric
646 Environment*, 88, 247-260, 10.1016/j.atmosenv.2014.01.046, 2014.

647 Millet, D. B., Baasandorj, M., Farmer, D. K., Thornton, J. A., Baumann, K., Brophy, P., Chaliyakunnel, S., de Gouw, J. A., Graus, M., and
648 Hu, L.: A large and ubiquitous source of atmospheric formic acid, *Atmospheric Chemistry and Physics*, 15, 6283-6304, 2015.

649 Mohr, C., Lopez-Hilfiker, F. D., Yli-Juuti, T., Heitto, A., Lutz, A., Hallquist, M., D'Ambro, E. L., Rissanen, M. P., Hao, L., and
650 Schobesberger, S.: Ambient observations of dimers from terpene oxidation in the gas phase: Implications for new particle formation and
651 growth, *Geophysical Research Letters*, 44, 2958-2966, 2017.

652 Nakashima, Y., and Kondo, Y.: Nitrous acid (HONO) emission factors for diesel vehicles determined using a chassis dynamometer, *Science
653 of The Total Environment*, 806, 150927, 2022.

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

656 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.,
657 Swietlicki, E., Svenningsson, B., Bohgard, M., Kulmala, M., Hallquist, M., and Pagels, J. H.: Secondary organic aerosol formation from

658 idling gasoline passenger vehicle emissions investigated in a smog chamber, *Atmospheric Chemistry and Physics*, 13, 6101-6116,
659 10.5194/acp-13-6101-2013, 2013.

660 Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., and Graus, M.: Real-time
661 measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area,
662 *Atmospheric Chemistry and Physics*, 16, 7411-7433, 2016.

663 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
664 secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor, *Atmospheric Chemistry and Physics*, 16,
665 2943-2970, 2016.

666 Paulot, F., Wunch, D., Crouse, J. D., Toon, G., Millet, D. B., DeCarlo, P. F., Vigouroux, C., Deutscher, N. M., González Abad, G., and
667 Notholt, J.: Importance of secondary sources in the atmospheric budgets of formic and acetic acids, *Atmospheric Chemistry and Physics*,
668 11, 1989-2013, 2011.

669 Pflaum, H., Hofmann, P., Geringer, B., and Weissel, W.: Potential of hydrogenated vegetable oil (HVO) in a modern diesel engine, SAE
670 Technical Paper0148-7191, 2010.

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

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

676 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.,
677 Drinovec, L., Mocnik, G., Mohler, O., Richter, R., Barmet, P., Bianchi, F., Baltensperger, U., and Prevot, A. S. H.: Secondary organic aerosol
678 formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, *Atmospheric Chemistry and Physics*, 13, 9141-
679 9158, 10.5194/acp-13-9141-2013, 2013.

680 Preble, C. V., Dallmann, T. R., Kreisberg, N. M., Hering, S. V., Harley, R. A., and Kirchstetter, T. W.: Effects of Particle Filters and Selective
681 Catalytic Reduction on Heavy-Duty Diesel Drayage Truck Emissions at the Port of Oakland, *Environmental Science & Technology*, 49,
682 8864-8871, 10.1021/acs.est.5b01117, 2015.

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

685 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,
686 R.: Isocyanic acid in the atmosphere and its possible link to smoke-related health effects, *Proceedings of the National Academy of Sciences*,
687 108, 8966-8971, 2011.

688 Saliba, G., Saleh, R., Zhao, Y., Presto, A. A., Lambe, A. T., Frodin, B., Sardar, S., Maldonado, H., Maddox, C., and May, A. A.: Comparison
689 of gasoline direct-injection (GDI) and port fuel injection (PFI) vehicle emissions: emission certification standards, cold-start, secondary
690 organic aerosol formation potential, and potential climate impacts, *Environmental science & technology*, 51, 6542-6552, 2017.

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

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

696 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,
697 A. L.: Secondary Organic Aerosol Formation from in-Use Motor Vehicle Emissions Using a Potential Aerosol Mass Reactor, *Environmental*
698 *Science & Technology*, 48, 11235-11242, 10.1021/es502239v, 2014.

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

701 Usmanov, R. A., Mazanov, S. V., Gabitova, A. R., Miftakhova, L. K., Gumerov, F. M., Musin, R. Z., and Abdulgatov, I. M.: The effect of
702 fatty acid ethyl esters concentration on the kinematic viscosity of biodiesel fuel, *Journal of Chemical & Engineering Data*, 60, 3404-3413,
703 2015.

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

706 Vourliotakis, G., and Platsakis, O.: ETC CM report 2022/02: Greenhouse gas intensities of transport fuels in the EU in 2020 - Monitoring
707 under the Fuel Quality Directive, European Topic Centre on Climate change mitigation, 2022.

708 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
709 monitoring of on-road emission factors by comparing concurrent PEMS measurements, *Science of the Total Environment*, 736, 139507,
710 2020.

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

713 Wang, Z., Nicholls, S. J., Rodriguez, E. R., Kummu, O., Hörkkö, S., Barnard, J., Reynolds, W. F., Topol, E. J., DiDonato, J. A., and Hazen,
714 S. L.: Protein carbamylation links inflammation, smoking, uremia and atherogenesis, *Nature medicine*, 13, 1176-1184, 2007.

715 Watne, A. K., Psychoudaki, M., Ljungstrom, E., Le Breton, M., Hallquist, M., Jerksjo, M., Fallgren, H., Jutterstrom, S., and Hallquist, A.
716 M.: Fresh and Oxidized Emissions from In-Use Transit Buses Running on Diesel, Biodiesel, and CNG, *Environ Sci Technol*, 52, 7720-7728,
717 <https://doi.org/10.1021/acs.est.8b01394>, 2018.

718 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
719 acids in diesel exhaust: a relevant source of HNCO?, *Environ Sci Technol*, 47, 7663-7671, 10.1021/es401127j, 2013.

720 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
721 China: Precursors and aging processes, *Environmental Pollution*, 309, 119778, 2022.

722 Yao, X., Fang, M., and Chan, C. K.: Size distributions and formation of dicarboxylic acids in atmospheric particles, *Atmospheric*
723 *Environment*, 36, 2099-2107, 2002.

724 Yuan, B., Veres, P., Warneke, C., Roberts, J., Gilman, J., Koss, A., Edwards, P., Graus, M., Kuster, W., and Li, S.-M.: Investigation of
725 secondary formation of formic acid: urban environment vs. oil and gas producing region, *Atmospheric Chemistry and Physics*, 15, 1975-
726 1993, 2015.

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

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

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

733 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
734 secondary organic aerosol formation from gasoline vehicle exhaust, *Proceedings of the National Academy of Sciences*, 114, 6984-6989,
735 2017.

736 Zhao, Y., Lambe, A. T., Saleh, R., Saliba, G., and Robinson, A. L.: Secondary Organic Aerosol Production from Gasoline Vehicle Exhaust:
737 Effects of Engine Technology, Cold Start, and Emission Certification Standard, *Environ Sci Technol*, 52, 1253-1261,
738 <https://doi.org/10.1021/acs.est.7b05045>, 2018.

739 Zhou, L., Hallquist, Å. M., Hallquist, M., Salvador, C. M., Gaita, S. M., Sjödin, Å., Jerksjö, M., Salberg, H., Wängberg, I., and Mellqvist,
740 J.: A transition of atmospheric emissions of particles and gases from on-road heavy-duty trucks, *Atmospheric Chemistry and Physics*, 20,
741 1701-1722, 2020.

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

745