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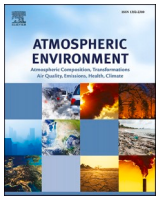

Chemical speciation of PM emissions from heavy-duty vehicles

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HIGHLIGHTS

- PM emission factors were higher for Euro V than Euro VI diesel heavy-duty vehicles.
- The lowest PM emissions were obtained for the Euro V vehicle fuelled with GTL.
- Na and Sr were the most abundant PM-bound elements, followed by Al and Ca.
- Several oxygenated organic compounds were detected in exhaust particulates.
- Benzenedicarboxylic acids were higher in emissions from Euro VI compared to Euro V.

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ABSTRACT

Particulate matter (PM) is recognised as the deadliest form of air pollution, with vehicle emissions being one of its most important sources. Verification of compliance with the emission standards has been reported in numerous works. However, the detailed chemical speciation of PM is still very poorly understood. In this study, different heavy-duty vehicles (HDV) were tested on a chassis dynamometer under different driving cycles. Particulate matter (PM) emission factors for Euro V and Euro VI vehicles ranged from 24.9 to 51.2 mg kWh^{-1} and from 8.4 to 14.7 mg kWh^{-1}, respectively. Major and trace elements, in their oxidised form, accounted for PM mass fractions between 6.3 and 58%. The lowest PM values were obtained for the Euro V vehicle fuelled with gas-to-liquids (GTL) under the world harmonised vehicle cycle (WHVC) with cold start, while the highest amounts were observed for the Euro VI vehicle fuelled with diesel over the hot start WHVC cycle. In general, Na and Sr were the most abundant elements, followed by Al and Ca. Several oxygenated organic compounds were detected, as far as we know, for the first time in exhaust particulates. Greater varieties (from C11 to C31 with no preference for odd versus even carbon numbers) and amounts of n-alkanes were detected in the emitted particulate matter (up to 7938 μg per g of PM) for the GTL fuelled vehicle (Euro V) tested by the WHVC driving cycle with cold start. The start-up phase mass fractions of ∑18PAHs were much higher (552 μg g^{-1}) when the diesel-powered Euro V vehicle followed the VTT cycle than in the following tests (28.8–48.1 μg g^{-1}). A homologous series of n-alkanoic acids, from C8 to C22, were found in the exhausts, accounting for particulate mass fractions ranging from 0.50 to 19.4 mg g^{-1}, and peaking at C14, C16 and C18. Benzenedicarboxylic acids were observed at higher concentrations in emissions from Euro VI vehicles compared to Euro V. n-Alkanols from C8 to C30, with a clear dominance of C18 were detected in all PM samples. Ethylene glycol and other glycols were always present.

1. Introduction

Air pollution is the single largest environmental health risk in Europe (EEA, 2021a). Poor air quality caused by certain pollutant emissions has negative impacts on the environment and human health, as it has been linked to climate change, and respiratory and cardiovascular diseases, respectively (Almeida et al., 2014; EEA, 2019; Kelly and Fussell, 2011; WHO, 2022). In Europe, about 75% of the population lives in urban

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areas (Eurostat, 2016) and road traffic is one of the main sources of air pollution (Custódio et al., 2016; Heydari et al., 2020; Pant and Harrison, 2013; Reche et al., 2012). In 2019, most of the urban population in the European Union (EU) was exposed to health-damaging levels of key air pollutants. Specifically, 97% of the urban population was exposed to concentrations of inhalable particulate matter with a diameter of 2.5 μm or less ($PM_{2.5}$) above the new World Health Organisation (WHO) guideline level of 5 μg m^{-3} (EEA, 2021b).

Road transportation emissions can be subdivided into exhaust emissions from combustion and non-exhaust emissions, which comprise particles from brake and tyre wear, road surface abrasion and dust resuspension (Thorpe and Harrison, 2008). Vehicle exhaust emissions are a relevant source of some pollutants, namely PM, black carbon (BC), carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NOx) and other toxic air pollutants (Sassykova et al., 2019). On-road diesel vehicles are the leading contributor to air pollution and associated disease burdens (Jin et al., 2021). HDVs are freight vehicles over 3.5 tonnes (e.g., trucks) or passenger transport vehicles of more than 8 seats (e.g., buses), and the vast majority are powered by diesel engines in Europe (Muncrief and Sharpe, 2015). HDVs accounted for 78% of on-road diesel BC emissions in 2017, though they made up less than a quarter of the diesel vehicle fleet (Miller and Jin, 2019). BC from diesel engine exhaust severely affects the climate since particles produce significant near-term climate warming, in addition to the impact on air quality and public health. The WHO reports that children who live near roads with HDV traffic have twice the risk of respiratory problems than those who live near streets with less traffic (WHO, 2022).

To reduce exhaust emissions, in the last decades, vehicle emission standards and exhaust after-treatment technologies, such as catalytic converters and diesel particulate filters, have been adopted, and changes in fuel quality have been introduced (Anenberg et al., 2019). Emission regulations have become more stringent over the years. In Europe, vehicle emissions are regulated by the "Euro standards", which set limits for CO, PM, hydrocarbons (HC), and NOx. For HDV, the emission standards currently in force are Euro VI (originally set out in Regulation 595/2009, with further amendments in Regulations 582/2011 and 133/2014), which have established a large reduction in the NOx emission limit and included for the first time a particle number (PN) limit (Lindqvist, 2012). The Euro VI emission limits went into effect in 2013 for new type approvals and in 2014 for all registrations. Although the application of strict enforcement policies has led to considerable reductions in exhaust emissions, traffic sites continue to register most of the exceedances of PM_{10} values (EEA, 2020). In 2021, the WHO imposed stricter new air quality guidelines as recent scientific evidence shows how air pollution harms human health (EEA, 2021a).

Road transport plays a key role in the economy, so there are some conflicting demands for transport policies. Achieving levels of good air quality is still a challenge, especially in urban areas with high volumes of traffic (WHO, 2022). Chemical fingerprints of exhaust emissions depend on engine age and type, after-treatment technologies, fuel and lubricating oil properties, and driving conditions. It is essential to better understand the chemical fingerprint of vehicle emissions. Knowing in detail the chemical composition, especially carcinogenic polyaromatic hydrocarbons, of the exhaust particles is of utmost importance not only to establish which constituents induce toxicity, but also to use emission profiles as input data for receptor models and, in this way, make source apportionments more accurate to implement adequate mitigation measures. Although several studies on PM-bound constituents from the exhaust of HDVs have been published, vehicle technology is constantly evolving, so it is crucial to update the available information about the chemical fingerprints of exhaust emissions. This paper aims to create PM speciation profiles for exhaust emissions from heavy-duty vehicles, including a vast array of elements and apolar and polar organic compounds. The new data set can contribute to European emission inventories and may help to increase the completeness of the SPECIEUROPE database. Furthermore, the results can provide useful information for toxicologists to better define the type of bioassay to apply and the doses to test.

2. Materials and methods

2.1. Sampling

In this study, 15 chassis dynamometer test cycles were carried out by the VTT Technical Research Centre of Finland, whose facility is equipped with a full-flow dilution tunnel and an AVL PSS i60 particulate matter sampler. PM was collected on 47 mm diameter filters (Pallflex® Filter Emfab™ Tx40Hi20Ww 47 mm). Three different HDVvehicles were tested under different test cycles and type of fuels (Table 1). HDV I is a truck, while HDV II and HDV III are buses. Some of the vehicles were with automatic transmission.

Vehicles were operated on a chassis dynamometer and the test cycles applied were the VTT cycle, the World Harmonised Vehicle Cycle (WHVC), and the Braunschweig cycle (Fig. S1). Both hot and cold start tests were performed to take into account the effect of engine temperature on emissions. The VTT test cycle is an urban cycle representing driving conditions in urban areas with multiple projected stops (through a road load model based on deceleration measurements and vehicle speed below 60 km h^{-1}). The test has a duration of 1200 s (Söderena et al., 2019). The German Braunschweig city driving cycle is performed on a chassis dynamometer and simulates driving a city bus with frequent stops and has a duration of 1740 s in a hot start test (Pelkmans and Keukeleere, 2000). The WHVC is a chassis dynamometer test developed based on the same dataset used for the development of the World Harmonised Transient Cycle (WHTC). It is performed as a combination of a cold start test and a hot start test, with an immersion time of 10 ± 1 min between them and with weighting factors for the final emission factors of 14% and 86%, respectively. The test duration is 1800 s and includes three segments, representing urban (900 s), rural (481 s), and motorway (419 s) driving (García et al., 2017). The densities of GTL, diesel 1 and diesel 2 (at 15 °C) were 782.4, 839.8 and 835.6 g l^{-1}, respectively. Both diesel fuels were normal EN590 blends, but while diesel 1 contained up to 7% of bio components, diesel 2 had 0%.

2.2. Analytical determinations

The filters were weighed on a Sartorius SE 2-F microbalance that meets the ISO 8178 requirements. Before and after sampling, the filters were weighed after a 2 h conditioning period in a temperature (22 °C ± 1 °C) and relative humidity-controlled (45% ± 8%) clean room.

Filters were cut for distinct chemical analysis: i) elements, ii) organic compounds. Blank filters were analysed and subtracted from the experimental values.

A punch of 1.9 cm of each filter was digested in closed Teflon 60 mL reactors using a 1.25 mL HNO_3: 2.5 mL HF: 1.25 mL $HClO_4$ mixture (Querol et al., 2001). The standard reference material (SRM) 1633b (bituminous coal fly ash from NIST, Gaithersburg, MD, USA) was also digested to determine the accuracy of the analytical and digestion methods. Three multi-elemental solutions from CPI International (Santa Rosa, CA, USA) and Sigma-Aldrich (St. Louis, MO, USA) were used to create external calibration curves: Spec® 1 - rare earth elements, Spec® 2 - alkalis, earth alkalis, and metals, and Spec® 4 - Nb. Trace and major elements were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific, iCAP 6500 Radial) and inductively coupled plasma mass spectroscopy (ICP-MS, Thermo Scientific, X-Series II), respectively. Three multi-elemental solutions (Spec® 1 - rare earth elements, Spec® 2 - alkalis, earth alkalis, and metals, and Spec® 4 - Nb) were used to create external calibration curves. To control the mean precision and accuracy, analyses of 0.025 mg of NBS1633b (fly ash) reference material (NIST, Gaithersburg, MD, USA) were carried out. They fell in the ranges 3–5% for ICP-AES and <10% for ICP-MS. The detection limits were 0.01 ng m^{-3} for most trace

Table 1
Details of the heavy-duty vehicles tested.

	Test cycle	Fuel	Vehicle model year	Emission standard	Driven distance (km)	Pos. work [kWh]
HDV I	VTT	Diesel 1	2013	Euro V	3.761	7.759
	VTT	Diesel 1	2013	Euro V	3.733	7.835
	VTT	Diesel 1	2013	Euro V	3.649	7.637
	WHVC cold	Diesel 1	2013	Euro V	19.879	17.435
	WHVC cold[a]	Diesel 1	2013	Euro V	19.918	17.383
	WHVC cold	GTL	2013	Euro V	20.003	17.314
	WHVC cold[a]	GTL	2013	Euro V	20.014	17.425
HDV II	WHVC cold	Diesel 2	2016	Euro VI	19.763	16.612
	WHVC hot	Diesel 2	2016	Euro VI	19.767	16.584
	WHVC hot	Diesel 2	2016	Euro VI	19.796	16.647
	WHVC hot	Diesel 2	2016	Euro VI	19.776	16.569
	WHVC hot	Diesel 2	2016	Euro VI	19.829	16.654
HDV III	Braunschweig hot	Diesel 2	2016	Euro VI	10.428	14.182
	Braunschweig hot	Diesel 2	2016	Euro VI	10.427	14.271

Gas-to-liquids (GTL).
[a] This test is a repetition of the previous one on the same day, so the engine does not actually start cold as the first one.

elements.

The remaining part of each filter was sequentially extracted with dichloromethane and methanol. After filtration of both solvents, the combined organic extract was concentrated to a volume of 0.5 mL in a TurboVap® evaporator workstation from Biotage and then dried under a gentle nitrogen stream. Flash vacuum silica gel column chromatography was employed to separate the extracts into five groups of organic compounds using eluents of increasing polarity. Before speciation by gas chromatography–mass spectrometry (GC–MS), the polar extracts containing oxygenated functional groups were subjected to trimethylsilyl (TMS) derivatisation with N,O-bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane (BSTFA + TMCS 99:1, from Merck) for 3 h at 70 °C. The TMS derivatives were analysed in a GC–MS from Thermo Scientific (Trace Ultra, quadrupole DSQ II) equipped with a TRB-5MS 60 m × 0.25 mm × 0.25 μm column. Aliphatic and polycyclic aromatic hydrocarbons (PAHs) were quantified in a Shimadzu QP5050A equipped with a TRB-5MS 30 m × 0.25 mm × 0.25 μm column. Six deuterated compounds (acenaphthene-d10, chrysene-d12, 1,4 dichlorobenzene d4, naphthalene-d8, perylene-d12, and phenanthrene-d10) contained in the EPA 8270 semi-volatile internal standard mix (Supelco), benzo [a]pyrene-d12 (Supelco) and fluorene-d10 (Aldrich) were used to spike the PAH extracts. Extracts from other functional groups were spiked with 3 internal standards (1-chlorohexadecane and 1-chlorododecane, both from Merck, and tetracosane-d50, from Aldrich). About 200 analytical standards were used to perform multipoint calibrations. Data were acquired in both full scan and selected ion monitoring (SIM) modes. The analytical methodology was fully detailed by Alves et al. (2011). Throughout the manuscript only the concentrations of constituents with values above the detection limits are discussed. The detection limit was defined as the concentration of the analyte giving a signal equal to the blank plus 3 × the standard deviation of the blank.

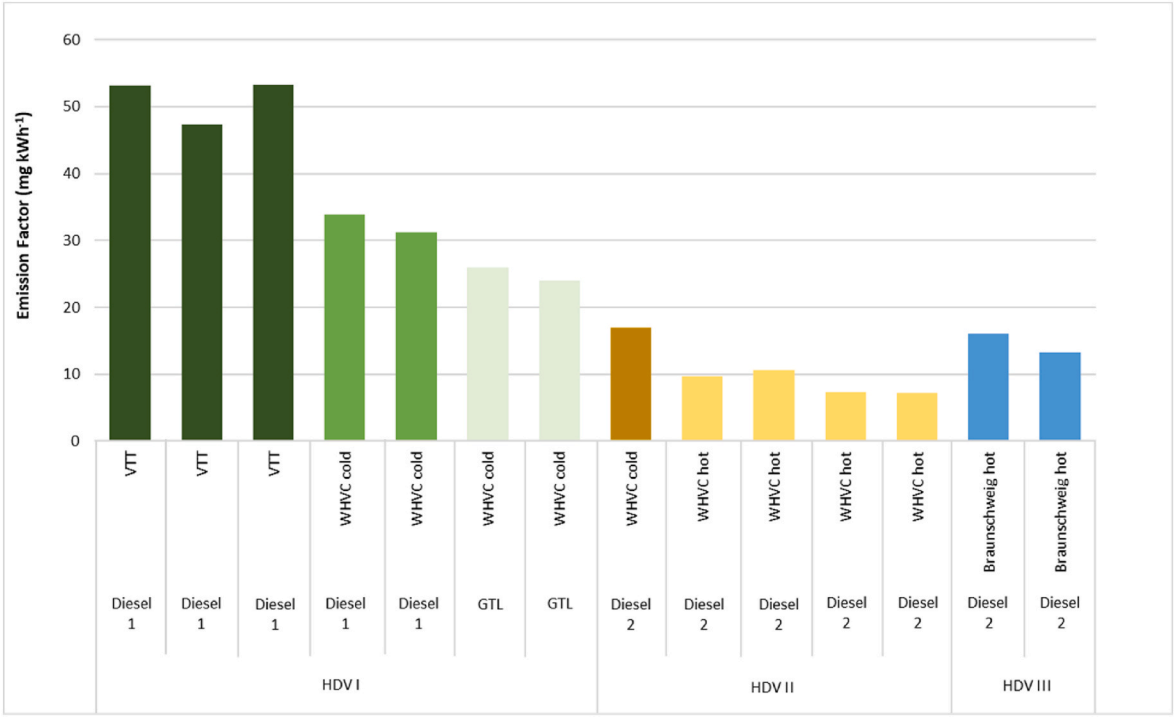

Fig. 1. PM emission factors for the three heavy-duty vehicles under three different test cycles and fuels.

3. Results and discussion

3.1. p.m. emission factors

The PM emission factors of the three heavy-duty vehicles under different test cycles are shown in Fig. 1 as mass of pollutant per kWh of engine work produced.

As expected, the Euro V vehicle (HDV I) presented higher PM emission factors than the Euro VI vehicles (HDV II and HDV III). The PM emission factors for HDV I ranged from 24.4 to 53.3 mg kWh^{-1}, while those from HDV II and HDV III ranged from 7.15 to 16.9 mg kWh^{-1} and from 13.3 to 16.1 mg kWh^{-1}, respectively. Statistically significant differences ($p < 0.0001$) were observed between the mean of the particle emission factor obtained for the VTT cycle of the HDV I and the mean of the other cycles for the same vehicle. The mean emission factor for all HDV III driving cycles was also statistically different ($p < 0.0001$) from the mean value found for HDV II.

The "Euro standards" for PM determined for HDV under standardised test cycles, such as the European Stationary Cycle (ESC) and the European Transient Cycle (ETC), have been replaced by the World Harmonised Transient Cycle (WHTC) and the World Harmonised Stationary Cycle (WHSC) since 2013 (Lindqvist, 2012). For diesel and gas vehicles, the PM emission standard for Euro V heavy vehicles is 30 mg kWh^{-1} under ETC (which simulates typical driving patterns) and 10 mg kWh^{-1} for Euro VI vehicles. The PM emission factors obtained for HDV I, HDV II and HDV III exceed the emission standards, except for HDV I under WHVC cold start with GTL (24.9 mg kWh^{-1}) and WHVC hot start with diesel 2 (8.4 mg kWh^{-1}). However, these comparisons should be taken as indicative only, as the emission standards are set for a different driving cycle, the ETC. Zhou et al. (2019) and Fontaras et al. (2012) tested HDV diesel engines using an engine dynamometer and reported PM emission factors from 15.0 to 26.8 mg kWh^{-1} and from 3.5 to 12.7 mg kWh^{-1} for China V and Euro V HDV diesel engines, respectively. These values were slightly lower than those reported in this study since PM emission factor of HDV I diesel under VTT was 51.2 ± 2.79 mg kWh^{-1} and under WHVC cold start was 32.5 ± 1.37 mg kWh^{-1}. As shown in previous studies, PM emission factors depend on the driving test cycle and fuel quality.

3.2. p.m.-bound chemical constituents

3.2.1. Elemental composition

Most of the metal (loid)s in vehicle exhaust particles comes from fuel combustion, lubricants and abrasion of engine components (Hao et al., 2019; Wang et al., 2003).

In the particles emitted by the different vehicles under distinct driving cycles, 47 elements were detected (Table 2). Major and trace elements, in their oxidised form, accounted for PM mass fractions between 6.3 and 58%. In the present study, the mass fractions represented by the elements in the exhaust particles of Euro VI vehicles were not lower than those of the Euro V vehicle. The lowest values were obtained for vehicle I fuelled with GTL under the WHVC with cold start, while the highest amounts were observed for vehicle II fuelled with diesel over the WHVC with hot start.

In general, the elements Na and Sr composed the largest PM fraction (averaging 44.9 mg g^{-1} and 30.6 mg g^{-1}, respectively), followed by Al and Ca (averaging 10.6 mg g^{-1} and 9.42 mg g^{-1}, respectively). Cu and Cr also accounted for high mass fractions (average of 3518 μg g^{-1} and 3473 μg g^{-1}, respectively). These two later elements, as well as Ca, Ni and Pb, are associated with exhaust emissions as they are commonly used as additives in lubricants oils and linings (Kostenidou et al., 2021; Pulles et al., 2012). Sr is used as stabilising agent in the wash coat of catalytic converters (Van Noorden, 2010; Wei et al., 2018). Al is generally connected to cylinder block and liner alloy, so high fractions of this element can be attributed to the abrasion of these components (Agarwal et al., 2015; Hao et al., 2019). In previous studies, Na has been

Table 2
Elemental content (average ± standard deviation) in particulate matter emissions from different vehicles and driving cycles. Values are in μg g^{-1}.

	HDV I			HDV II		HDV III
	VTT cycle D1	WHVC cold D1	WHVC cold GTL	WHVC cold D2	WHVC hot D2	Braunschweig hot D2
Li	1291 ± 87.6	1067 ± 17.5	956 ± 158	1199	3496 ± 957	2261 ± 184
Be	23.7	6.68	3.50	–	83.2 ± 32.7	71.8 ± 17.1
Sc	148 ± 10.5	147 ± 14.3	141 ± 17.4	180	551 ± 172	370 ± 9.25
Ti	–	2588 ± 292	–	–	–	–
V	190 ± 29.4	343 ± 53	216	1113	1613 ± 427	404 ± 57.2
Cr	3127 ± 321	2417 ± 331	2306 ± 393	3224	5491 ± 1826	4271 ± 1472
Mn	266 ± 55.4	307 ± 23.3	271 ± 25.4	601	1561 ± 478	805 ± 76.3
Co	30.9 ± 2.11	34.3 ± 3.58	32.8 ± 1.77	83.1	160 ± 37.4	68.7 ± 8.30
Ni	181 ± 12.2	137 ± 19.4	146 ± 5.03	415	843 ± 202	415 ± 18.1
Cu	1741 ± 700	1442 ± 144	2139 ± 168	2790	6209 ± 1615	6788 ± 885
Ga	52.7 ± 21.5	103 ± 22.8	88.6 ± 19.7	102.9	378 ± 159	216 ± 7.84
Ge	17.1 ± 5.05	16.7 ± 1.45	13.3 ± 1.36	32.8	53.6 ± 12.6	41.1 ± 0.445
Se	14.8	3.86 ± 1.18	17.7 ± 10.1	–	148 ± 88.3	32.3
Rb	176 ± 18.2	233 ± 32.3	193 ± 44.9	153	816 ± 202	561 ± 46.7
Sr	21903 ± 4256	20394 ± 4924	14578 ± 9117	11664	89250 ± 43162	25953 ± 7233
Y	62.4 ± 29.3	81.1 ± 39.0	111	–	305 ± 281	69.7
Zr	–	1558 ± 11.0	856 ± 17.1	2943	7927 ± 2736	1290 ± 732
Nb	–	–	–	–	–	53.3
Cd	18.4 ± 1.19	14.5 ± 0.488	14.3 ± 1.91	37.0	64.7 ± 11.7	42.3 ± 5.76
Sn	60.3 ± 3.89	49.7 ± 14.1	39.6 ± 0.567	90.6	157 ± 31.9	181 ± 45.1
Sb	294 ± 105	257 ± 17.4	170 ± 8.82	245	217 ± 124	624 ± 32.6
Cs	6.17 ± 1.07	7.56 ± 1.11	6.05 ± 0.666	8.01	35.4 ± 15.4	17.1 ± 0.0101
La	92.2 ± 14.1	110 ± 74.2	129	–	575 ± 447	90.4
Ce	39.0	164	180	–	744 ± 675	–
Pr	14.5 ± 2.03	20.5 ± 18.2	27.5	–	127 ± 92.9	8.71
Nd	67.2 ± 8.81	89.2 ± 70.1	111	–	508 ± 391	78.0
Sm	8.36	16.5 ± 14.3	25.6	–	91.7 ± 72.8	1.31
Eu	25.0 ± 3.28	29.0	15.5	–	78.0	– –
Gd	13.4 ± 5.08	19.5 ± 13.9	25.0	–	108 ± 73.1	11.5
Tb	–	4.46	4.65	–	26.6	–
Dy	16.0 ± 9.36	25.5 ± 8.99	30.7	–	92.4 ± 67.5	22.6
Ho	5.70	6.51	6.32	–	27.5 ± 14.2	–
Er	13.8 ± 3.60	13.7 ± 3.95	16.6	–	44.7 ± 31.5	9.21 ± 6.95
Yb	16.5 ± 3.93	14.4 ± 4.71	9.93 ± 8.70	–	49.6 ± 31.4	13.1 ± 2.96
Hf	101 ± 12.9	109 ± 5.67	94.2 ± 2.85	271	503 ± 171	204 ± 22.7
W	–	–	–	–	–	149

(continued on next page)

Table 2 (*continued*)

	HDV I			HDV II		HDV III
	VTT cycle D1	WHVC cold D1	WHVC cold GTL	WHVC cold D2	WHVC hot D2	Braunschweig hot D2
Pb	254 ± 48.2	195 ± 22.5	148 ± 41.7	148	785 ± 442	426 ± 31.9
Th	29.8 ± 11.7	34.5 ± 21.3	49.9	–	137 ± 146	36.1
U	68.0 ± 5.68	55.2 ± 2.61	56.4 ± 1.35	93.0	175 ± 44.5	115 ± 1.89
Al	6226 ± 1242	8062 ± 4283	5120 ± 3383	–	25976 ± 13738	7846 ± 3884
Ca	2271 ± 1074	12931	5891	–	22691 ± 19955	3301
Fe	270 ± 88.7	208 ± 27.5	156 ± 1.58	285	751 ± 202	531 ± 50.9
K	818 ± 420	525 ± 720	365	–	–	977
Mg	–	1962	633	–	7900	–
Na	33192 ± 1938	22868 ± 803	22075 ± 1604	43286	90190 ± 19803	57956 ± 3068
P	32.4 ± 10.3	29.3 ± 11.3	6.61 ± 3.06	17.2	22.3	46.7 ± 2.65
S	36.8 ± 31.8	52.8 ± 1.83	37.2 ± 1.36	–	–	–

"-" not detected or below the detection limit.

also detected in high amounts. This inorganic element is associated with fuel additives (Huang et al., 2022). Sulphur was only detected in emissions from the Euro V vehicle. Most of the S in the fuel is emitted as SO2 (gas phase) in the combustion process, while only a very small part reacts then from SO2 to SO3 and further to SO4 and ends up in particle phase (measured as part of PM). How much SO2 turns to SO3 depends on the conditions (temperature, dilution, catalyst available, etc.). Furthermore, this element is a component of crude oil, but some pollution abatement strategies have forced the S content of fuels to be lowered to levels close to zero.

Heavy-duty vehicle I (Euro V, 2013) was tested under the VTT driving cycle with diesel 1 and the WHVC, under cold start, with diesel 1 and GTL. Both driving cycles that used diesel as fuel (72.3 mg g^{-1} for VTT and 71.2 mg g^{-1} for WHVC) recorded a mass fraction around 1.3 times higher than the GTL fuel (53.6 mg g^{-1}). HDV II (Euro VI, 2016) fuelled with diesel 2 was tested under WHVC with cold and hot start conditions. Under hot conditions, the total PM mass fraction represented by elements was 3.7 times higher (257 mg g^{-1}) than in cold conditions (69.0 mg g^{-1}). Under cold conditions, lanthanides were not detected. Furthermore, Al and Ca, which were elements detected at high particulate mass fractions in the other driving cycles, were not present over the cold start WHVC in this vehicle. HDV III (Euro VI, 2016) was tested with only one type of fuel (diesel) and a driving cycle with two repetitions. Mean particulate mass fractions of 114 ± 8.58 mg g^{-1} were obtained. Comparing the two hot driving cycles, emissions from the Braunschweig cycle presented a considerably lower particulate elemental content when compared to the WHVC with hot start condition (PM mass fraction = 258 ± 99.1 mg g^{-1}). However, these two hot driving cycles presented, on average, higher contents of many elements (Li, Be, Sc, Cr, Mn, Cu, Ga, Ge, Se, Rb, Sr, Cd, Sn, Cs, Pb, U, Na, Fe), especially a considerably higher Cu mass fraction (6.21 and 6.79 mg g^{-1}, respectively) comparing to the other cycles (WHVC cold start and VTT). In a previous study carried out in a chassis dynamometer with light-duty vehicles, the emission values for an urban driving cycle with a hot start were about two times higher than those obtained under cold start conditions, suggesting that higher temperature would likely enhance the volatilisation of metals, which upon cooling, condense or adsorb onto other particulate components (Alves et al., 2015).

3.2.2. Particulate organic compounds

Several classes of organic compounds were identified in the particulate matter of vehicle exhausts, including alkanes, alkanes, PAHs, alcohols, various types of acids, alkyl esters of fatty acids, phenolic compounds, plasticizers, glycols, among others.

Fossil fuels contain n-alkanes whose composition depends on the manufacturing distillation boiling points. High boiling points yield fuels with higher molecular weight constituents. GTL is produced from natural gas through the Fischer–Tropsch process. The process yields a synthetic crude oil that is made up of a wide variety of alkanes but that is essentially free of unsaturated or aromatic constituents. In the case of refined lubricating oils, only trace amounts of the n-alkanes are generally detected. Since the ability to pump lube oil through the engine depends on its waxy content, crude oil fractions must be dewaxed. This dewaxing process removes a substantial part of n-alkanes, but most of the n-alkyl moieties remain present. However, the elevated temperature during engine operation may lead to thermal cracking of these n-alkyl hydrocarbons and to the detection of high molecular weight n-alkanes in exhaust emissions, even if fuels or lube oils were originally deficient in those constituents. Thus, the aliphatic content in exhaust emissions is difficult to interpret because it depends not only on the composition of the fuel and lubricating oil, but also on the temperatures reached by the engine. In the present study, the particulate mass fractions of alkanes, alkanes and isoprenoid alkanes did not show statistically significant differences when the means of the various tests for each of the 3 vehicles were compared ($p > 0.5$). Greater varieties (from C_{11} to C_{31} with no preference for odd versus even carbon numbers) and amounts of n-alkanes were detected in the emitted particulate matter (up to 7938 μg per g of PM) for the GTL fuelled vehicle (Euro V) tested by the WHVC driving cycle with cold start (Table 3). In this case, the highest n-alkane mass fractions were observed for homologous compounds $\geq C_{19}$. Much lower n-alkane emissions, although quite variable (54.7–468 μg g^{-1}), were recorded for the same cold start WHVC driving cycle, but when the Euro V vehicle was fuelled with diesel. The diesel-powered Euro V HDV under the VTT driving cycle recorded the 2nd highest n-alkane mass fraction (1855 ± 1141 μg g^{-1}). Heavy vehicle number 2, classified as Euro VI, when driven according to the WHVC test cycle, generated particulate n-alkane mass fractions of 457 ± 338 μg g^{-1} for hot start conditions, while the corresponding value for cold start was 279 μg g^{-1}. Mass fractions ranging from 134 to 789 μg g^{-1}, averaging 462 μg g^{-1}, were obtained for the diesel-powered Euro V HDV under the Braunschweig cycle. It should be noted that when two consecutive tests are classified as "cold start", they do not represent real replicates because the 2nd one is a repetition on the same day; therefore, the engine does not actually start cold, although there was a cool-down period between tests.

Some alkenes were detected in particulate matter emissions with no clear pattern: tetradecene, hexadecene, octadecene, nonadecene, eicosene and tricosene. Two isoprenoid alkanes, pristane and phytane, were also present. The highest contents were recorded in emissions from the GTL powered Euro V vehicle and from the same vehicle when driven on the VTT cycle.

Although the mechanisms of PAH generation during combustion in vehicle engines are not fully understood, it has long been argued that radical formation dominates the pyrolysis process. Gaseous hydrocarbon radicals rearrange rapidly leading to PAH formation and growth. It has been discussed that the addition of hydrocarbon radicals to lower molecular weight PAH conducts via alkyl-PAH to the production of higher PAHs (Rogge et al., 1993). In addition to fuels, lubricating oils are also a significant source of PAH emissions (Brandenberger et al., 2005). It has been shown that diesel PAH-bound particulate emissions during both fuel firing and motoring in the absence of fuel increase with oil contamination which in turn reflects the build-up of PAH with oil age (Williams et al., 1989). Vieira de Souza and Corrêa (2016) determined PAH concentrations in diesel fuel sold in Brazil and in lubricant oil sampled in different usage times. The researchers concluded that 95–99% of the PAHs identified in diesel fuel were destroyed, converted

Table 3
Aliphatic content in particulate matter emissions from different vehicles and driving cycles.

	Test cycle	Fuel	Emission standard	Particulate mass fractions (μg g^{-1})		
				n-Alkanes	n-Alkenes	Isoprenoid alkanes
Heavy-duty vehicle I	VTT	Diesel 1	Euro V	1591	306	595
	VTT	Diesel 1	Euro V	2140	120	274
	VTT	Diesel 1	Euro V	426	55.3	56.8
	WHVC cold	Diesel 1	Euro V	54.7	5.73	4.29
	WHVC cold	Diesel 1	Euro V	468	6.42	78.0
	WHVC cold	GTL	Euro V	713	114	510
	WHVC cold	GTL	Euro V	7938	172	712
Heavy-duty vehicle II	WHVC cold	Diesel 2	Euro VI	279	24.5	37.2
	WHVC hot	Diesel 2	Euro VI	894	86.7	206
	WHVC hot	Diesel 2	Euro VI	205	133	31.8
	WHVC hot	Diesel 2	Euro VI	553	60.6	121
	WHVC hot	Diesel 2	Euro VI	177	37.4	nd
Heavy-duty vehicle III	Braunschweig hot	Diesel 2	Euro VI	134	24.3	nd
	Braunschweig hot	Diesel 2	Euro VI	789	166	223

nd - not detected.

into other compounds during the combustion, and/or retained in the lubricant oil reservoir. They also observed that the PAH profile of lubricant oil was similar to those of diesel and exhaust, indicating that both the PAHs retained in the lubricant oil and those released by the exhaust have mostly a petrogenic origin. Moreover, it was noted that PAHs with lower molecular weight (mainly naphthalene) are less processed and/or destroyed during combustion and/or have a higher contribution from other sources, such as engine lubricant oil or pyrosynthesis.

In the present study, when the diesel-powered Euro V vehicle followed the VTT cycle, the start-up phase mass fractions of Σ_{18}PAHs were much higher (552 μg g^{-1}) than in the following tests (28.8–48.1 μg g^{-1}). The start-up phase also led to the emission of several PAHs that were not detected in the particulate matter from the replicates of the same VTT cycle, such as benzo [a]anthracene, chrysene, benzo [b]fluoranthene, benzo [k]fluoranthene, benzo [e]pyrene, benzo [a]pyrene, perylene, indeno [1,2,3-cd]pyrene, dibenzo [a,h]anthracene and benzo [g,h,i] perylene. PAHs with 6 rings were also detected in emissions from the same Euro V vehicle during cold start of the WHVC cycle but were not observed for either the GTL or the Euro VI diesel vehicles. As reported for the VTT cycle, the cold start phase of the Euro V vehicle in the WHVC test produced much higher overall PAH emissions (Σ_{18}PAHs = 109 μg g^{-1}) compared to the already slightly warmed-up engine (Σ_{18}PAHs = 31.2 μg g^{-1}). It has been demonstrated that the emission of PAH compounds from the incomplete combustion of diesel fuel greatly depends on the source of the fuel and the driving patterns. During cold start, higher PAH concentrations of high molecular weights have been observed during idling cycle, while acceleration cycles lead to higher concentrations than the steady-state conditions (Borrás et al., 2009). Particulate PAH mass fractions in the same range (Σ_{18}PAHs = 32–125 μg g^{-1}) were recorded for Euro VI vehicles tested under the WHVC and Braunschweig hot start driving cycles. Regardless of the vehicle and driving cycle, fluorene (13.0–99.7 μg g^{-1}) and fluoranthene (1.37–29.0 μg g^{-1}) were always present. Retene (1-methyl-7-isopropyl phenanthrene), with mass fractions up to 9.35 μg g^{-1}, was also a ubiquitous compound. It has been used as a molecular tracer of softwood combustion (Ramdahl, 1983), but its detection in particles collected in a road tunnel (Alves et al., 2016) and resulting from the interaction between pavements and tyres (Alves et al., 2020) raised questions about its suitability as a marker of biomass burning. Despite the variability in individual speciation, mean values of ΣPAH particulate mass fractions for the various driving cycles of each vehicle did not show statistically significant differences between the 3 HDVs ($p > 0.5$).

Some alkylated PAHs (C2-naphthalene and C1-phenanthrenes) were detected in particulate matter emissions from all tests, except the Braunschweig driving cycle. The highest global emissions of these compounds were recorded for the start-up phase of the VTT cycle when the diesel-powered Euro V was driven (57.4 μg g^{-1}), followed by the same vehicle, but powered by GTL, under the WHVC cold start test (21.1 μg g^{-1}). Alkyl-PAHs had already been detected in diesel and biodiesel exhaust emissions by Casal et al. (2014).

A homologous series of n-alkanoic acids, ranging from C_8 to C_{22}, were found in the exhaust particulates. Globally, n-alkanoic acids accounted for particulate mass fractions ranging from 0.50 to 19.4 mg g^{-1} (Fig. 2). The most abundant acids were tetradecanoic, hexadecanoic and octadecanoic (Fig. 3). Diacids from C_2 (oxalic) to C_{10} (sebacic) were also detected. n-Alkanols from C_8 to C_{30}, with a clear dominance of octadecanol (C_{18}) were observed in all particulate matter samples. Emissions of organic acids and other oxygenated compounds highly depend on fuel types, air/fuel ratios, driving conditions and engine start modes (Cheung et al., 2010; Li et al., 2015, 2021). Large amounts of carboxylic acids and alcohols are supposed to come from lubricating oils. Li et al. (2015) and Liang et al. (2005) presented a comparative analysis of lubricating oil and diesel, revealing the absence of carboxylic acids and alcohols from the fuel, but appreciable amounts in the oil. Under heavier engine loads and higher temperatures, larger amounts of lubricants are used, enhancing their evaporation, and leading to the presence of their constituents in the exhaust particulates. However, oxidative pyrolysis and the partial oxidation of aliphatic hydrocarbons from the fuel could substantially increase the amount of oxygenated organic compounds (Li et al., 2015).

Benzenedicarboxylic acids (phthalic, terephthalic and isophthalic), which are the basis in the production of polyesters, were observed at higher concentrations in emissions from Euro VI vehicles compared to Euro V. Of the 3 acids, the only one that was always encountered, irrespective of the driving cycle or the vehicle, was terephthalic.

Isocyanic acid (HNCO) was detected in one particulate matter sample from the Euro V diesel vehicle over the WHVC cycle (73.1 μg g^{-1}), and at much higher mass fractions in emissions from Euro VI diesel vehicles either over the same WHVC cycle (16.1–24.1 mg g^{-1}) or over the Braunschweig driving test (26.1–34.7 mg g^{-1}). This acid has been demonstrated to be highly toxic and a potential health concern due to its dissociation at physiological pH (Roberts et al., 2011). It has been suggested that HNCO may be generated as a by-product of vehicle exhaust after-treatment technologies (Li et al., 2021, and references therein). To decrease emissions, the automotive industry has introduced a series of different after-treatment systems over the last years. HNCO is an intermediate product of the conversion of urea into NH_3. In selective catalytic reduction, and aqueous solution of urea is used as a source of NH_3, to reduce NO_x. If the urea injection is high and the temperature too low for proper decomposition, there may be NH_3 slip and even HNCO slip. Recent studies have already reported the presence of HNCO in exhaust emissions of various types of vehicles (Brady et al., 2014; Li et al., 2021; Suarez-Bertoa and Astorga, 2016; Wren et al., 2018).

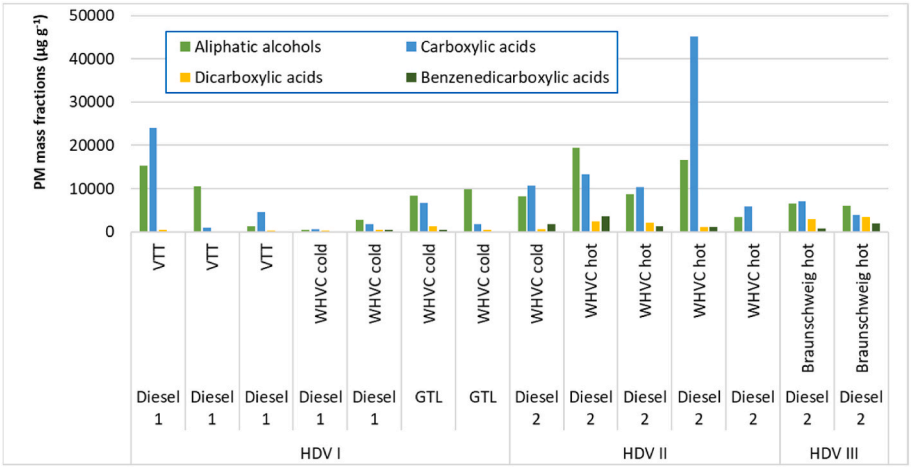

Fig. 2. Mean PM mass fractions of some classes of organic compounds.

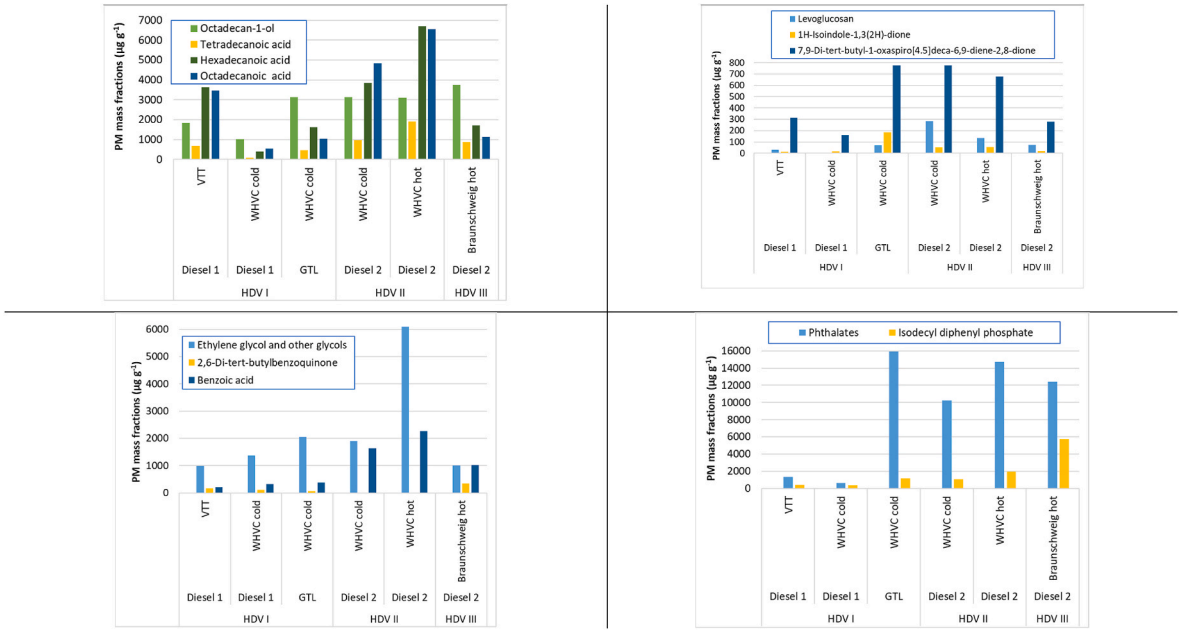

Fig. 3. Particulate mass fractions of various organic compounds.

Ethylene glycol and other glycols were found in the samples but did not follow any vehicle- or driving-cycle dependent pattern. So far, many oxygen-containing hydrocarbons, especially glycol-based additives, have been added to diesel fuel to reduce emissions from combustion engines (Gómez-Cuenca et al., 2011; Guo et al., 2016; Safieddin Ardebili et al., 2021). Ethylene glycol is also used as engine coolant for most on-road vehicles and its concentrations has been measured in the Caldecott Tunnel near San Francisco by Wood et al. (2015).

Several oxygenated organic compounds were detected, as far as we know, for the first time in exhaust particulates. Given the absence of studies, it is difficult to establish comparisons and even explain their formation or origin. This is the case, for example, of levoglucosan, a thermal degradation product from cellulose, recurrently used as a tracer of biomass burning in source apportionment studies (Vicente and Alves, 2018). Recently, this anhydrosugar has been described as a component of non-exhaust particles generated from wear between pavements and tyres, although at mass fractions much lower than those found in biomass burning emissions (Alves et al., 2020). It was hypothesised that temperatures reached either in the vulcanisation process or in the friction between tyres and pavements during vehicle running can convert part of the cellulose fibres into sugars. The detection of levoglucosan in the exhaust particles of the present study may be associated with the thermal degradation of cellulosic components of the vehicles, but this is an assumption that needs further investigation. Levoglucosan was detected in all driving, although in higher amounts in vehicle II emissions (Fig. 3). The mean mass fraction of levoglucosan in particulate matter from the various driving cycles of the Euro V vehicle showed to be significantly different of those from Euro VI vehicles ($p < 0.03$).

1H-Isoindole-1,3(2H)-dione, also known as phthalimide, was present in most samples, for any vehicle or driving conditions. No statistically significant differences were found between the mean phthalimide mass fractions for the 3 vehicles ($p > 0.06$). This derivative of phthalic anhydride is probably formed at the high temperature reached in engines through the reaction of its plasticizer precursor with ammonium compounds or urea during the selective catalytic reduction process. Once again, this hypothesis needs experimental confirmation. Another plasticizer related compound, also used as a lubricant additive, found in exhaust particulates was isodecyl diphenyl phosphate. Its mass fractions were higher during the during the Braunschweig cycle. The mean value for this cycle was statistically different from the mean values obtained

for the tests of the other two vehicles ($p \leq 0.0001$). 7,9-di-tert-butyl-1-oxaspiro [4.5]deca-6,9-diene-2,8-dione was another ever-present compound. It is likely a product of Irganox®, which represents a broad range of antioxidants used to prevent degradation of polymers, such as plastics and synthetic fibres, from heat exposure. 2,6-di-tert-butyl benzoquinone, previously observed in ambient air (Delgado-Saborit et al., 2013), was also present in several exhaust samples. It is likely a product of the oxidation of 2,6-di-t-butyl phenol, a common antioxidant additive, or of butylated hydroxytoluene (BHT), usually used in fuels, lubricants, oils, waxes, synthetics, rubber, plastics and elastomers to prevent those materials from oxidation. Many other plasticizers were detected, including multiple phthalates and bis(2-ethylhexyl) adipate. The highest global mass fraction was achieved for the Euro VI diesel vehicle over the WHVC hot start cycle (4.1–29.2 mg g^{-1}), while the lowest were recorded for the Euro V diesel vehicle over the WHVC cold start cycle (0.134–1.16 mg g^{-1}).

4. Conclusions

In this study, three HDVs were tested under different cycles with different fuels to estimate the PM emission factors and chemical composition. PM emission factors for Euro V and VI ranged from 24.9 to 51.2 mg kWh^{-1} and from 8.4 to 14.7 mg kWh^{-1}, respectively. Major and trace elements, in their oxidised form, accounted for PM mass fractions between 6.3 and 58%. The lowest values were obtained for the Euro V vehicle fuelled with GTL under the WHVC with cold start, while the highest amounts were observed for the Euro VI vehicle fuelled with diesel over the hot start WHVC cycle. In general, Na and Sr were the most abundant elements, followed by Al and Ca. Several classes of organic compounds were identified in the PM of vehicle exhausts, including alkanes, alkanes, PAHs, alcohols, various types of acids, alkyl esters of fatty acids, phenolic compounds, plasticizers, glycols, among others. Compounds from oil lubricants (e.g., isodecyl diphenyl phosphate), components of the cooling system fluids (e.g. ethylene glycols), by-products of after-treatment technologies (isocyanic acid and 1H-isoindole-1,3(2H)-dione), thermal degradation products of cellulosic components (levoglucosan), and antioxidants leached from polymeric materials (e.g. oxidised Irgafos® 168) were observed in the exhaust particles.

The vehicle emission profiles generated by PM characterisation can contribute to improve emission inventories, to more accurately apply source apportionment models and to implement adequate mitigation measures. Furthermore, the results can provide useful information for toxicologists to better define the type of bioassay to apply and the doses to test. Nevertheless, emission testing with additional vehicles is necessary since PM emissions depend on engine age and type, after-treatment technologies, fuel and lubricating oil properties, and driving conditions.

CRediT authorship contribution statement

I. Cunha-Lopes: Conceptualization, Formal analysis, Methodology, Validation, Writing – original draft, Writing – review & editing. **K. Lehtoranta:** Investigation, Resources, Writing – review & editing. **S.M. Almeida:** Resources, Writing – review & editing. **M. Evtyugina:** Methodology, Writing – review & editing. **A. Vicente:** Methodology, Writing – review & editing. **E. Vicente:** Data curation, Writing – review & editing. **H. Kuutti:** Investigation, Resources. **F. Amato:** Methodology. **C.A. Alves:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Data curation, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2023.119823.

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