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Environmental significance

Urban air pollution is strongly influenced by on-road vehicles, which continue to emit substantial amounts of pollutants, particularly during their cold starts, despite advances in emission control technologies. However, cold start emissions remain poorly understood under real-world conditions. To address this, emissions of approximately 20,000 cars were quantified and chemically characterized through measurements conducted inside an underground parking garage. The findings of this work (cold start emission factors, composition, volatility distribution, etc.) can be used to improve emission inventories and support more accurate simulation of vehicle emissions in chemical transport models.

Measurements of Real-World Cold Start Emissions in a Parking Garage

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Abstract

Motor vehicles are an important source of urban air pollution, with their cold starts substantially contributing to their total emissions. To quantify these cold start emissions under real-world conditions, measurements were conducted inside an underground parking garage in Greece, capturing approximately 21,000 cold starts with an average soak time of 1.5 h. Emitted particulate matter (PM₁) was primarily carbonaceous, consisting of 61% organic aerosol (OA), mainly composed of hydrocarbons (O:C=0.03), and 39% of black carbon (BC). Volatile organic compound (VOC) cold start emissions were dominated by light (C₆–C₉) aromatics (65%), followed by small oxygenated C₁–C₄ species (12%), hydrocarbon fragments (C₂–C₇, 7%), and aliphatic C₇–C₂₈ hydrocarbons (3%). Intermediate- and semi-volatile organic compounds (IVOCs and SVOCs) comprised 3% and 0.8% of the total gas-phase organic cold start emissions, respectively. The findings of this work highlight the importance of cold starts under short soak conditions and can be used to improve emission inventories and evaluate vehicle emission models under real-world conditions.

1. Introduction

Despite advancements in vehicle emission control systems, on-road vehicles remain a significant source of urban air pollution, releasing pollutants in both the particulate and

gas phases.^{1,2} These emissions have adverse impacts on human health³ and also contribute to climate change, through the release of carbon dioxide (CO₂) and black carbon (BC)⁴.

Vehicle exhaust emissions can be separated into cold start and hot-running emissions. Emissions under hot-running conditions have decreased over time with advances in engines and aftertreatment technologies. As a result, the relative importance of cold start emissions, has increased.^{5–8} Cold start emissions occur during a vehicle's warm-up phase, defined as the first few minutes of operation following a period of engine inactivity (soak time). Such emissions may occur after any engine start as long as engine and catalyst temperatures are below optimal, with their magnitude and duration largely determined by soak time.^{9–11} Cold start emissions of several pollutants, generally increase with longer soak times, reaching a maximum after approximately six hours of inactivity^{8,9}, while NO_x emissions peak after 1–2 h^{8,12,13}.

In Europe, passenger cars account for more than 80% of total passenger-kilometers driven.¹⁴ According to RIVM¹⁵, about 95% of cold starts occur in urban areas. In Greece, the average passenger car fleet composition in 2023 is dominated by Euro 3 vehicles (33%), followed by Euro 2 and Euro 6 (17% each), Euro 4 and Euro 5 (9% each), and pre-Euro and Euro 1 vehicles (8% each) (data provided by the Netherlands Organisation for Applied Scientific Research (TNO)). Most of the fleet (91%) is gasoline-powered, with diesel vehicles accounting for 9%, while vehicles running on liquefied petroleum (LPG) or compressed natural gas (CNG) account for only 0.2%.

To quantify cold start emissions, studies have conducted measurements of individual vehicles either on a chassis dynamometer^{12,16–18} or more recently under real-world driving conditions^{5,7,8,19–22}. Emissions have been generally found to be substantially elevated during the first 60–200 s of operation^{12,19,23}. Several studies^{6,24–27} have reported substantial discrepancies between laboratory and on-road measurements, showing that conventional chassis dynamometer procedures often fail to capture the variability and dynamics of real-world driving. Concerns about the representativeness of laboratory tests intensified after investigations revealed that some manufacturers employed strategies that reduced emissions only under controlled conditions.²⁸ These findings accelerated the development of real-world testing protocols with the use of portable emissions measurement systems (PEMS), which enable the quantification of regulated pollutants under diverse driving conditions. However, PEMS lack chemical resolution and cannot characterize non-regulated pollutants. At the same time, equipping passenger cars with high-resolution instrumentation capable of resolving detailed chemical composition of

the emitted VOCs and particles is challenging. As a result, important aspects of real-world emissions, including the chemical characteristics of cold start emissions, remain insufficiently constrained, limiting the ability of emission models and inventories to fully assess the impact of vehicle emissions on urban air quality and human health.

To address these challenges, the present study focuses on quantifying and characterizing cold start emissions of several pollutants from passenger cars under realistic conditions that are not fully represented by chassis dynamometer testing. To capture the emissions of a European fleet of light-duty vehicles, measurements were conducted inside an underground parking garage. This confined environment provided stable ambient conditions and encompassed a broad range of cold start events that naturally occur in urban areas, accounting for different soak times and idling durations prior to driving. The stationary setup also enabled detailed chemical characterization using state-of-the-art high-resolution instrumentation, addressing a main limitation of PEMS. This work aims to estimate real-world cold start emissions that can be used to improve emission inventories.

2. Methodology

2.1. Sampling site

Vehicle emissions were measured inside an underground parking garage located beneath a commercial shopping center in Patras, Greece (38°14'15.3"N, 21°43'34.3"E). The garage consists of two levels, with the sampling site located at the second level below ground (Fig. S1). This level includes 246 parking spaces. The maximum clearance of 2.7 m limits access to the facility only to light-duty vehicles. The shopping center also houses a cinema and several food and beverage establishments, contributing to sustained vehicle activity during the late afternoon and evening hours. The garage was closed to the public during the early morning hours, typically between 2:00 and 6:00 local time (LT). Measurements were conducted over a three-week period, from November 29 to December 20, 2024.

2.2. Instrumentation and methods

Particle number size distributions in the 10–490 nm range were measured using a scanning mobility particle sizer (SMPS, model 3034, TSI). Black carbon (BC)

concentrations were determined by an aethalometer (AE33, Magee Scientific). The chemical composition of non-refractory submicron aerosol was measured using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Inc.).

The organic gas and particle phases were characterized by a high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik Inc) coupled to a chemical analysis of aerosol on-line (CHARON) inlet. Details about the instrument's operation are provided in Table S1. The CHARON/PTR-MS sampled for 8 min the gas-phase and for 13 min the particulate phase. During the first 4 min of each aerosol cycle, the inlet passed through the PTR-MS HEPA filter to quantify the corresponding background. Gas-phase background measurements were performed once per day for approximately 30 min placing an activated carbon filter before the inlet.

Both mass spectrometers switched their sampling every 21 minutes between the garage and the outflow of an oxidation flow reactor (OFR), used for quantifying secondary organic aerosol (SOA) formation. The OFR results are presented in a separate publication.²⁹

The concentrations of inorganic trace gases such as nitrogen monoxide (NO) and dioxide (NO₂) (model APNA-370, Horiba), carbon monoxide (CO) (model 300E, Teledyne) and dioxide (CO₂) (model T360, Teledyne), ozone (O₃) (model 400E, Teledyne) and sulfur dioxide SO₂ (Thermo, model 43iTLE) were continuously monitored.

To investigate the spatial distribution of the pollutants inside the garage, six calibrated CO₂ Aranet sensors were deployed at eight different locations as shown in Fig. S1. Two of the sensors were relocated midway. During the last week of the measuring period, one low-cost ENSENSIA sensor system³⁰, capable of measuring NO, NO₂, CO, CO₂, O₃, total VOCs and PM_{2.5} was installed outside of the parking garage to monitor ambient background conditions. Details on the calibration and evaluation of the ENSENSIA measurements are provided in Supplementary Section S1. Briefly, the ENSENSIA measurements, averaged over 5 min, showed good agreement with reference instruments, with R² above 0.8 and normalized mean absolute error (nMAE) below 14% (Table S2).

Pre-conditioned sorbent tubes (C1-AAXX-5003, Tenax TA, Markes International Ltd), preceded by a Teflon filter, were employed to collect organic vapors. Each sampling period lasted for approximately one day, starting around 10:00 AM, with a flow rate of 0.016 L min⁻¹, collecting approximately 23 L of air. The tubes were analyzed offline using

a thermal desorption system (TD, UNITY–252 Air Server-xr, Markes International Ltd.) coupled with a gas chromatograph-mass spectrometer (GC-MS, Shimadzu QP2010), following the method parameters provided in Table S3. After each analysis, a cleaning cycle was applied to remove interferences from previous samples. An overview of the analytical framework used for the characterization of gas- and particle-phase organic compounds and the specific role of each instrument is provided in Table S4.

Vehicle activity was continuously monitored using motion-activated cameras installed at both the entrance and exit of the garage, enabling the quantification of traffic flow on a minute-by-minute basis through manual analysis of the recorded footage.

3. Data analysis

3.1. HR-ToF-AMS

The HR-ToF-AMS data were analyzed using SQUIRREL (SeQUential Igor data RetRiEvaL, v1.66G) and PIKA (Peak Integration by Key Analysis, v1.26G) within Igor Pro (WaveMetrics, Lake Oswego, OR). The algorithm of Kostenidou et al.³¹ was used to correct the AMS measurements for the collection efficiency (CE) of the instrument and to estimate the organic aerosol (OA) density. This method was used to combine the particle size distributions of AMS and SMPS over 1 h intervals, accounting for BC, which is assumed to follow the same size distribution as the OA. The resulting average values of CE and OA density were 0.71 ± 0.23 and $1.30 \pm 0.42 \text{ g cm}^{-3}$, respectively. Elemental ratios of OA were determined following the method proposed by Canagaratna et al.³².

3.2. CHARON/PTR-MS

The data of CHARON/PTR-MS were analyzed using the Ionicon data analyzer (IDA, Ionicon Analytik GmbH). Approximately 1300 peaks were detected by IDA within the m/z 15–450 range. Peaks associated with the instrument operation and with a signal-to-noise ratio (S/N) below 0.5 for the gas-phase, following the EPA PMF guidelines³⁴, and 0.1 for the particle-phase were excluded. The lower threshold was adopted as a screening criterion for the particle-phase because higher S/N thresholds resulted in the exclusion of most particle-phase ions. The estimation of S/N is described in Section S2. Ion assignments were performed by comparing the measured and theoretical m/z values, selecting in each case the molecular formula with the smallest mass deviation (in ppm)

among those within ± 60 ppm and containing only C, H, O and N atoms. Molecular formulas were constrained to contain integer values of double bond equivalents (DBE), and among possible candidates, those with chemically reasonable DBE values ($\text{DBE} \geq 0$) were retained. From the above analysis, measurements of 195 gas-phase and 116 particle-phase species were retained, and molecular formulas were assigned to 176 and 100 of them, respectively. The retained peaks accounted for 54% of the cumulative mixing ratio in both phases. A proton transfer rate constant of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was applied for all gas-phase ions while particle signals were corrected using an enhancement factor of 8. To account for the time required by the instrument to re-equilibrate after each phase transition, the initial 2 min of gas and the first 3 min of each aerosol sampling period, were excluded from the analysis. Background signals, determined from the corresponding blank measurements, were subtracted from the recorded data prior to further processing. For the gas phase, the daily mean background signal (Fig. S2) of each ion was subtracted from all corresponding data for that day. VOC data collected between December 14, 10:00 and December 15, 12:00 were discarded due to interference from emissions associated with the painting of a few parking spots in the morning of December 14.

3.3. Source apportionment

Positive matrix factorization (PMF)³³ analysis was applied to the high-resolution OA spectra (mass-to-charge, m/z : 12–200) measured by HR-ToF-AMS and to the PTR-MS gas-phase measurements to resolve emissions from vehicles and contributions from the external environment. AMS data were analyzed using the Source Finder (SoFi, v6.F2) interface, while PTR-MS data were processed with EPA-PMF 5.0, using 20 min averaged VOC mixing ratios. Measurement uncertainties for the PTR-MS data were estimated following the approach of Chow et al.³⁵, as described in Section S2. Methanol and ethanol were excluded from the PTR-MS PMF analysis, as their high abundance and diverse origins prevent their meaningful apportionment within a simple PMF solution that was pursued in this study. Among the remaining 193 gas-phase species used in the PMF input, 36 had S/N ratios between 0.5 and 2 (“weak” variables), and their uncertainties were increased threefold, following the EPA-PMF guidelines³⁴.

For both AMS and PTR-MS, the PMF solutions, and consequently the resulting factors, were initially evaluated using the goodness-of-fit parameter (Q/Q_{exp}) and the corresponding residuals. Solutions were then further assessed for physical consistency,

based on the presence of known tracer compounds and the temporal agreement with co-located measurements. In addition, AMS factor spectra were compared with literature profiles using the theta angle (θ), a quantitative metric of similarity treating spectra as vectors, with smaller θ values indicating higher agreement.³⁶

Source apportionment of black carbon was performed following the model of Sandradewi et al.³⁷, which assumes that the optical absorption coefficient is the sum of contributions from biomass burning and fossil fuels.

Finally, to estimate the contributions of sources to each compound measured by TD-GC-MS, the average fractions of the PTR-MS VOC factors were applied in a multilinear regression over the Tenax sampling periods.

3.4. Emission factor estimation

A box model was applied to quantify pollutant vehicle emissions (E_p) inside the parking garage. The model focused on tailpipe emissions, as contributions from engine oil leakage, tires, brakes, and resuspension from the parking surface were considered negligible. Assuming that the parking was well mixed, the indoor pollutant concentration ($C(t)$) can be described by the following mass balance equation:

$$V \frac{dC(t)}{dt} = E_p(t) - k(t)V(C(t) - C_{out}(t)) \quad (1)$$

where V (19,000 m³) is the garage volume, $k(t)$ is the ventilation rate constant, and $C_{out}(t)$ is the outdoor concentration of the pollutant. Concentration measurements represent 20 min averages and were smoothed to reduce noise. The time derivative of the concentration was then estimated numerically. Since the ventilation rate was unknown, $k(t)$ was determined from the CO₂ concentration using Eq. (1) and assuming known emissions, as described below. The resulting temporal profile of $k(t)$ is presented in Fig. S3. Outdoor concentrations of CO, CO₂, NO and NO₂ were based on the ENSENSIA measurements. For periods without concurrent outdoor ENSENSIA measurements, the corresponding outdoor concentrations were derived from the average diurnal profiles calculated from the available data. For OA, BC and VOCs, the source-apportioned concentrations were used, assuming negligible outdoor vehicle influence as their levels in the parking were much higher than their levels outdoors. The outdoor concentrations of SO₂ and particle number (N_{10}) were estimated from their average background levels, calculated during the early morning hours (4:30–5:30 LT) when no traffic was present inside the parking and

concentrations were assumed to approach ambient values. These background concentrations were then linearly interpolated between days to provide continuous outdoor values.

The total vehicle emissions of a pollutant ($E_p(t)$) were expressed as the sum of contributions from cold start and hot-engine emissions:

$$E_p(t) = N_c(t)e_{p,c} + N_h(t)e_{p,h} \quad (2)$$

where $N_c(t)$ is the cold start rate, $e_{p,c}$ is the pollutant mass emitted per cold start, $N_h(t)$ is the arrival rate of hot-running engine vehicles, and $e_{p,h}$ is the pollutant mass emitted per hot engine. $N_c(t)$ was assumed to be equal to the vehicle exit rate, while $N_h(t)$ was derived from camera counts at the entrance to the second level of the parking garage. Both $N_c(t)$ and $N_h(t)$ correspond to 20 min averages. The emission factors $e_{p,c}$ and $e_{p,h}$ were assumed constant and were determined by solving Eq. (2) using a linear least squares approach. For VOC measurements obtained by TD-GC-MS, the hot-running contribution to tailpipe emissions was assumed negligible in order to solve Eq. (1) and (2) using daily averages. The reported $e_{p,c}$ was corrected by a factor of 2.9 to account for the partial capture of the cold start period within the parking garage. This factor was derived from the ratio of the time vehicles spent inside the garage after starting, estimated based on multiple driving tests to be 45 s, to the average duration of a typical cold start, 130 ± 70 s^{12,19,23}.

The CO₂ emissions used in Eq. (1) to derive the ventilation rate constant were calculated from Eq. (2), assuming CO₂ emission factors from the TNO emission inventory (Section 3.5). A CO₂ emission factor for hot-running engines ($e_{\text{CO}_2,h}$) of 15.9 g per vehicle was adopted for urban environments. This factor corresponds to a travel distance of 70 m, representing the mean travel distance in the parking garage (Fig. S1). For cold starts, the inventory does not provide a CO₂ emission factor ($e_{\text{CO}_2,c}$). Therefore, $e_{\text{CO}_2,c}$ was estimated by scaling the hot-running CO₂ emission factor using the cold-to-hot ratio of CO emission factors of 2.6 and adjusted to account for the fraction of the cold start phase occurring inside the garage, yielding 206 g CO₂ per cold start. The sensitivity of our results to these choices of CO₂ emissions is investigated in a subsequent section.

3.5. TNO emission inventory

The TNO emission inventory covers cold-start and hot-operation emissions for both regulated pollutants and total particle number (TPN) using a framework that combines

pollutant-specific emission factors with detailed activity data. The TPN corresponds actually to particles larger than 10 nm (N_{10}).

For regulated pollutants, emission factors were primarily derived from the Dutch emission registration (ER) system¹⁵, which provides detailed real-world values by vehicle category and road type and explicitly accounts for cold-start effects. These factors implicitly reflect vehicle ageing and fleet characteristics and are therefore well suited for realistic emission modelling under European conditions. To enhance consistency and robustness, ER values were evaluated against the EMEP/EEA Guidebook², and Guidebook values were adopted where substantial discrepancies were identified.

Particle number emission factors, in the 10–325 nm size range, were developed using a hybrid approach combining existing datasets, an extensive literature review, and measurement data, reflecting the lack of harmonized methodologies for particle number emissions in conventional inventories. Both laboratory and real-world measurements were used to characterise cold start and hot-operation emissions, with cold starts identified based on engine coolant temperature at the beginning of a trip (below 70 °C).

Cold start emission factors were expressed per cold start event, defined as an engine start following at least two hours of inactivity. The frequency of cold starts was estimated following the Dutch national inventory methodology¹⁵, which relates cold-start occurrence to annual mileage and assumes that approximately 60% of all starts are cold starts, predominantly occurring under urban driving conditions. These emission factors were combined with activity data from COPERT to construct the emission inventory, following the general framework of the CAMS-REG inventory³⁸.

3.6. Organic gas-phase emission volatility distribution

The volatility distribution of gas-phase organic cold start emissions was estimated within the 1-D volatility basis set (VBS) framework by combining PTR-MS and TD-GC-MS measurements.³⁹ The effective saturation mass concentration (C^*) of individual compounds measured by the PTR-MS was estimated according to Li et al.⁴⁰. For gas-phase compounds identified by TD-GC-MS analysis, the volatility was calculated based on the chromatographic profile of Tenax tubes, following the approach of Zhao et al.⁴¹ and Sinha et al.⁴² as described in Supplementary Section S3. Briefly, the chromatograph was segregated into volatility bins using the retention times of n-alkanes and the concentration of these bins was estimated using the response factor of the corresponding

n-alkane in each bin. The resulting profile included VOCs (C^* between 10^7 – 10^{11} $\mu\text{g m}^{-3}$), intermediate volatility organic compounds (IVOCs, C^* between 10^3 – 10^6 $\mu\text{g m}^{-3}$), and semi-volatile organic compounds (SVOCs, C^* between 10^0 – 10^2 $\mu\text{g m}^{-3}$).

4. Results and discussion

4.1. Garage conditions and spatial distribution

The temperature inside the parking garage was mild and relatively stable, averaging 21.1 ± 0.9 °C (Fig. S4b). Relative humidity exhibited larger variability, with an average of 55.4 ± 8.5 % and values exceeding 70% in some days (Fig. S4a).

CO₂ levels varied by less than 10% across the garage (Fig. S5). This indicates that the garage can be treated as well mixed to a first approximation. This does not, however, necessarily imply equivalent mixing of all pollutants emitted directly by vehicles, especially those that are more reactive.

4.2. Vehicle activity

During the measurement period, a total of 20,616 cars entered and exited the parking garage. Traffic was dominated by passenger cars, with only a small number of vans, and practically no motorcycles. Cold start events are attributed to the vehicles exiting the facility. Fig. 1 presents the average diurnal profile of cold start and vehicle arrival rate for the garage, while the full time series for the entire campaign is shown in Fig. S6. The arrival rate corresponds to vehicles entering with hot-running engines.

Cold starts had a midday peak, between 12:00 until 14:00 LT and a second peak in the evening around 19:30 LT. Vehicle arrivals peaked earlier, at about 11:00 LT and 18:30 LT. During the early morning hours (from 6:00 to 9:00 LT), vehicle activity consisted mainly of entries, driven by the arrival of shopping center personnel and the first customers of the day, with few departures. Cold starts represented nearly the entirety of traffic during nighttime periods. Even during peak arrival times, cold starts still accounted for approximately half of the total traffic.

Throughout the campaign, the daily number of cold starts remained above 600, exceeded 800 on 73% of the days, and averaged 976 ± 255 per day. The final day of the campaign, December 20, was excluded from this analysis as sampling ended in the

morning and the data coverage was limited. The highest traffic volume was observed on December 1, with 1,621 cold starts recorded.

The average soak time in the garage during the measurement period was 84 ± 10 min, with the estimated daily averages shown in Fig. S7. For each day, the soak time was estimated as the time integral of the number of cars inside the garage divided by the total number of vehicle departures that day, as described in Section S4.

4.3. Sources of PM_{10}

4.3.1 Organic aerosol

The parking air quality was also affected by outside air pollution sources due to its ventilation system. To distinguish the different sources of submicron aerosol inside the parking garage and to assess the contribution of vehicles, the high-resolution OA mass spectra were analyzed using PMF. Three factors were identified, namely: hydrocarbon-like organic aerosol (HOA) that accounted on average for 36% of the total PM_{10} OA, biomass burning organic aerosol (BBOA) contributing 32% and oxidized organic aerosol (OOA) accounting for the remaining 31%. HOA is typically linked to traffic emissions, BBOA corresponds to fresh residential wood burning and OOA represents more aged organics.

The spectra of these factors are shown in Fig. S8. HOA is dominated by hydrocarbon ion fragments, with strong signals at m/z 41, 43, 55, 57, 67, 69, 71, 81, 83, 85, 95 and 97. BBOA is identified by its distinctive peaks at m/z 60 and 73, fragments commonly associated with levoglucosan, a well-established tracer of fresh biomass burning⁴³. The BBOA spectrum also exhibits pronounced signals at m/z 27, 28, 29, 39, 41, 44, 55 and 57. OOA shows a clear enhancement of oxygenated fragments with dominant peaks at m/z 28 and 44 (CO_2^+) and lower ones at m/z 27, 29, 39, 41, 43 and 55.

The O:C of HOA was 0.03, reflecting the dominance of fresh vehicle emissions. This value is comparable to previous studies in Patras (0.1 reported by Kostenidou et al.⁴⁴ and by Florou et al.⁴⁵; 0.08 by Kaltsonoudis et al.⁴⁶). BBOA had an O:C of 0.31, close to the values of 0.3 found by Florou et al.⁴⁵ and 0.43 by Kaltsonoudis et al.⁴⁶. The O:C of OOA was 0.46, which is lower than the values reported in the three past campaigns in Patras^{44–46}.

The resulting factors were compared with reference spectra (excluding m/z 39) from a previous winter campaign in Patras⁴⁶. The theta angles were 8° for HOA, 13° for BBOA

(corresponding to the fresh BBOA factor in that study), and 15° for OOA. These values indicate good agreement for HOA and BBOA, while OOA shows slightly larger deviations, consistent with its more variable composition depending on its aging state.

The time series of the OA sources is given in Fig. 2. During the operating hours (6:00–2:00 LT) of the garage, the average concentration of HOA was $8 \mu\text{g m}^{-3}$, with hourly values reaching up to $50 \mu\text{g m}^{-3}$ (December 11). The HOA diurnal profile presented two distinct peaks, one around midday (13:00 LT) and a higher one in the early evening (19:00 LT), with average concentrations of $13 \mu\text{g m}^{-3}$ and $18 \mu\text{g m}^{-3}$, respectively (Fig. 3a). These patterns are consistent with the vehicle activity inside the garage (Fig. 1), highly correlating with the diurnal average profile of cold starts ($R^2=0.96$).

The mean concentration of BBOA was $8 \mu\text{g m}^{-3}$ during the operating hours of the garage, with hourly levels exceeding $30 \mu\text{g m}^{-3}$ on several days. On average, BBOA concentrations began to rise in the afternoon, with a pronounced peak at 20:00 LT with an average value of $23 \mu\text{g m}^{-3}$ (Fig. 3b). This behavior is consistent with residential wood burning in Patras.^{45,46}

OOA averaged $3.9 \mu\text{g m}^{-3}$, with a smaller peak during the late morning to early afternoon (10:00–16:00 LT) and a higher peak in the evening (18:00 LT), at $6 \mu\text{g m}^{-3}$ (Fig. 3c). The peak during the afternoon is influenced by the enhanced residential biomass burning.⁴⁶

The relative contribution of the identified OA sources varied both across the campaign and within the day. Throughout the day, HOA contributed most between 9:00 LT and 19:00 LT (Fig. 3d). BBOA was more prominent during the evening and night hours, from 19:00 up to 5:00 LT. OOA played a relatively larger role in the early morning hours (5:00–9:00 LT).

The total CHARON/PTR-MS OA ($\text{OA}_{\text{CHARON}}$) was strongly correlated with the BBOA factor ($R^2=0.75$) and its average diurnal profile ($R^2=0.96$). Consistent with the BBOA behavior, the $\text{OA}_{\text{CHARON}}$ increased in the afternoon and peaked in the late evening (19:00 LT), remaining elevated until midnight (Fig. S9). The correlations of $\text{OA}_{\text{CHARON}}$ with the other factors were considerably weaker, with R^2 values of 0.11 and 0.52, for the HOA and OOA diurnal profiles, respectively. These results indicate that CHARON predominantly captures OA components related to biomass burning and has a small sensitivity to the hydrocarbon-rich OA from fresh vehicle emissions. The average concentration of $\text{OA}_{\text{CHARON}}$ during the operating hours of the parking facility was $3 \mu\text{g m}^{-3}$ with hourly levels surpassing $20 \mu\text{g m}^{-3}$ on December 4 and 18 due to strong biomass

burning influence. On average, the OA mass loading measured by CHARON accounted for approximately 15% of the OA mass measured by the AMS.

The average mass spectrum measured by CHARON/PTR-MS is shown in Fig. S10. The OA_{CHARON} was primarily composed of oxygenated compounds (CHO, 75%), followed by nitrogen-containing oxygenated compounds (CHNO, 22%), while hydrocarbon-like species (CH) contributed only 2%. Protonated levoglucosan fragments at m/z 85, 127 and 145 contributed 12%. The most abundant species showed at m/z 69.03 (C_4H_4O ; furan)^{47,48}, 156.03 ($C_6H_5NO_4$; 4-nitrocatechol)^{49,50}, 170.05 ($C_7H_7NO_4$; methyl-nitrocatechol)⁴⁹, 209.08 ($C_{11}H_{12}O_4$; sinapaldehyde)⁴⁹ and 211.09 ($C_{11}H_{12}O_4$; syringyl acetone, propionyl syringol, or sinapyl alcohol)⁴⁹.

4.3.2 Black carbon

Fossil fuel combustion (BC_{ff}) was the main contributor to BC inside the garage, with average concentrations of $3.3 \mu g m^{-3}$ during operating hours, accounting for 58% of total BC (Fig. S11). BC_{ff} reached an hourly maximum of $13.5 \mu g m^{-3}$ (December 1). The diurnal profile (Fig. 4a) of BC_{ff} showed two distinct peaks, around midday (12:00 LT, $4.8 \mu g m^{-3}$) and in the early evening (20:00 LT, $6.4 \mu g m^{-3}$), closely following cold start activity ($R^2=0.98$) and HOA ($R^2=0.95$).

Biomass burning BC (BC_{bb}) peaked at 20:00 LT with an average value of $5.2 \mu g m^{-3}$, and its diurnal profile (Fig. 4b) was well correlated with that of BBOA ($R^2=0.84$).

4.4. Vehicle-related PM characteristics

To better capture the characteristics of PM related to vehicle emissions, the analysis of this section focuses exclusively on periods when HOA accounted for at least 80% of the total OA (Fig. 2), providing a strict criterion for vehicle-dominated conditions while retaining sufficient data for characterization. These HOA-dominated periods represent 41 hours (out of 513 hours of available data) and all reported averages in this section refer to them. A sensitivity analysis using HOA thresholds of 70% and 90% showed only minor changes in the resulting PM characteristics (Table S5).

For these periods, hourly PM_1 concentrations ranged from 12.1 up to $42.7 \mu g m^{-3}$, with an average of $20.8 \pm 7.8 \mu g m^{-3}$ (Fig. S12). PM_1 consisted primarily of organics, which accounted for $62 \pm 10\%$ ($13.2 \pm 6.7 \mu g m^{-3}$) and black carbon with $35 \pm 10\%$ ($6.8 \pm 2.1 \mu g m^{-3}$), while the remaining was sulfate (2%), ammonium (1%), and nitrate (1%).

PM_{2.5} black carbon is assumed to be in the PM₁ range. The average particle mass size distribution (Fig. S13) peaked at 300 nm.

Particle number concentration (N_{10}) averaged $2.3 \pm 0.5 \times 10^4 \text{ cm}^{-3}$, with hourly peak levels frequently exceeding $40,000 \text{ cm}^{-3}$ (Fig. S14). On average the particle number size distribution (Fig. S15) peaked at 60 nm with a standard deviation of 12 nm. Fig. S16 presents the comparison between the average normalized particle number size distribution measured inside the parking garage and the distribution estimated from the emission inventory. The two distributions show good agreement, with an overlap coefficient of 0.95.

4.5. Gas-phase pollutants

4.5.1 Inorganic gases

Hourly concentrations of CO, CO₂, NO and SO₂ were strongly correlated with each other ($R^2 > 0.84$; Table S6), indicating that the concentrations of these gases were predominantly driven by a common source—vehicle activity. The same gases had a mild correlation with NO₂ (R^2 between 0.60–0.81; Table S6), indicating that NO₂ was more influenced by outdoor sources and processes. None of the inorganic trace gases correlated with O₃ (R^2 below 0.05; Table S6), which remained at low concentrations largely due to its rapid removal through reaction with the elevated NO levels inside the parking. The hourly time series of the measured inorganic gases (CO, CO₂, NO, NO₂, SO₂ and O₃) inside the parking garage are given in Fig. S17. Their mean concentrations under periods of strong fresh exhaust emissions influence within the garage, are provided in Table S7.

The average diurnal profiles of CO, CO₂, NO, NO₂ and SO₂ (Fig. 5) followed similar temporal patterns, with one peak around midday (12:00 LT–14:00 LT) and a higher one in the early evening (19:00 LT), strongly correlating with the diurnal profile of cold starts, HOA and BC_{ff} ($R^2 \approx 0.94$).

The outdoor hourly concentrations measured by the ENSENSIA are shown in Fig. S18. CO levels ranged from 0.1 to 2.9 ppm, while CO₂ averaged $480 \pm 38 \text{ ppm}$. NO concentration was generally low throughout the day, with occasional early-morning peaks, resulting in an average of $7.4 \pm 20.2 \text{ ppb}$. The average NO₂ concentration was $21.7 \pm 9.3 \text{ ppb}$, close to the average observed inside the parking garage, indicating that background levels strongly influence indoor NO₂. The hourly NO₂ concentrations inside

and outside of the garage showed a strong correlation ($R^2=0.85$) over the period measured by ENSENSIA.

4.5.2 Organic gases

The PTR-MS quantified 195 compounds with a mixing ratio of 169 ± 28 ppb. TD-GC-MS identified 29 additional compounds that were not detected by PTR-MS as their proton affinities are lower than the one of water. It should be noted, however, that the Tenax sorbent does not efficiently retain hydrocarbons lighter than hexane due to breakthrough, while hexane itself was excluded from the analysis because of potential interference arising from its use as a solvent.

A relatively small subset of compounds accounted for 77% of the total VOC mixing ratio measured by PTR-MS during the HOA-dominated periods. These included toluene (17%), C₈ aromatics (C₈H₁₀, 17%), acetaldehyde (10%), hydrocarbon fragments (C₃H₆, C₄H₆ and C₇H₆, 8%), C₉ aromatics (C₉H₁₂, 7%), benzene (7%), acetone (4%), methanol (3%), formaldehyde (2%) and the C₂H₂O fragment (2%). Average concentrations of these major compounds over the same periods are summarized in Table S8, with diurnal profiles shown in Fig. S19.

Aromatic VOCs and the summed hydrocarbon fragments had pronounced midday (13:00 LT) and evening (18:00 LT–20:00 LT) peaks, closely tracking cold starts and primary vehicle emission tracers (HOA, BC_{ff}, CO, CO₂ and NO; $R^2>0.85$; Table S9). Major oxygenated VOCs (OVOCs) showed smoother diurnal variability, with a morning rise (10:00 LT) and evening maximum (19:00 LT), reflecting mixed influences from vehicle emissions and outdoor air. The average diurnal profiles of formaldehyde, acetone and acetaldehyde were strongly correlated with those of cold starts and vehicle-related emission tracers ($R^2>0.85$), whereas C₂H₂O showed moderate correlations (R^2 : 0.70–0.85). Methanol differed, correlating weakly with vehicle activity and traffic emission tracers ($R^2 < 0.56$) but strongly with biomass burning markers (BBOA, BC_{bb}, OA_{CHARON}; $R^2>0.9$).

4.5.3 VOC sources

PMF analysis of VOCs measured by PTR-MS resolved two factors. The first was associated with vehicle activity, while the second represented non-vehicle sources. The two-factor solution explained 99% of the variance in the VOC dataset, with the vehicle-related factor accounting, on average, for 55% of the total VOC mixing ratio considered

in the PMF analysis, after excluding methanol and ethanol. Attempts to retrieve a higher number of factors resulted in overfitting, causing the vehicle-related factor to split.

Fig. 6 shows the 30 VOCs with the highest average mixing ratios in each factor, which together account for 91% of the vehicle-related factor and 81% of the non-vehicle sources. The remaining signal is distributed among the other 186 m/z values. Toluene (21%), C₈ aromatics (21%, e.g. xylenes, ethylbenzene), fragments of larger alkanes or alkenes (C₃H₆, C₄H₆ and C₇H₆, 9%), benzene (8%), C₉ aromatics (8%, e.g. trimethylbenzenes) and acetaldehyde (8%) mainly constituted the vehicle-related factor signal, all of which have been previously found in gasoline exhaust emissions^{51,52}. This composition is also consistent with that observed during the HOA-dominated periods, where the same compounds dominated the measured VOCs. In contrast, the non-vehicle factor mixing ratio was enriched in OVOCs, particularly acetaldehyde (18%), acetone (9%), C₂H₂O (5%), and formaldehyde (5%), with notable contributions of aromatics, including C₈ aromatics (7%), toluene (6%), C₉ aromatics (4%) and benzene (2%).

Vehicle-related VOCs averaged 123.2 ± 83.2 ppb during the facility operating hours (Fig. S20) and had two distinct peaks (Fig. 7a), around 13:00 and 18:00 LT, strongly correlating with the diurnal profiles of HOA, BC_{ff} and cold start rate ($R^2 > 0.89$). Over the same period, non-vehicle VOCs averaged 48.1 ± 26.9 ppb and showed a small increase at 14:00 LT, followed by a peak at 20:00 LT (Fig. 7b), correlating well with BBOA, BC_{bb}, OA_{CHARON} ($R^2 > 0.8$).

Fuel evaporation from parked vehicles can also contribute to VOC levels in parking garages. However, these emissions are dominated by light alkanes (C₄–C₅), with a smaller contribution of aromatic hydrocarbons.^{53–56} Wu et al.⁵⁶ estimated that evaporative emissions accounted for less than 15% of total VOCs when garage activity was dominated by cold starts. Given that light alkanes were not captured by the measurement setup of this work, fuel evaporation is expected to have a minor contribution to the measured VOCs.

4.6. Cold start emissions

The cold start emission factors for the measured pollutants, calculated as detailed in Section 3.4, together with the uncertainty ranges derived from the CO₂ cold start emission factor sensitivity analysis (Section 4.6.2), are summarized in Table 1. Hot-running emissions were found to be negligible (Table S10). Source-apportioned concentrations

were used for OA, BC and VOCs to isolate vehicle contributions, while measured outdoor concentrations were included in the estimation for the remaining pollutants. Sulfate, nitrate, and ammonium were not source apportioned and were excluded from the cold start emission factor analysis, as they represented only a minor fraction of the vehicle-related PM_{10} (Section 4.4). Model performance was evaluated by applying the derived emission factors to predict pollutant concentrations inside the garage.

These predicted concentrations were then compared against the measurements at a 20 min temporal resolution. The model reproduces inorganic gas-phase pollutants well, as CO, NO, NO₂, SO₂ show low normalized mean absolute errors (nMAE<31%; Table S11) and good agreement with measurements ($R^2>0.9$; Fig. S21). Total VOCs measured by PTR-MS were adequately captured (nMAE=31%, $R^2=0.89$). Among particulate pollutants, N_{10} shows the best agreement (nMAE=29%, $R^2=0.89$), while BC shows a more moderate agreement (nMAE=35%, $R^2=0.85$).

After CO₂, the highest cold start emissions in mass were observed for CO (9.0 ± 2.5 g per cold start). NO_x emissions were approximately one order of magnitude lower (0.50 ± 0.13 g per cold start), with NO accounting for 93% of the total NO_x. Among the inorganic trace gases, SO₂ showed the lowest cold start emissions.

Most of the cold start VOC emissions (96%) were quantified by PTR-MS and consisted predominantly of C₈ aromatics (25%), toluene (22%), C₉ aromatics (11%), benzene (7%), C₂–C₇ hydrocarbon fragments (7%) and acetaldehyde (4%). The remaining 4% of cold start VOC emissions was detected by TD-GC-MS and consisted primarily of linear alkanes, with heptane representing the single largest contributor (0.9%), followed by C₈–C₁₁ alkanes, each contributing roughly 0.3% to the total VOCs. TD-GC-MS speciation showed that C₈ aromatics were largely xylenes (o-, m-, and p-; 85%), with ethylbenzene making up the remaining 15%, whereas C₉ aromatics were dominated by trimethylbenzenes (1,2,3-, 1,2,4-, 1,3,5-; 60%) and ethyltoluenes (o-, m-, and p-; 40%).

The total characterized organic cold start emissions in the gas phase were distributed in the VBS following the approach described in Section 3.6. Most of the gas-phase emitted mass was in the VOC range (96%), with smaller contributions from IVOCs (3.0%) and SVOCs (0.8%) (Fig. 8). Gas-phase IVOC cold start emissions were mainly composed of C₁₁ aromatics (C₁₁H₁₆, 11%), followed by methylnaphthalene (7%), C₄H₈N₂O₂ (6%), dodecane (5%), cyclopentylbenzene (5%), and around 3% each from CH₃NO₂, C₁₃, and C₁₄ linear alkanes. In contrast, gas-phase SVOC cold start emissions consisted primarily

of long-chain linear alkanes (C_{22} – C_{28}) accounting for 55% of the SVOC fraction. The mass ratios of gas-phase IVOCs and SVOCs were 1.9 ± 0.8 and 0.5 ± 0.2 relative to OA, compared with 3.0 ± 1.2 and 0.8 ± 0.4 to BC, respectively. The uncertainties reported for these ratios include those from the emission factor estimation (Table 1) and the TD-GC-MS quantification, with the latter estimated at approximately 21% as described in Section S3. A bias can also be introduced when n-alkane retention times are used to assign the volatility of aromatic and oxygenated compounds,⁵⁷ as was done in this study (Section S3). However, this was not included in the uncertainty propagation, as the use of decade-wide volatility bins reduces the sensitivity to such differences.⁵⁸

4.6.1 Comparison with the TNO emission inventory

Fig. 9 summarizes the estimated ranges of cold start emissions for each pollutant along with the corresponding values from the reference emission inventory. The reported ranges reflect the uncertainty associated with the assumed CO_2 cold start emission factor, based on the sensitivity analysis discussed in Section 4.6.2. Except for NO_x and IVOCs, the mean cold start emissions obtained in this study were lower than the inventory values. SO_2 emissions, on the other hand, are not included in the inventory due to their low magnitude compared to the other inorganic gases.

Only the non-aliphatic VOCs are compared due to limitations in the measurements of this study, which did not capture light alkanes (C_nH_{2n+2} , $n \leq 6$). Cold start emissions of selected major VOC species are compared with the composition of the hot-running emissions (Table S12), which is assumed to represent cold starts in the inventory, in Fig. S22. Benzene shows the closest agreement with the inventory (16% deviation), while toluene and xylenes were 1.8 and 2 times higher, respectively. In contrast, trimethylbenzenes were nearly a factor of two lower than the assumed value. Acetaldehyde was 82% higher compared to the aldehydes group of the inventory. Formaldehyde and the “other aromatics” group (C_nH_{2n-6}) were lower than the inventory by roughly a factor of three. The latter may be influenced by fragmentation of larger aromatics within the PTR-MS.

Cold start IVOC emissions in the gas phase were 59% higher than the inventory, whereas gas-phase SVOC emissions represented only 33% of the total cold start SVOCs in the inventory, reflecting the uncharacterized particulate fraction. PM_1 OA cold start emissions were nearly a factor of two lower than the reference $PM_{2.5}$ OA values, while BC showed good agreement, with only 17% deviation. Particle number (N_{10}) emissions

per cold start were about a factor of five lower than the inventory value, which corresponds to the same size range. Since particle number emissions are known to be sensitive to ambient temperature⁵⁹ due to its influence on nucleation and condensation processes, this effect could also contribute to the observed differences.

4.6.2 Emission factor sensitivity analysis

A sensitivity analysis was conducted to assess the impact of uncertainties in key assumptions on the derived emission factors (Fig. S23). The influence of the CO₂ cold start emission factor was evaluated by varying its value by 30%, which resulted in an almost proportional response of the derived pollutant cold start emission factors, with average changes of 29% for both the increased and decreased cases, indicating a near linear propagation of uncertainty.

Uncertainty related to the assumed partial capture of cold start emissions within the garage was further examined by exploring cold start correction factors between 1 and 6.7. This range reflects the variability in the fraction of the cold start period occurring inside the garage, based on the assumed residence time of vehicles in the garage after engine start-up (45 ± 15 s) relative to the duration of a typical cold start (130 ± 70 s)^{12,19,23}. A correction factor of 1, corresponding to all cold start emissions occurring inside the parking garage, decreased the derived emission factors by an average of 3% (Table S13). In contrast, a correction factor of 6.7 increased them by an average of 7%. Overall, the influence of the assumed fraction of cold start emissions captured inside the garage is small, as the correction factor influences both the derived ventilation rate constant, through the assumed CO₂ cold start emissions, and the cold start emission estimates.

The assumption that all vehicle exits corresponded to cold starts was evaluated by reducing the number of cold starts to 60% of the observed exits and treating the remaining 40% as hot-running vehicles. Under this assumption, the estimated cold start emission factors increased by an average of 7% compared with the base case.

For VOCs, the potential effect of peaks excluded from the PTR-MS analysis was evaluated by assuming that the entire excluded analyte signal was vehicle-related. This assumption increased the VOC cold start emission factor by 25%.

For N_{10} , two additional sensitivity tests were performed, as its vehicle contribution could not be source apportioned. Restricting vehicle-related N_{10} to the HOA-associated fraction reduced its cold start emissions by nearly half relative to the base scenario. The

assumed background concentration effect was examined by doubling the assumed outdoor levels. This resulted in a 21% decrease in the cold start emissions of N_{10} .

4.7. Limitations

The analysis in this work is subject to several methodological limitations that are discussed in this section. First, the ventilation rate was not measured independently but was derived from the CO_2 mass balance using assumed CO_2 emission factors. As examined in the sensitivity analysis, uncertainties in these emission factors propagate to the derived pollutant emission factors. Another limitation is the well-mixed assumption of the box model used to estimate the emission factors, which is supported by the spatial CO_2 measurements. However, equivalent spatial measurements were not available for the other pollutants, which may exhibit stronger spatial gradients due to their chemical reactivity.

Individual vehicle soak times could not be determined from the camera measurements, and all vehicle exits were assumed to correspond to cold starts. Despite this, the sensitivity analysis indicated that this assumption had only a small effect on the derived cold start emission factors. In addition, the measurements directly capture only the emissions released while vehicles remain inside the parking garage. Total cold start emissions were therefore estimated using a correction factor based on the assumed vehicle residence time after engine start and the duration of a typical cold start. Although the sensitivity analysis indicated a relatively small effect on the derived emission factors, this extrapolation represents an additional source of uncertainty.

Limitations in the measurements also concern VOCs, as the applied measurement techniques were not able to capture light alkanes, which can contribute substantially to total VOC emissions (Table S12) and are important indicators of fuel evaporation. As a result, the contribution of fuel evaporation could not be separated from tailpipe VOC emissions.

Finally, the measurements were conducted during a single winter campaign at one parking facility. Therefore, the derived emission factors may not be representative of other seasons, temperatures, parking configurations, or vehicle fleets.

5. Conclusions

Cold start emissions were quantified and characterized inside an underground parking garage during a three-week winter period in Patras, Greece, based on 20,616 recorded vehicle exits. Under the conditions of this study, where the average vehicle soak time was 1.5 h, vehicle emissions were driven almost entirely by cold starts.

PM emitted during cold starts consisted almost entirely of carbonaceous species, consisting of 61% OA and 39% BC. The emitted OA was primarily composed of hydrocarbons (C_xH_y), resulting in an O:C of 0.03. Cold start VOC emissions mainly consisted of light aromatic compounds (C_6 - C_9 , 65%), followed by small oxygenated C_1 - C_4 species (12%), C_2 - C_7 hydrocarbon fragments (7%) and aliphatic C_7 - C_{28} hydrocarbons (3%). The contributions of IVOCs and SVOCs represented 3.0% and 0.8% of the total characterized gas-phase organic cold start emissions. The IVOC/OA mass ratio was 1.9 ± 0.8 and the SVOC/OA was 0.5 ± 0.2 , at 21 °C and an OA concentration of $13.2 \mu\text{g m}^{-3}$. The corresponding IVOC/BC ratio was 3.0 ± 1.2 and SVOC/BC was 0.8 ± 0.4 .

Air quality inside the garage was also strongly influenced by transported outdoor pollution, particularly during periods of residential biomass burning. This underscores the importance of outdoor air impact in confined environments and the strong wintertime contribution of biomass-burning emissions.

Overall, the results of this study can be used to improve cold start emission factors of inventories and to evaluate models that simulate vehicle emissions. These findings also highlight the importance of additional real-world measurements of vehicle fleets under representative conditions to improve emission inventories and support urban air quality assessments.

Author contributions

S. N. P. contributed to conceptualization; D. P., C. K., S. A., A. M., I. D. A., J. K., and M. E. M. contributed to formal analysis; D. P. wrote the original draft; all authors contributed to investigation, review, and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data set is publicly accessible at <https://doi.org/10.5281/zenodo.18683999>. The data of the current study are restricted and are available from the corresponding author (Spyros N. Pandis) on reasonable request.

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References

- 1 P. Gireesh Kumar, P. Lekhana, M. Tejaswi and S. Chandrakala, Effects of vehicular emissions on the urban environment- a state of the art, *Mater. Today: Proc.*, 2021, **45**, 6314–6320.
- 2 European Environment Agency, EEA, *EMEP/EEA air pollutant emission inventory guidebook 2023 – update 2024: 1.a.3.b.i-iv road transport*, 2023.
- 3 N. J. Hime, G. B. Marks and C. T. Cowie, A comparison of the health effects of ambient particulate matter air pollution from five emission sources, *Int. J. Environ. Res. Public Health*, 2018, **15**, 1206.
- 4 J. Lelieveld, K. Klingmüller, A. Pozzer, R. T. Burnett, A. Haines and V. Ramanathan, Effects of fossil fuel and total anthropogenic emission removal on public health and climate, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 7192–7197.
- 5 A. Kontses, G. Triantafyllopoulos, L. Ntziachristos and Z. Samaras, Particle number (PN) emissions from gasoline, diesel, LPG, CNG and hybrid-electric light-duty vehicles under real-world driving conditions, *Atmos. Environ.*, 2020, **222**, 117126.
- 6 S. M. A. Rahman, I. M. R. Fattah, H. C. Ong, F. R. Ashik, M. M. Hassan, M. T. Murshed, M. A. Imran, M. H. Rahman, M. A. Rahman, M. A. M. Hasan and T. M. I. Mahlia, State-of-the-art of establishing test procedures for real driving gaseous emissions from light- and heavy-duty vehicles, *Energies*, 2021, **14**, 4195.
- 7 J. Hu, H. C. Frey and B. Y. Boroujeni, Contribution of cold starts to real-world trip emissions for light-duty gasoline vehicles, *Atmosphere*, 2022, **14**, 35.
- 8 Z. Zhai, J. Xu, M. Zhang, A. Wang and M. Hatzopoulou, Quantifying start emissions and impact of reducing cold and warm starts for gasoline and hybrid vehicles, *Atmos. Pollut. Res.*, 2023, **14**, 101646.
- 9 M. F. Weilenmann, P. Soltic and S. Hausberger, The cold start emissions of light-duty-vehicle fleets: A simplified physics-based model for the estimation of CO₂ and pollutants, *Sci. Total Environ.*, 2013, **444**, 161–176.
- 10 M. S. Reiter and K. M. Kockelman, The problem of cold starts: A closer look at mobile source emissions levels, *Transportation Research Part D: Transport and Environment*, 2016, **43**, 123–132.
- 11 European Commission. Joint Research Centre., *Including cold-start emissions in the Real-Driving Emissions (RDE) test procedure: an assessment of cold start frequencies and emission effects.*, Publications Office, LU, 2017.

- 12 Y. Wen, S. Zhang, L. He, S. Yang, X. Wu and Y. Wu, Characterizing start emissions of gasoline vehicles and the seasonal, diurnal and spatial variabilities in China, *Atmos. Environ.*, 2021, **245**, 118040.
- 13 U.S. Environmental Protection Agency, *Exhaust emission rates for light-duty onroad vehicles in MOVES3*, 2020.
- 14 European Commission, Eurostat, *Modal split of inland passenger transport*, Publication Office of the European Union, 2025.
- 15 National Institute for Public Health and the Environment, RIVM, *Methods for calculating the emissions of transport in the Netherlands*, 2024.
- 16 L. Chen, Z. Liang, X. Zhang and S. Shuai, Characterizing particulate matter emissions from GDI and PFI vehicles under transient and cold start conditions, *Fuel*, 2017, **189**, 131–140.
- 17 J.-Y. Favez, M. Weilenmann and J. Stilli, Cold start extra emissions as a function of engine stop time: Evolution over the last 10 years, *Atmos. Environ.*, 2009, **43**, 996–1007.
- 18 M. Weilenmann, P. Soltic, C. Saxer, A.-M. Forss and N. Heeb, Regulated and nonregulated diesel and gasoline cold start emissions at different temperatures, *Atmos. Environ.*, 2005, **39**, 2433–2441.
- 19 B. Du, L. Zhang, Y. Geng, Y. Zhang, H. Xu and G. Xiang, Testing and evaluation of cold-start emissions in a real driving emissions test, *Transportation Research Part D: Transport and Environment*, 2020, **86**, 102447.
- 20 M. V. Faria, R. A. Varella, G. O. Duarte, T. L. Farias and P. C. Baptista, Engine cold start analysis using naturalistic driving data: City level impacts on local pollutants emissions and energy consumption, *Sci. Total Environ.*, 2018, **630**, 544–559.
- 21 L. He, Y. You, X. Zheng, S. Zhang, Z. Li, Z. Zhang, Y. Wu and J. Hao, The impacts from cold start and road grade on real-world emissions and fuel consumption of gasoline, diesel and hybrid-electric light-duty passenger vehicles, *Sci. Total Environ.*, 2022, **851**, 158045.
- 22 C. McCaffery, H. Zhu, C. Li, T. D. Durbin, K. C. Johnson, H. Jung, R. Brezny, M. Geller and G. Karavalakis, On-road gaseous and particulate emissions from GDI vehicles with and without gasoline particulate filters (GPFs) using portable emissions measurement systems (PEMS), *Sci. Total Environ.*, 2020, **710**, 136366.
- 23 O. I. Awad, X. Ma, M. Kamil, O. M. Ali, Z. Zhang and S. Shuai, Particulate emissions from gasoline direct injection engines: A review of how current emission regulations are being met by automobile manufacturers, *Sci. Total Environ.*, 2020, **718**, 137302.
- 24 J. Andersson, J. May, C. Favre, D. Bosteels, S. De Vries, M. Heaney, M. Keenan and J. Mansell, On-road and chassis dynamometer evaluations of emissions from two euro 6 diesel vehicles, *SAE Int. J. Fuels Lubr.*, 2014, **07**, 919–934.
- 25 J. May, D. Bosteels and C. Favre, An assessment of emissions from light-duty vehicles using PEMS and chassis dynamometer testing, *SAE Int. J. Engines*, 2014, **07**, 1326–1335.
- 26 G. Fontaras, N.-G. Zacharof and B. Ciuffo, Fuel consumption and CO₂ emissions from passenger cars in europe – laboratory versus real-world emissions, *Prog. Energy Combust. Sci.*, 2017, **60**, 97–131.
- 27 G. P. Chossière, R. Malina, F. Allroggen, S. D. Eastham, R. L. Speth and S. R. H. Barrett, Country- and manufacturer-level attribution of air quality impacts due to excess NO_x emissions from diesel passenger vehicles in Europe, *Atmos. Environ.*, 2018, **189**, 89–97.
- 28 J. R. Krall and R. D. Peng, The volkswagen scandal: deception, driving and deaths, *Significance*, 2015, **12**, 12–15.

- 29 C. Kaltsonoudis, D. Pavlidis, A. Matrali, C. N. Vasilakopoulou, S. Androulakis, C. Christopoulou, G. A. Argyropoulou, K. Seitanidi, Y. Chen, A. S. H. Prevot and S. N. Pandis, Chemical aging of passenger car emissions, *in preparation*.
- 30 I. D. Apostolopoulos, G. Fouskas and S. N. Pandis, Field calibration of a low-cost air quality monitoring device in an urban background site using machine learning models, *Atmosphere*, 2023, **14**, 368.
- 31 E. Kostenidou, R. K. Pathak and S. N. Pandis, An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, *Aerosol Sci. Technol.*, 2007, **41**, 1002–1010.
- 32 M. R. Canagaratna, J. L. Jimenez, J. H. Kroll, Q. Chen, S. H. Kessler, P. Massoli, L. Hildebrandt Ruiz, E. Fortner, L. R. Williams, K. R. Wilson, J. D. Surratt, N. M. Donahue, J. T. Jayne and D. R. Worsnop, Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 2015, **15**, 253–272.
- 33 P. Paatero and U. Tapper, Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, 1994, **5**, 111–126.
- 34 U.S. Environmental Protection Agency, *EPA positive matrix factorization (PMF) 5.0 fundamentals and user guide*, 2014.
- 35 J. C. Chow, J. G. Watson, K. Park, N. F. Robinson, D. H. Lowenthal, K. Park and K. A. Magliano, Comparison of particle light scattering and fine particulate matter mass in central California, *J. Air Waste Manage. Assoc.*, 2006, **56**, 398–410.
- 36 E. Kostenidou, B.-H. Lee, G. J. Engelhart, J. R. Pierce and S. N. Pandis, Mass spectra deconvolution of low, medium, and high volatility biogenic secondary organic aerosol, *Environ. Sci. Technol.*, 2009, **43**, 4884–4889.
- 37 J. Sandradewi, A. S. H. Prévôt, S. Szidat, N. Perron, M. R. Alfarra, V. A. Lanz, E. Weingartner and U. Baltensperger, Using Aerosol Light Absorption Measurements for the Quantitative Determination of Wood Burning and Traffic Emission Contributions to Particulate Matter, *Environ. Sci. Technol.*, 2008, **42**, 3316–3323.
- 38 J. Kuenen, S. Dellaert, A. Visschedijk, J.-P. Jalkanen, I. Super and H. Denier Van Der Gon, CAMS-REG-v4: a state-of-the-art high-resolution European emission inventory for air quality modelling, *Earth Syst. Sci. Data*, 2022, **14**, 491–515.
- 39 N. M. Donahue, A. L. Robinson, C. O. Stanier and S. N. Pandis, Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 2006, **40**, 2635–2643.
- 40 Y. Li, U. Pöschl and M. Shiraiwa, Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols, *Atmos. Chem. Phys.*, 2016, **16**, 3327–3344.
- 41 Y. Zhao, N. T. Nguyen, A. A. Presto, C. J. Hennigan, A. A. May and A. L. Robinson, Intermediate volatility organic compound emissions from on-road diesel vehicles: chemical composition, emission factors, and estimated secondary organic aerosol production, *Environ. Sci. Technol.*, 2015, **49**, 11516–11526.
- 42 A. Sinha, I. George, A. Holder, W. Preston, M. Hays and A. P. Grieshop, Development of volatility distributions for organic matter in biomass burning emissions, *Environ. Sci.: Atmos.*, 2023, **3**, 11–23.
- 43 M. R. Alfarra, A. S. H. Prevot, S. Szidat, J. Sandradewi, S. Weimer, V. A. Lanz, D. Schreiber, M. Mohr and U. Baltensperger, Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions, *Environ. Sci. Technol.*, 2007, **41**, 5770–5777.

- 44 E. Kostenidou, K. Florou, C. Kaltsonoudis, M. Tsiflikiotou, S. Vratolis, K. Eleftheriadis and S. N. Pandis, Sources and chemical characterization of organic aerosol during the summer in the eastern Mediterranean, *Atmos. Chem. Phys.*, 2015, **15**, 11355–11371.
- 45 K. Florou, D. K. Papanastasiou, M. Pikridas, C. Kaltsonoudis, E. Louvaris, G. I. Gkatzelis, D. Patoulas, N. Mihalopoulos and S. N. Pandis, The contribution of wood burning and other pollution sources to wintertime organic aerosol levels in two Greek cities, *Atmos. Chem. Phys.*, 2017, **17**, 3145–3163.
- 46 C. Kaltsonoudis, K. Florou, J. K. Kodros, S. D. Jorga, C. N. Vasilakopoulou, H. D. Baliaka, A. Matrali, A. Aktypis, M. P. Georgopoulou, A. Nenes and S. N. Pandis, Significant contributions of fresh and aged biomass burning organic aerosol from residential burning in a wintertime urban environment, *Atmos. Environ.*, 2025, **343**, 121018.
- 47 B. B. Palm, Q. Peng, C. D. Fredrickson, B. H. Lee, L. A. Garofalo, M. A. Pothier, S. M. Kreidenweis, D. K. Farmer, R. P. Pokhrel, Y. Shen, S. M. Murphy, W. Permar, L. Hu, T. L. Campos, S. R. Hall, K. Ullmann, X. Zhang, F. Flocke, E. V. Fischer and J. A. Thornton, Quantification of organic aerosol and brown carbon evolution in fresh wildfire plumes, *Proc. Natl. Acad. Sci. U.S.A.*, 2020, **117**, 29469–29477.
- 48 A. Ijaz, B. Temime-Roussel, B. Chazeau, S. Albertin, S. R. Arnold, B. Barret, S. Bekki, N. Brett, M. Cesler-Maloney, E. Dieudonne, K. K. Dingilian, J. G. Fochesatto, J. Mao, A. Moon, J. Savarino, W. Simpson, R. J. Weber, K. S. Law and B. D'Anna, Complementary aerosol mass spectrometry elucidates sources of wintertime submicron particle pollution in Fairbanks, Alaska, during ALPACA 2022, *Atmos. Chem. Phys.*, 2025, **25**, 11789–11811.
- 49 A. Bertrand, G. Stefenelli, C. N. Jen, S. M. Pieber, E. A. Bruns, H. Ni, B. Temime-Roussel, J. G. Slowik, A. H. Goldstein, I. El Haddad, U. Baltensperger, A. S. H. Prévôt, H. Wortham and N. Marchand, Evolution of the chemical fingerprint of biomass burning organic aerosol during aging, *Atmos. Chem. Phys.*, 2018, **18**, 7607–7624.
- 50 Z. Finewax, J. A. De Gouw and P. J. Ziemann, Identification and quantification of 4-nitrocatechol formed from OH and NO₃ radical-initiated reactions of catechol in air in the presence of NO_x: implications for secondary organic aerosol formation from biomass burning, *Environ. Sci. Technol.*, 2018, **52**, 1981–1989.
- 51 S. M. Pieber, N. K. Kumar, F. Klein, P. Comte, D. Bhattu, J. Dommen, E. A. Bruns, D. Kılıç, I. El Haddad, A. Keller, J. Czerwinski, N. Heeb, U. Baltensperger, J. G. Slowik and A. S. H. Prévôt, Gas-phase composition and secondary organic aerosol formation from standard and particle filter-retrofitted gasoline direct injection vehicles investigated in a batch and flow reactor, *Atmos. Chem. Phys.*, 2018, **18**, 9929–9954.
- 52 E. Kostenidou, B. Marques, B. Temime-Roussel, Y. Liu, B. Vansevenant, K. Sartelet and B. D'Anna, Secondary organic aerosol formed by Euro 5 gasoline vehicle emissions: chemical composition and gas-to-particle phase partitioning, *Atmos. Chem. Phys.*, 2024, **24**, 2705–2729.
- 53 Y. Liu, M. Shao, L. Fu, S. Lu, L. Zeng and D. Tang, Source profiles of volatile organic compounds (VOCs) measured in China: Part I, *Atmos. Environ.*, 2008, **42**, 6247–6260.
- 54 Q. Sha, M. Zhu, H. Huang, Y. Wang, Z. Huang, X. Zhang, M. Tang, M. Lu, C. Chen, B. Shi, Z. Chen, L. Wu, Z. Zhong, C. Li, Y. Xu, F. Yu, G. Jia, S. Liao, X. Cui, J. Liu and J. Zheng, A newly integrated dataset of volatile organic compounds (VOCs)

- source profiles and implications for the future development of VOCs profiles in China, *Sci. Total Environ.*, 2021, **793**, 148348.
- 55 D. Wang, J. Zhou, L. Han, W. Tian, C. Wang, Y. Li and J. Chen, Source apportionment of VOCs and ozone formation potential and transport in Chengdu, China, *Atmos. Pollut. Res.*, 2023, **14**, 101730.
- 56 Y. Wu, Y. Liu, P. Liu, L. Sun, P. Song, J. Peng, R. Li, N. Wei, L. Wu, T. Wang, L. Zhang, N. Yang and H. Mao, Evaluating vehicular exhaust and evaporative emissions via VOC measurement in an underground parking garage, *Environ. Pollut.*, 2023, **333**, 122022.
- 57 A. A. Presto, C. J. Hennigan, N. T. Nguyen and A. L. Robinson, Determination of volatility distributions of primary organic aerosol emissions from internal combustion engines using thermal desorption gas chromatography mass spectrometry, *Aerosol Sci. Technol.*, 2012, **46**, 1129–1139.
- 58 Q. Lu, Y. Zhao and A. L. Robinson, Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions, *Atmos. Chem. Phys.*, 2018, **18**, 17637–17654.
- 59 R. Suarez-Bertoa and C. Astorga, Impact of cold temperature on Euro 6 passenger car emissions, *Environ. Pollut.*, 2018, **234**, 318–329.

Table 1. Cold start emission factors.

Pollutant	Cold start emissions^a (units per cold start)
CO (g)	9.0 ± 2.5
NO (g)	0.46 ± 0.13
NO ₂ (g)	0.03 ± 0.01
SO ₂ (mg)	7.5 ± 2.1
Total VOCs (g)	0.54 ± 0.15
IVOCs (mg)	16.5 ± 3.6
SVOCs (mg)	4.3 ± 1.3
OA ^b (mg)	8.7 ± 2.6
BC (mg)	5.5 ± 1.5
N_{10}	$2.8 \pm 0.8 \times 10^{13}$

^aThe reported ranges reflect the uncertainty associated with the sensitivity analysis of the assumed CO₂ cold start emission factor

^bEstimated under conditions of an average OA concentration of $13.2 \mu\text{g m}^{-3}$ and a temperature of 21 °C

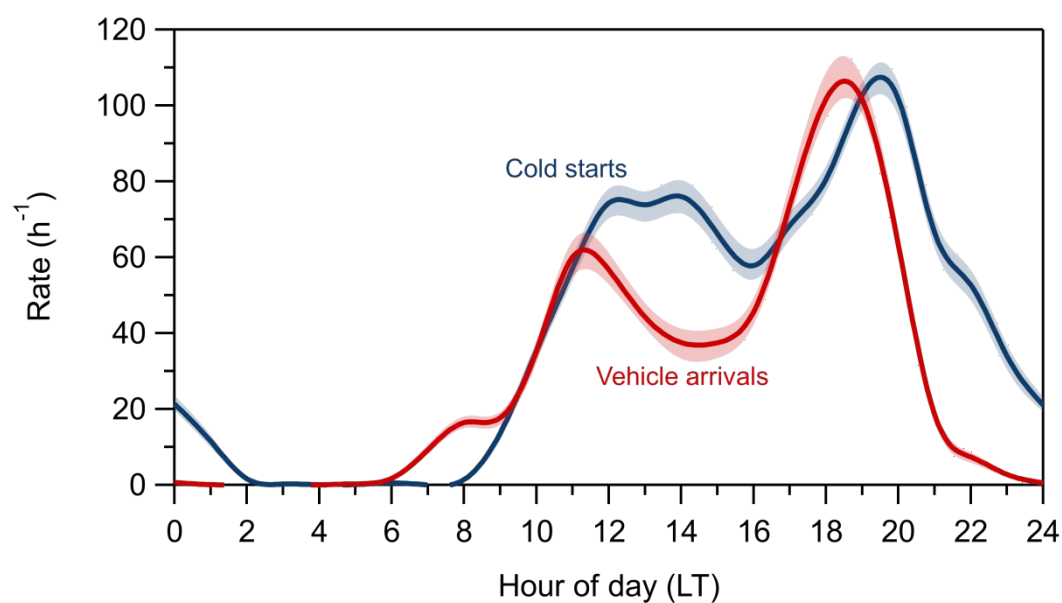


Fig. 1. Average diurnal profiles of cold start rate (blue) and vehicle arrival rate (red). The shaded areas correspond to one standard deviation of the hourly mean values.

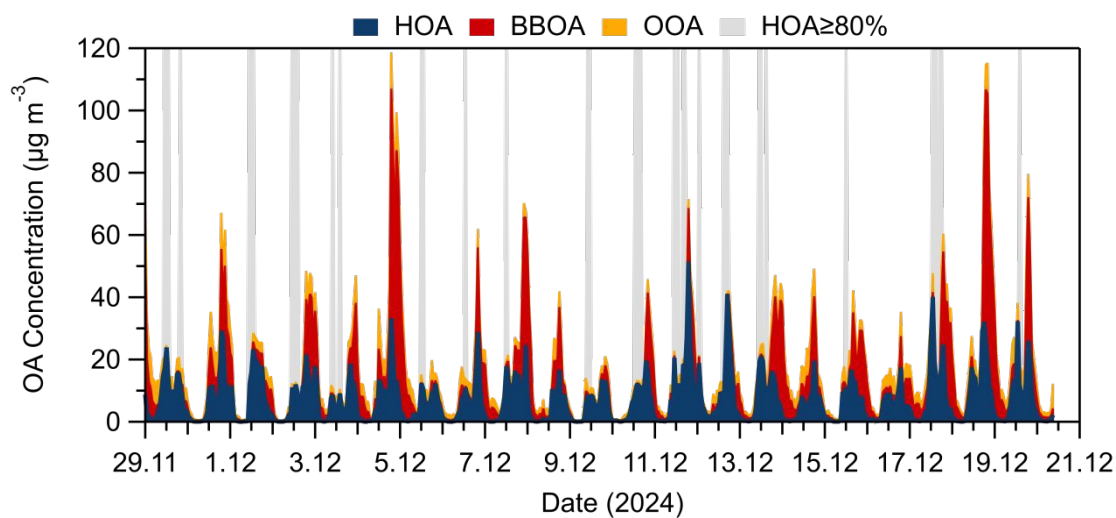


Fig. 2. Hourly average time series of the OA components. Shaded areas indicate periods dominated by vehicle emissions.

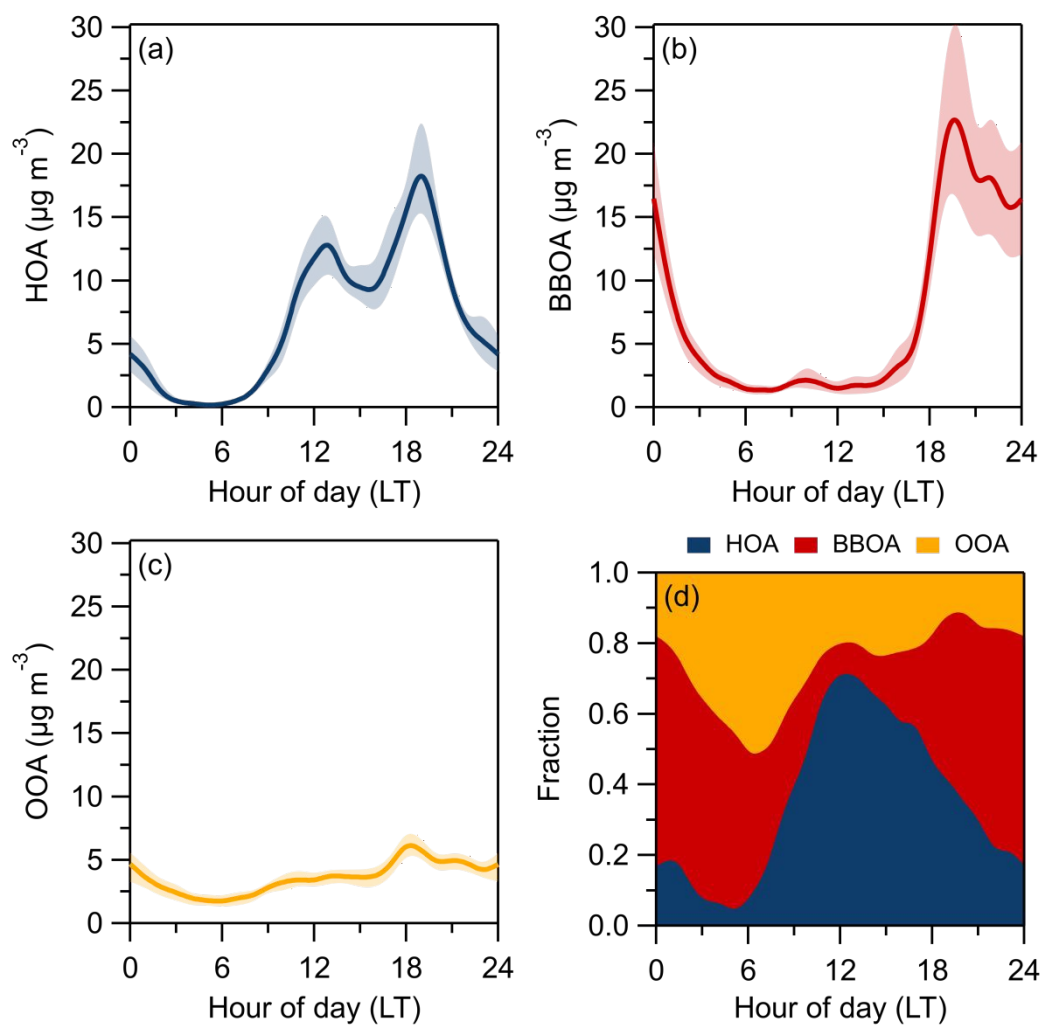


Fig. 3. Diurnal profiles of the PMF factors: (a) HOA, (b) BBOA, (c) OOA and (d) their relative diurnal contribution. The shaded areas correspond to one standard deviation of the hourly mean values.

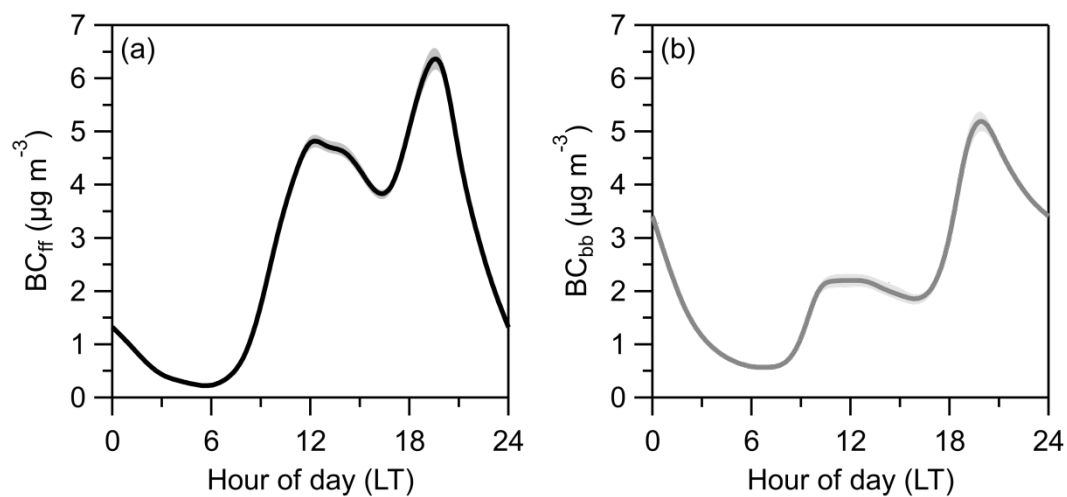


Fig. 4. Average diurnal profiles of (a) fossil fuel BC and (b) biomass burning BC inside the garage. The shaded areas correspond to one standard deviation of the hourly mean values.

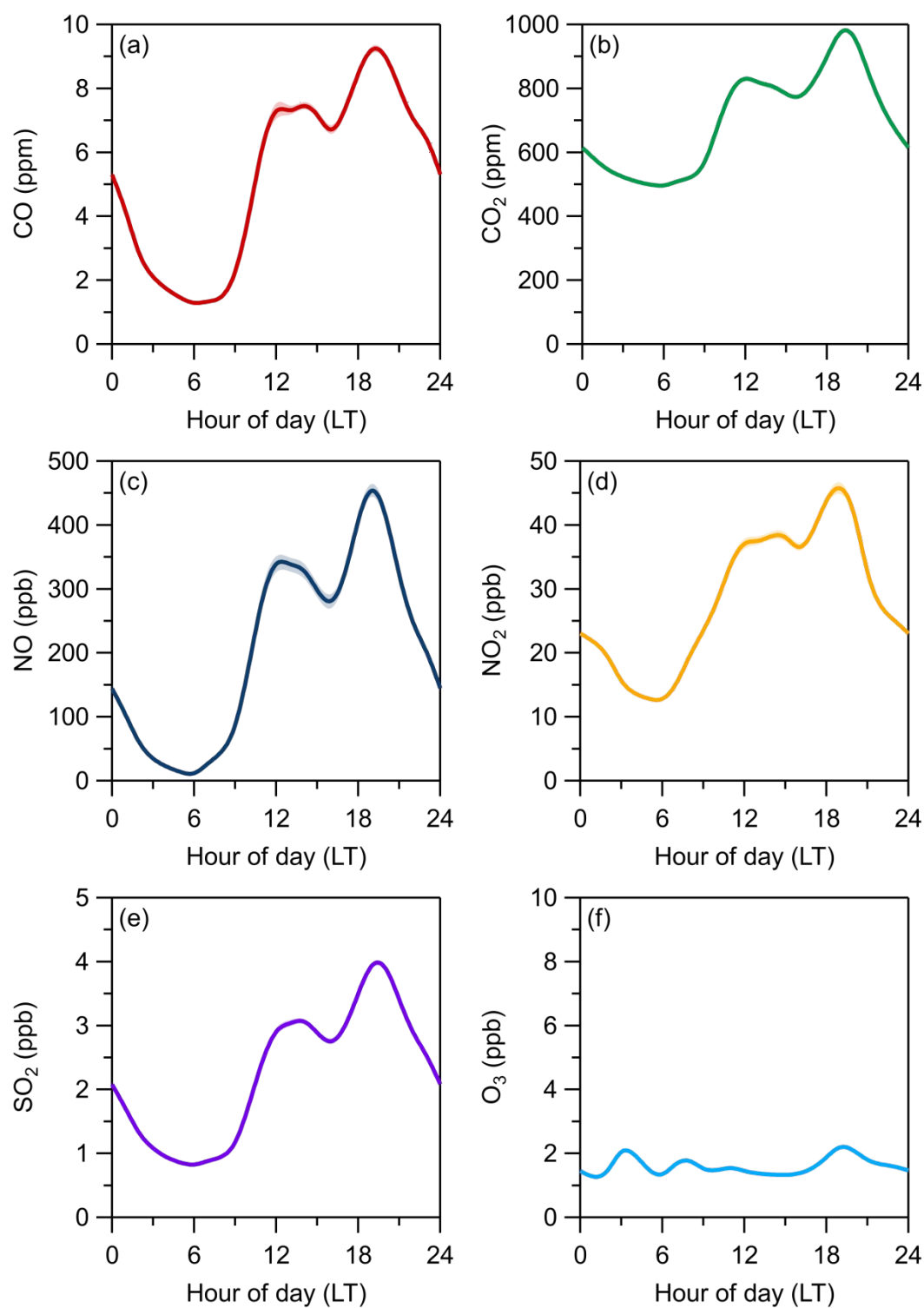


Fig. 5. Diurnal profiles of (a) CO, (b) CO₂, (c) NO, (d) NO₂, (e) SO₂ and (f) O₃. The shaded areas correspond to one standard deviation of the hourly mean values.

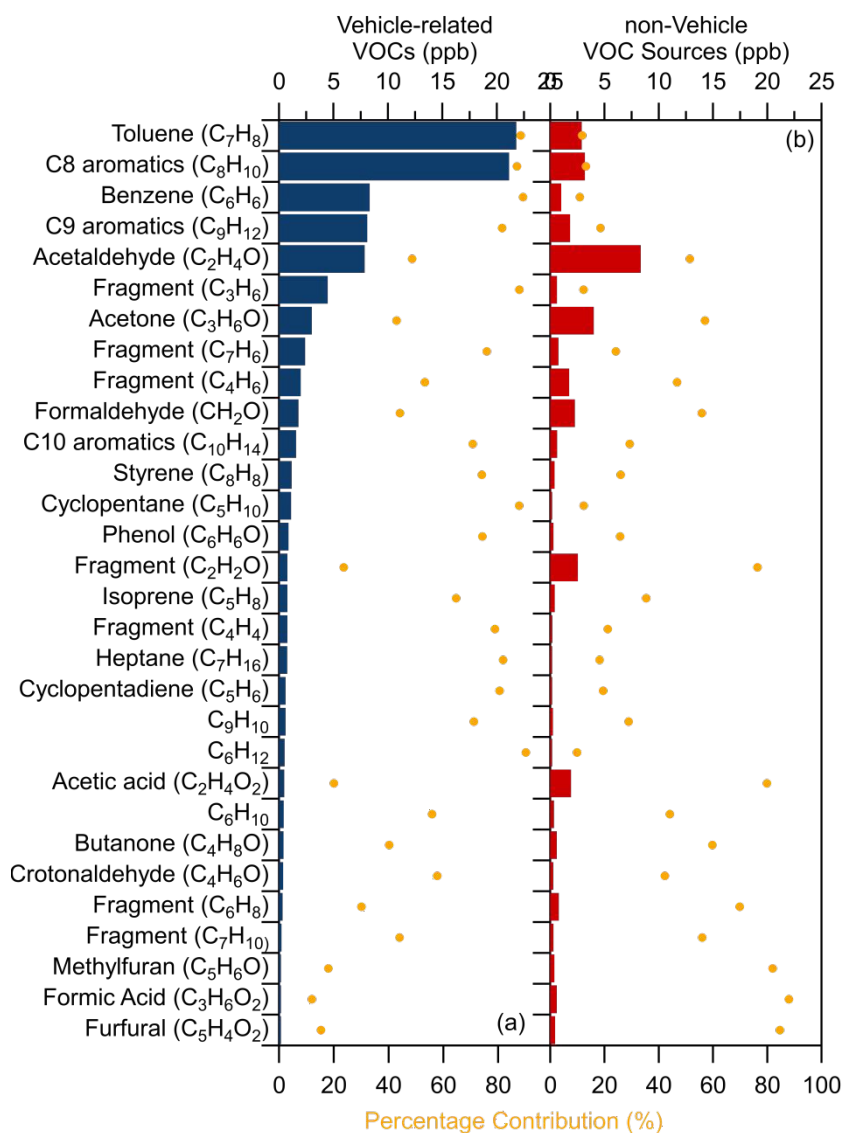


Fig. 6. Average mixing ratios of the 30 most abundant VOCs associated with (a) the vehicle-related factor and (b) non-vehicle sources. The bottom axis shows the percentage contribution of each VOC to the corresponding factor.

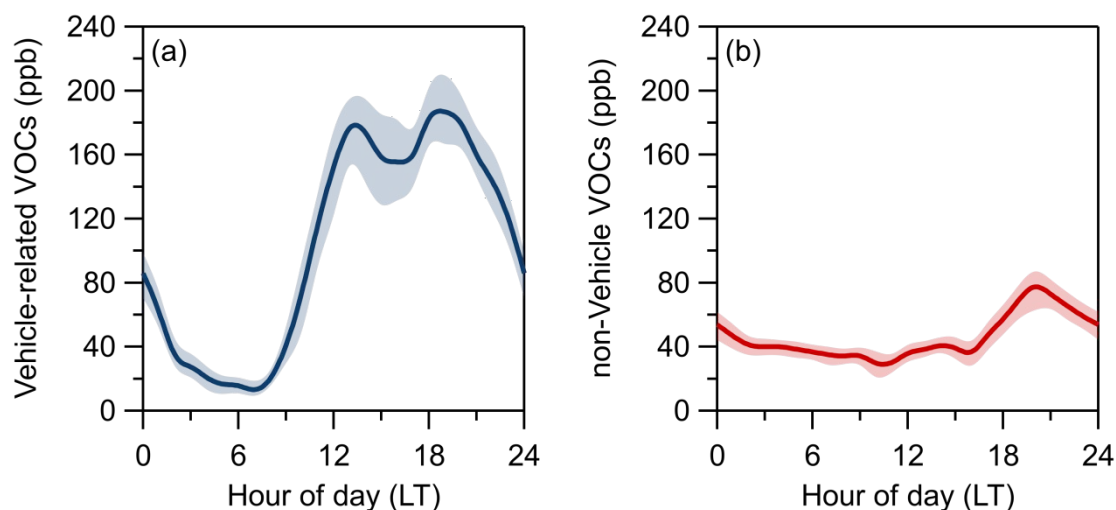


Fig. 7. Average diurnal profiles of (a) vehicle-related and (b) non-vehicle VOCs inside the garage. The shaded areas correspond to one standard deviation of the hourly mean values.

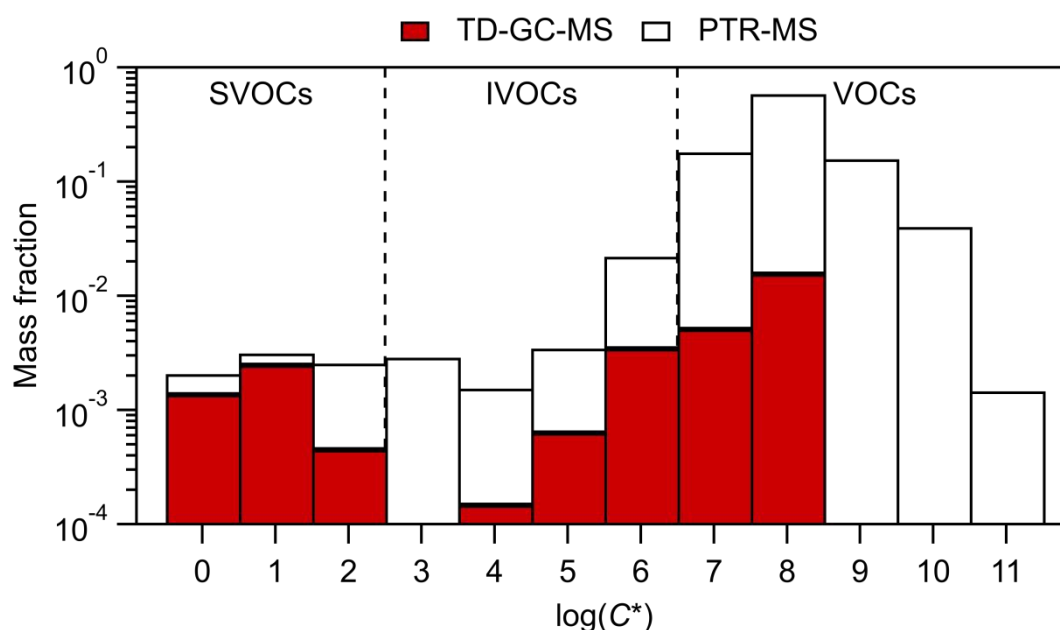


Fig. 8. Volatility distribution of organic cold start emissions in the gas phase classified by measurement instrument used (red: TD-GC-MS, white: PTR-MS)

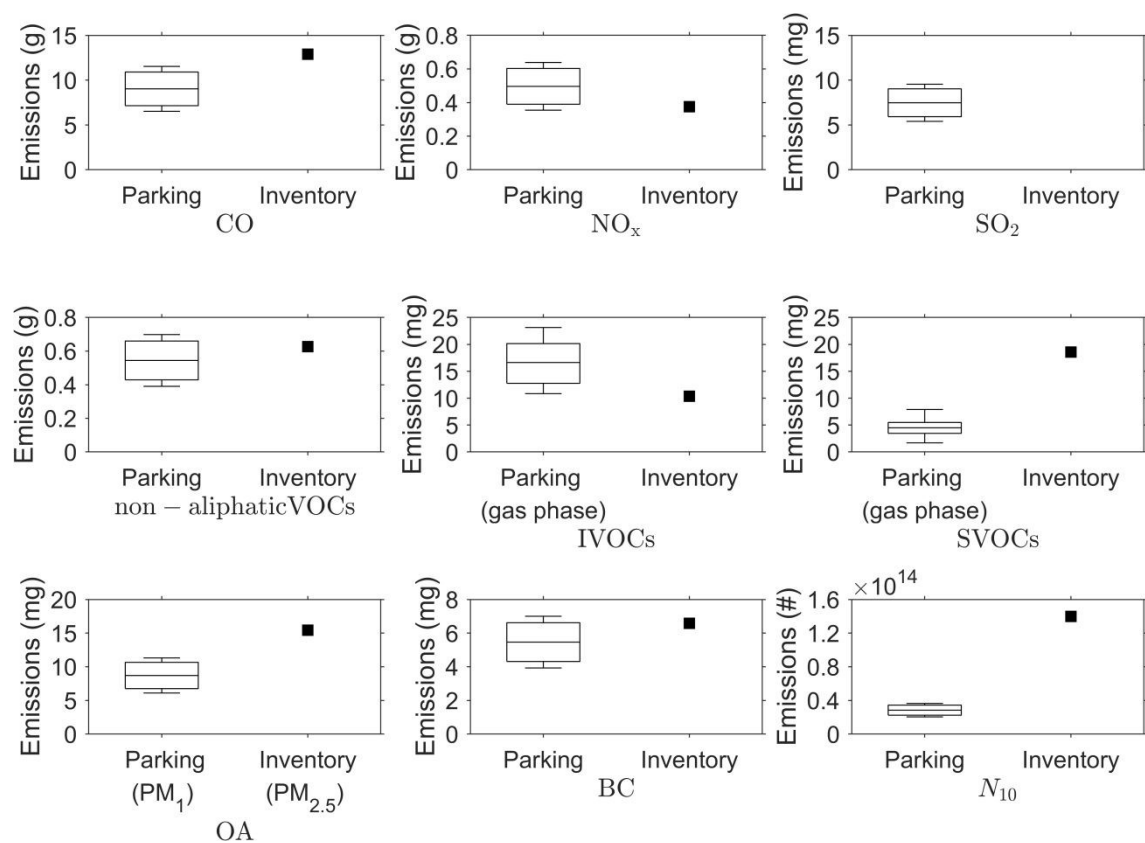


Fig. 9. Boxplots of the estimated pollutant emission factors per vehicle for a cold start compared to the emission inventory. The parking measurements were conducted at an average soak time of approximately 1.5 h, an OA concentration of 13.2 $\mu\text{g m}^{-3}$, and a temperature of 21 °C. The black line denotes the median value.

Data availability

The data set is publicly accessible at <https://doi.org/10.5281/zenodo.18683999>. The data of the current study are restricted and are available from the corresponding author (Spyros N. Pandis) on reasonable request.