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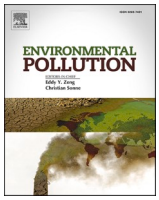

Exhaust particle number and composition for diesel and gasoline passenger cars under transient driving conditions: Real-world emissions down to 1.5 nm☆

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ABSTRACT

Recent recommendations given by WHO include systematic measurements of ambient particle number concentration and black carbon (BC) concentrations. In India and several other highly polluted areas, the air quality problems are severe and the need for air quality related information is urgent. This study focuses on particle number emissions and BC emissions of passenger cars that are technologically relevant from an Indian perspective. Particle number and BC were investigated under real-world conditions for driving cycles typical for Indian urban environments. Two mobile laboratories and advanced aerosol and trace gas instrumentation were utilized. Our study shows that passenger cars without exhaust particle filtration can emit in real-world conditions large number of particles, and especially at deceleration a significant fraction of particle number can be even in 1.5–10 nm particle sizes. The mass concentration of exhaust plume particles was dominated by BC that was emitted especially at acceleration conditions. However, exhaust particles contained also organic compounds, indicating the roles of engine oil and fuel in exhaust particle formation. In general, our study was motivated by serious Indian air quality problems, by the recognized lack of emission information related to Indian traffic, and by the recent WHO air quality guidance; our results emphasize the importance of monitoring particle number concentrations and BC also in Indian urban areas and especially in traffic environments where people can be significantly exposed to fresh exhaust emissions.

1. Introduction

Vehicular on-road traffic is a major contributor to air pollutants of urban areas affecting human population health, environment at local and regional scale, and global climate; e.g. gaseous CO_2 and methane as well as particulate black carbon (BC) are strong climate forcers, and particulate pollution, gaseous ozone and nitrogen compounds cause negative health effects (e.g. IPCC, 2018; Fu et al., 2020; Bond et al., 2013, Oberdörster et al., 2005; IARC, 2012; Su et al., 2008; Janssen et al., 2011; Monks et al., 2015; Bates, 2005). These detrimental effects of traffic emissions have caused the general need for emission regulation, aiming to improve the technologies used in vehicle fleet, decrease the emissions and improve air quality especially in cities where large number of people is exposed to the pollutants.

Ultrafine particles (particle diameter smaller than 100 nm) typically dominate the particle number concentrations of urban air. While inhaling urban air those particles deposit efficiently in the human respiratory tract (ICRP, 1994), and after the deposition, they can affect the human airway tissues or translocate to other parts of the body. Ultrafine particles can be formed in ambient air from initially gaseous

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atmospheric components (Alam et al., 2003), or they can be emitted to atmosphere from aerosol sources, in traffic influenced areas mostly from vehicle engines (Kumar et al., 2014; Rönkkö and Timonen, 2019). In general, exhaust emissions of vehicles contain primary emitted non-volatile soot agglomerates and ash particles (primary particle emissions) (Kittelson, 1998; Tobias et al., 2001; Sgro et al., 2012; Seong et al., 2014; Fushimi et al., 2011; Lähde et al., 2014) that are, the majority of them are in ultrafine particle size range, and gaseous compounds. Some of the emitted gaseous compounds can condense onto the surfaces of non-volatile particles or nucleate forming new particles already in cooling dilution process (fresh particle emissions) (Charron and Harrison, 2003; Arnold et al., 2006, 2012; Rönkkö et al., 2013; Shi and Harrison, 1999; Tobias et al., 2001; Schneider et al., 2005; Khalek et al., 2003; Pirjola et al., 2019), and some of them can contribute the particle mass and number concentration of urban air after they have underwent oxidizing processes in the atmosphere (secondary aerosol) (Kroll et al., 2012; Chirico et al., 2010; Gordon et al., 2014). Thus, the physical and chemical properties of ultrafine particles originated from traffic emissions are dynamic by nature, challenging the monitoring of their concentrations as well as emission reduction actions.

Recently, World Health Organization (WHO) (WHO, 2021) introduced particle number concentration as a new recommended air quality metric to monitor, which significantly increases need for understanding the characteristics and sources of ambient ultrafine particles. For instance, the understanding of the anthropogenic emissions of the smallest sub-3 nm particles is scarce, although their contribution to particle number concentrations have been reported to be large (e.g. Sgro et al., 2008; Alanen et al., 2015; Rönkkö et al., 2017). The number of different particle sources is large, and the emission profiles of those sources can have large variation, especially from particle number emission and particle composition point of view. For instance, diesel engines utilized both in heavy and light duty vehicles have been reported to emit primary soot and ash particles mostly being in ultrafine particle size range, but their actual emissions strongly depend on exhaust after-treatment devices and fuel characteristics (Maricq et al., 2002; Chirico et al., 2010; Gordon et al., 2014). Fuel sulphur inhibits the proper functioning of after-treatment systems designed to reduce tailpipe emissions and corrodes engines and pipes. For example, exhaust sulphur compounds may experience partial storage in the after-treatment system at low temperatures and occasionally release at higher exhaust temperatures leading to the short-term impact of fuel sulphur content. Besides, storage of sulphur compounds in the DOC decreases the DOC oxidation power ("sulphur poisoning") and thus can increase gaseous hydrocarbon emissions. As the DOC does not totally prevent formation of organic condensable gases, it might promote formation of sulphuric acid that is a key nucleation gas (Arnold et al., 2012). Primary and fresh particle emissions affect mostly the air quality near the emission sources, whereas the effect of the secondary processes are more important on a regional scale (Rönkkö and Timonen, 2019).

The particle emissions from gasoine vehicles have been reported to be significantly lower than diesel vehicles without particle filtration systems, but e.g. modern fuel injection strategies have been observed to result to elevated particulate emissions (Mathis et al., 2005; Raza et al., 2018; Rönkkö et al., 2023).

This study is a part of the project conducted in collaboration with Finnish and Indian research institutes. The main focus of that TAQIITA project was to understand the role of traffic in respct of air quality in India. In this study we characterized the effects of fuel and vehicle types on real-world exhaust particle number, size distribution and composition of passenger cars. We utilized comprehensive high time resolution instrumentation to study primary, fresh and secondary particle emissions at transient and steady driving conditions. To focus on exhaust plume concentrations and real emissions, the measurements were conducted by chasing the vehicles by two mobile laboratories equipped with different instrument setups. Particularly, the investigated particle size range includes even nanocluster aerosols (particles smaller than 3 nm), which have been reported to dominate roadside particle number concentrations (Rönkkö et al., 2017), but are only poorly studied in the literature of vehicular emissions.

The test vehicles, fuels and driving cycles were chosen to represent the passenger car fleet in India (Pirjola et al., 2019) where air pollution is a huge problem (Ravishankara et al., 2020; Martikainen et al., 2023). Simultaneously, the exhaust emissions of Indian vehicles are poorly understood, as well as the traffic emissions of many other highly polluted countries. This lack of information is even more clear when considering the recent air quality guidance from WHO which shifts the focus from mass-based particulate pollutant metrics more to particle number and composition (WHO, 2021). Thus, this study is one of the first systematic real-world experimental investigations that produced novel information for these purposes from "Indian" perspective. The results of this study can be used in assessment and designing new traffic fuel related policies, in air quality modelling, in emission inventories and when designing new emission and air quality regulations especially for heavily polluted urban environments.

2. Methods

2.1. Measurement site, test vehicles and fuels

Real-world driving tests were conducted by a chasing method for two passenger cars on an approximately 2 km long straight road in Alastaro, Finland. The location was suitable for emission measurements due to insignificant local pollutant sources and other traffic (Karjalainen et al., 2014; Wihersaari et al., 2020; Pirjola et al., 2015, 2019). The tested cars were a diesel vehicle Euro 4 Toyota Corolla 2.2 D-4D (4 cylinders, displacement 2.2 dm3, model year 2007, maximum power 100 kW), equipped with a diesel oxidation catalyst (DOC), and a gasoline vehicle Euro 4 Suzuki SX4 (4 cylinders, displacement 1.6 dm^3, model year 2005, maximum power 79 kW), multipoint injection (MPI) engine that was equipped with a three-way catalyst converter (TWC).

European diesel (EN590) with fuel sulphur content (FSC) of 6.1 mg/kg, and Indian diesel (BS IV) with higher FSC of 34.7 mg/kg. The diesel vehicle and diesel fuels were the same as used in Pirjola et al. (2019). The fuel properties can be found in Table S1 (see also the Supplement of Pirjola et al., 2019). The gasoline vehicle run with low sulphur (<10 mg/kg) 98-octane gasoline-ethanol blend fuel the ethanol concentration being below 10%. For both vehicles the used engine oil was fully synthetic high performance motor oil Neste City Pro LL 5 W-30 which allows extended oil drain intervals.

2.2. Mobile laboratories and instrumentation

Mobile laboratories Sniffer (e.g. Pirjola et al., 2004, 2016) and ATMo-Lab (Rönkkö et al., 2017) with different instrumentation were used to chase the cars. In Sniffer the sampling occurred above the front bumper at 0.7 m height from the ground, and the distance between Sniffer and the passenger car was kept constant ~10 m. With 1 s time resolution the number concentration of particles larger than 2.5 nm was measured by a CPC 3776 and number size distribution of particles (10 nm - 1 μm) by an ELPI (Electrical Low Pressure Impactor, Dekati Ltd.) (Keskinen et al., 1992) equipped with a filter stage (Marjamäki et al., 2002) and an additional impactor stage (Yli-Ojanperä et al., 2010). Fresh exhaust particles were measured before and primary exhaust particles after the thermodenuder (TD) (Rönkkö et al., 2011) where the sample temperature was raised to 265 °C and the evaporated components were removed by activated charcoal. Particle losses were corrected according to Heikkilä et al. (2009). The black carbon (BC) in the PM_1 size fraction was measured by a 7-wavelength (370, 470, 520, 590, 660, 880, and 950 nm) aethalometer (AE 33, Magee Scientific) (Drinovec et al., 2015) with a time resolution of 1 s. The 880 nm wavelength was used for the BC analyses. The CO_2 concentration was monitored with a LICOR LI-840A gas analyzer. A weather station on the roof at a

height of 2.9 m provided meteorological parameters (wind speed and direction, temperature and relative humidity). The Sniffer's speed was recorded by a GPS system (model GPS V; Garmin).

In the ATMo-Lab, the aerosol sample was drawn from the lower-mid sampling line at the front of the vehicle, which is located approximately 50 cm above ground at the hight of the front bumper. The sample was drawn to a CO_2 analyzer (Sick Maihak, Sidor), to a classic ELPI (Dekati Inc.) with additional stages, to a PSM (including Airmodus A20 CPC, particle sizes down to 1.5 nm), two CPCs (CPC 3776, 3775, TSI Inc) and TSAR (Simonen et al., 2017) operated with 5.5 lpm sample flow and 75% light intensity setting. A bridge diluter (DR 7.5) was used to dilute the sample flow to PSM and CPCs. Before the TSAR, additional ozone, CO, and water vapour were fed to the sample line. After the TSAR, the other ELPI was used downstream of the TSAR to measure the particle concentrations of aged aerosol sample, after an additional dilution. An addition dilution with the DR of 4.1 preceding the second ELPI was used to keep the total flow rate through the TSAR at 5.5 lpm. CO (Environnement S.A., CO12M), RH (Vaisala MI70) and ozone (Model 205, 2B Technologies) were measured after the TSAR. A soot-particle aerosol mass spectrometer (Onasch et al., 2012) (SP-AMS; Aerodyne Research Inc.) was used to measure the composition of particles, equipped with a valve to choose the aerosol from TSAR or from sampling line bypassing the TSAR.

The measurement instrumentation of both mobile laboratories can be found in the supplement Fig. S1.

2.3. Driving cycles

Constant speed tests at 20, 40 and 70 km/h with gears 2, 3 and 4, respectively, were carried out on three sequential days in September 2017. Mild wind of 1 m/s blew from north-east and temperature varied in the range of 10–15 °C. Furthermore, transient acceleration/deceleration tests were performed in the following way: Fast acceleration occurred from 20 km/h to 50 km/h with gear 2 or 3 followed by constant speed driving around 20 s after which the speed decelerated by engine braking back to 20 km/h. The cycles (20-50-20) were repeated 5–6 times. The other cycle (30-70-30) with gear 3 was repeated 4 times.

2.4. Data analyses methods

Quality of the measurement data were validated first in respect of the proper functioning of instruments and then aligned based on the measurement time. Particle number emission factors EF (#/km) were calculated by equation (1)

$$EF = \frac{\sum_{i=1}^{n}\left(\Delta N_j \bullet MAF_i\right)}{\rho_{exh} \bullet s} \bullet \frac{\sum_{i=1}^{n}\Delta CO_{2,i}^{raw}}{\sum_{i=1}^{n}\Delta CO_{2,i}^{dil}} \quad (1)$$

where n is the number of seconds considered, ΔN (cm^{-3}) and $\Delta\ CO_{2,i}^{dil}$ (ppm) are the momentary concentrations of particles and CO_2 when the background concentrations (bg) were subtracted, MAF_i is the exhaust mass flow (g/s), ρ_{exh} is the exhaust density (0.0012 g/cm^3) and s is the mileage in km. $\Delta\ CO_{2,i}^{raw}$ (ppm) refers to the momentary raw CO_2 concentration (bg subtracted) measured on the dynamometer over the same transient cycle.

For the steady state tests the OBD data including speed, engine load and exhaust mass flow (MAF) from both vehicles were available allowing the determinations of emission factors in #/km. For the transient cycles it was successfully saved only for the gasoline car, but the OBD parameters for the same transient cycles were measured later in the laboratory. Although run resistances in the laboratory conditions can slightly differ from the real-world conditions, these values could be used since the road in Alastaro was flat, wind speed was very low, no rain occurred, and no other traffic was available. Besides emission factors, also the $\Delta\ N_{mean}/\ \Delta\ CO_{2,mean}$ and $\Delta\ N_{median}/\ \Delta\ CO_{2,median}$ i.e., ratios of the mean and median values (over the measurement period) of the momentary Δ N and Δ CO_2 values, were calculated since those values might be interesting and valuable for the air quality researchers and authorities. These represent particle number emissions and can be compared to the ratios of Δ N and Δ CO_2 measured e.g. for traffic in urban environments (Rönkkö et al., 2017).

3. Results and discussions

3.1. Exhaust plume particle number concentrations

Fig. 1 shows temporal variation of vehicles' exhaust plume particle number concentrations measured with instruments with different cut-off sizes, i.e., particle number concentration for particles with diameter (Dp) larger than 1.5 nm, 2.5 nm and 4 nm. In addition, the figure shows the time series of vehicles' speed during the three subsequent cycles and the changes in plume CO_2 concentrations. These are shown separately for gasoline and diesel car, the latter with two different diesel fuels.

CO_2-trends shown in Fig. 1 describe how the combustion originated exhaust is seen in exhaust plume. In all situations studied here the CO_2 elevated especially in acceleration conditions and decreased in deceleration conditions. In this study, the deceleration was conducted mostly by engine braking, meaning the situation when no fuel is injected to the engine cylinders. In general, the CO_2 concentrations measured simultaneously with particle concentrations can be used to calculate the real fuel consumption specific emission factors and, on the other hand, to investigate the origin of the particles; previous studies have shown that the vehicles with internal combustion engines emit particles both during fuel combustion, in accelerations and steady driving (Maricq, 2007; Pirjola et al., 2015), and when fuel is not combusted in the engine, i.e. in engine braking conditions (e.g. Rönkkö et al., 2014; Karjalainen et al., 2014; Wihersaari et al., 2020).

The particle number emissions of gasoline car were significantly lower than the emissions of diesel car. Regarding the particle emissions of gasoline car, they were observed mostly in accelerations but minor increases in plume concentrations of particles were seen also during decelerations. In addition, higher exhaust plume concentrations were observed in 30–70 cycle than in 20–50 cycle, both of them conducted with 3rd gear, indicating that the driving pattern have significant effect particle emissions of gasoline cars. It should be noted that the change in particle number concentration patterns was associated especially with the emissions of small particles; while the particle number concentrations were relatively independent of the lower cut of size of the instrument during the 20–50 cycle, in 30–70 cycle the number concentrations were higher when measured with lower cut-off size instruments. Thus, the result indicates that the change in driving pattern affects especially the gasoline car exhaust particles smaller than 4 nm in particle size, and even the nanoclusters being below 2.5 nm in particle size.

With both diesel fuels, the particle emission from diesel car was even more than ten times higher than the particle emission from gasoline car. In addition, the temporal patterns of particle concentrations and thus also the instantaneous particle emissions were different; like the gasoline car, diesel particles were emitted during acceleration but also during deceleration. We did not observe large effects of diesel fuel quality on particle number concentrations in the exhaust plume; both diesel fuels produced relatively similar particle number concentrations during accelerations and decelerations. As well the effect of driving conditions on particle emissions during decelerations was similar with the both diesel fuels; high particle number concentrations were observed especially when decelerated from 50 km/h to 20 km/h with 2nd gear.

With diesel car, the sizes of emitted particles were clearly dependent on driving conditions; while during accelerations similar values were measured with all the instruments (Fig. 1), during decelerations significantly higher concentrations were measured with instruments with lower cut-off size (CPC and PSM). This means that the particles emitted during accelerations were larger than 4 nm in particle size and thus

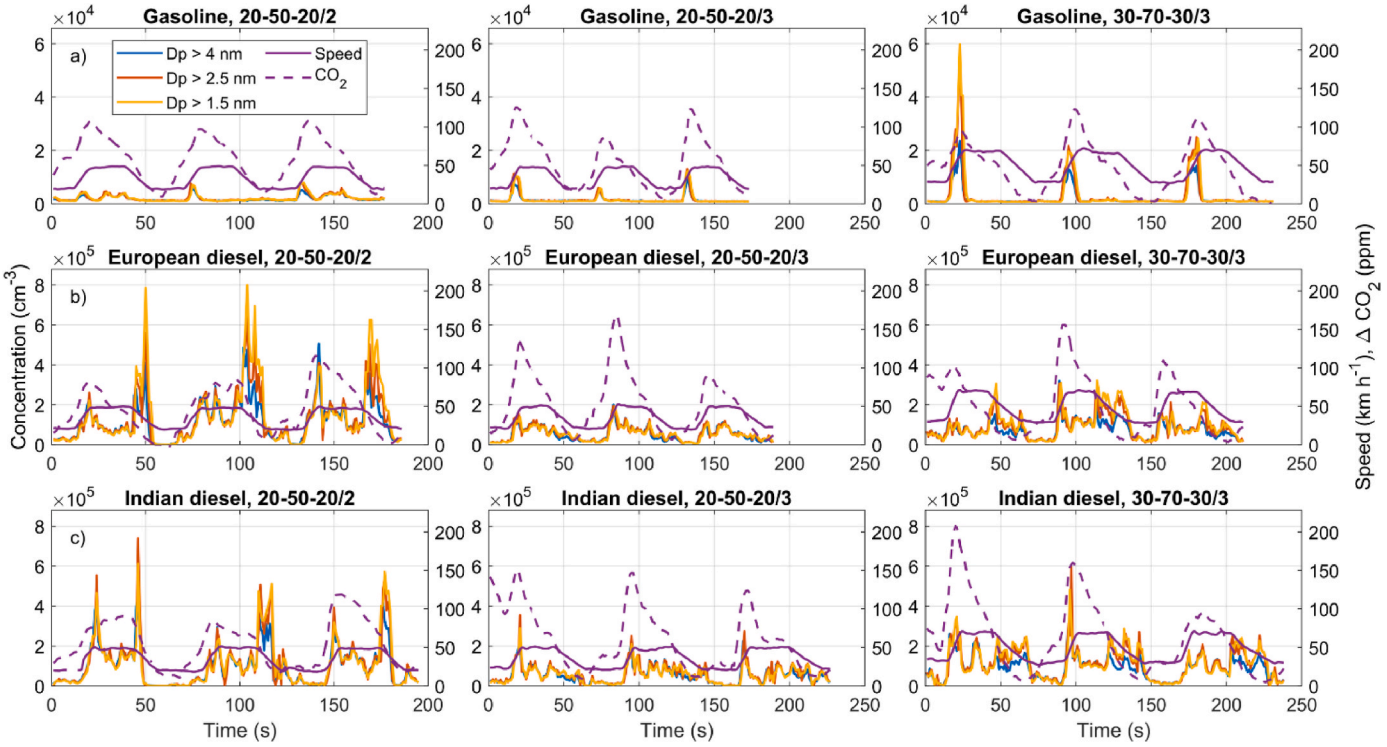

Fig. 1. Time series of exhaust plume particle number concentrations, i.e., fresh exhaust particle concentrations, speed, and increase of exhaust plume CO_2 concentration. Time series are shown for different speed profile and gear combinations and for different vehicle and fuels; a) gasoline, b) European diesel, c) Indian diesel. Three subsequent transient cycles are shown in each subfigure. The cutpoints of 4 nm, 2.5 nm and 1.5 nm correspond to measurement with CPC3775, CPC3776 and PSM, respectively. Note that the subfigures for gasoline car have different y-axes. The results in logaritmic scales are presented in supplementary material (Fig. S2). Background particles were not subtracted.

larger than the particles emitted during the decelerations. Hence, diesel cars are a source of sub-4 nm particles at motoring conditions.

3.2. Time resolved particle number size distributions of exhaust plumes

As an example, Fig. 2 shows the time series of particle number size distributions for the fresh and primary exhaust particles for all fuels during the three subsequent transient cycle 20-50-20 driven with the 2nd gear. The size distributions were measured by the ELPI, and the particles in the size range of 7–1000 nm are shown. The effect of background particles was subtracted. The particle number size distributions of exhaust plumes for two other driving cycles (20-50-20, 3rd gear; 30-70-30, 3rd gear) are presented in Figs. S3 and S4.

With all fuels the emitted particles were mostly in the ultrafine particle size range, i.e., smaller than 100 nm. However, particle emissions depended on driving conditions so that the largest emissions, in respect of particle concentrations and sizes, were observed during accelerations, even though with the gasoline vehicle the particle sizes and the concentrations were much lower than with the diesel-fuelled vehicle. This is in good agreement with Fig. 1. With both diesel fuels some particle emissions were seen during decelerations, whereas for the gasoline vehicle the particle emissions were negligible. With both cars, the particle concentrations were lower when running at the constant speed of 20 km/h than with the constant 50 km/h speed (Fig. 1). The particle size range was typically narrower at lower speed due to the significantly lower concentrations of nanosized particles (Dp < 20 nm).

Fig. 3 illustrates the results from the more detailed analysis of particle size distributions during acceleration and deceleration. Left hand side panels of Fig. 3 show average fresh and primary particle size distributions during acceleration conditions (acceleration larger than 1 m/s^2) and right-hand side panels show the single fresh exhaust particle size distributions for deceleration conditions conducted by engine braking so that the distributions dec1, dec2 and dec3 describe the beginning, the middle and the end of the deceleration. In addition, background aerosol particle size distributions (bg) are shown.

For the gasoline car the average fresh exhaust plume particle size distributions during acceleration were bi-modal; separate particle modes were observed in particle size ranges smaller and larger than 40 nm, peaking at around 20 nm and at around 70 nm. However, the mode at 70 nm was significantly affected by background aerosol particles, which can be seen from Fig. 3a (green line). The 96 h backward-trajectory analysis of FLEXTRA by NILU (Norwegian Institute for Air Research; Stohl et al., 1995) showed that an air mass was transported through central Russia and arrived in southern Finland (Fig. S5a) potentially carrying anthropogenic pollutants.

Furthermore, it should be kept in mind that the distributions shown in Fig. 3 are averages of size distributions measured during accelerations. Every individual size distribution can significantly deviate from the averaged value due to different phases of the acceleration and differences between the individual acceleration situation, e.g. driver's behaviour, driving direction, as well as slightly different acceleration of the test vehicle and chasing laboratory vehicle. This is indicated by Fig. 2 which shows how the exhaust plume particle size distributions change in time, and by Fig. S6 which shows the standard deviations for 20-50-20 case with 2nd gear.

The exhaust plume particle size distributions of gasoline cars were substantially affected by thermal treatment of the sampled aerosol (Fig. 2, right panel) and Fig. 3 left panel); this was observed especially with the particle mode at particle sizes larger than 40 nm (soot mode particles). However, also this effect seems to be originated by the effect on background aerosol particles (see the difference between solid and dashed green lines in Fig. 3a), and thus the effect on particles emitted by the car was minor. The thermodenuder slightly decreased the concentrations of the smallest particles emitted by gasoline car at two of three

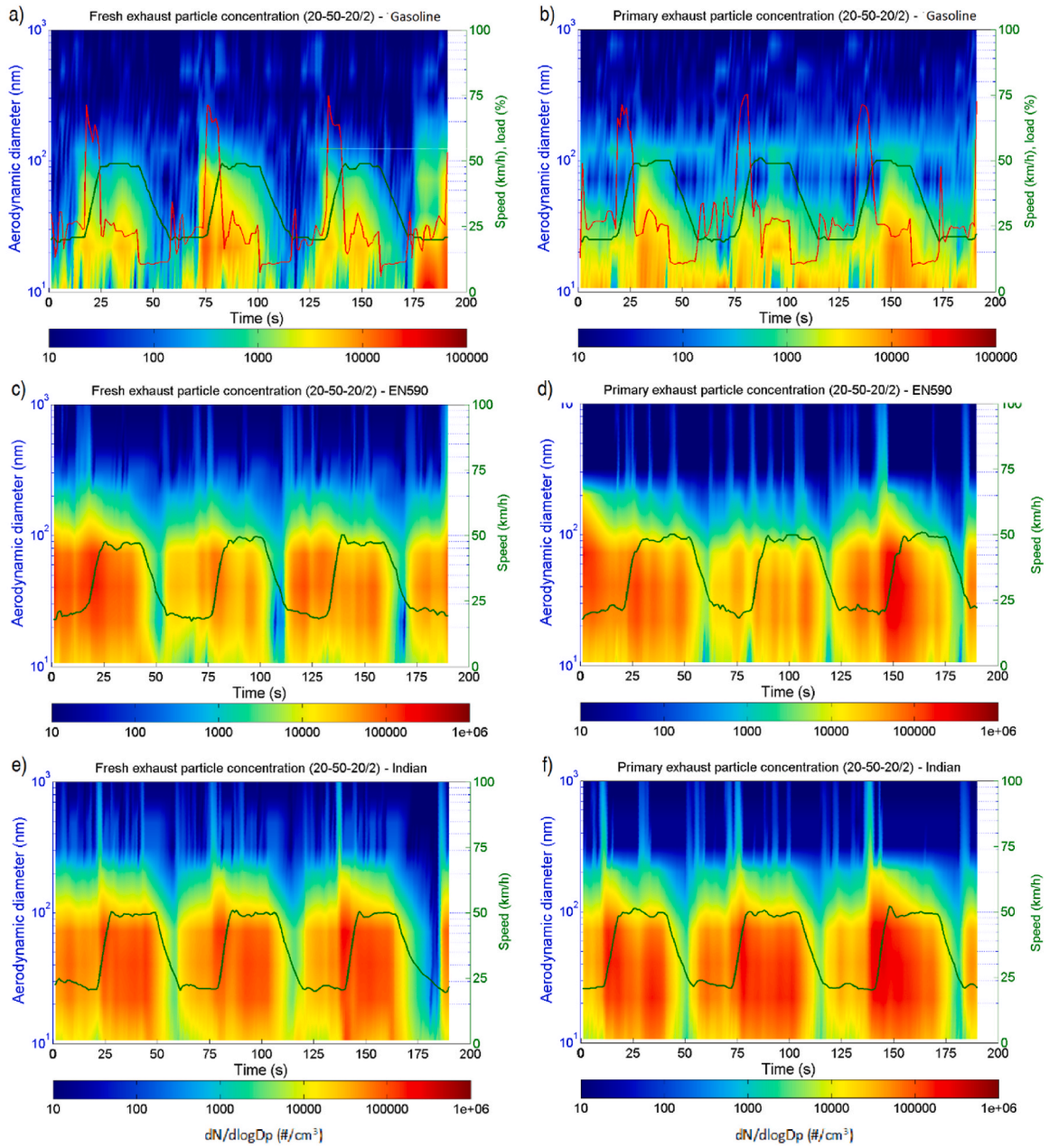

Fig. 2. Time resolved exhaust plume particle size distributions for fresh exhaust (left) and primary exhaust particles (right) during the driving cycle 20-50-20 km/h driven with 2nd gear. Size distributions are shown for gasoline car (a,b) and diesel car, for the latter separately for two different diesel fuels, European diesel (EN590) (c,d) and Indian diesel(e,f). Particle size in aerodynamic diameter (nm) is shown on the left y-axis, vehicle speed (km/h) on the right y-axis and particle concentrations (particles/cm^3) by colour scale.Engine load (%, orange curve) is shown for the gasoline car. Background particles were subtracted.

driving cycles. One should remember that when comparing the fresh and primary particle size distributions they were not measured simultaneously and, as indicated by Fig S6, the deviation of individual particle size distributions was large.

In case of diesel car, the averaged particle size distributions during acceleration were unimodal and relatively similar for both of the studied fuels, even though the distribution was somewhat higher and wider with the Indian diesel than with the European diesel. 20–80 nm particles dominated the concentrations. The effects of background particles cannot be ruled out, since during the Indian diesel measurements an airmass transported pollutants from central Russia (Fig. S5b) whereas during the European diesel measurements an airmass moved three days over the North Atlantic transporting cleaner air to the measurement location (Fig. S5c).

The thermodenuder slightly shifted the distributions towards smaller particle sizes (Fig. 3, at least when using EN590 diesel fuel. This shift of size distributions to smaller particle sizes can be interpreted as a result of evaporation of semivolatile compounds from surfaces of soot particles. The particle size distribution measurements combined with volatility measurements indicate higher emissions of solid black carbon/soot particles from diesel car compared to gasoline car. It is worth noting that the thermodenuder measurements did not indicate the presence of nucleation mode source in the size range observed by the ELPI. This differs from some previous studies reporting nucleation mode particle formation especially at elevated loads and when fuels with higher sulphur contents are used.

Regarding diesel exhaust emissions during deceleration, Fig. 1 showed that high number concentration of particles smaller than 4 nm

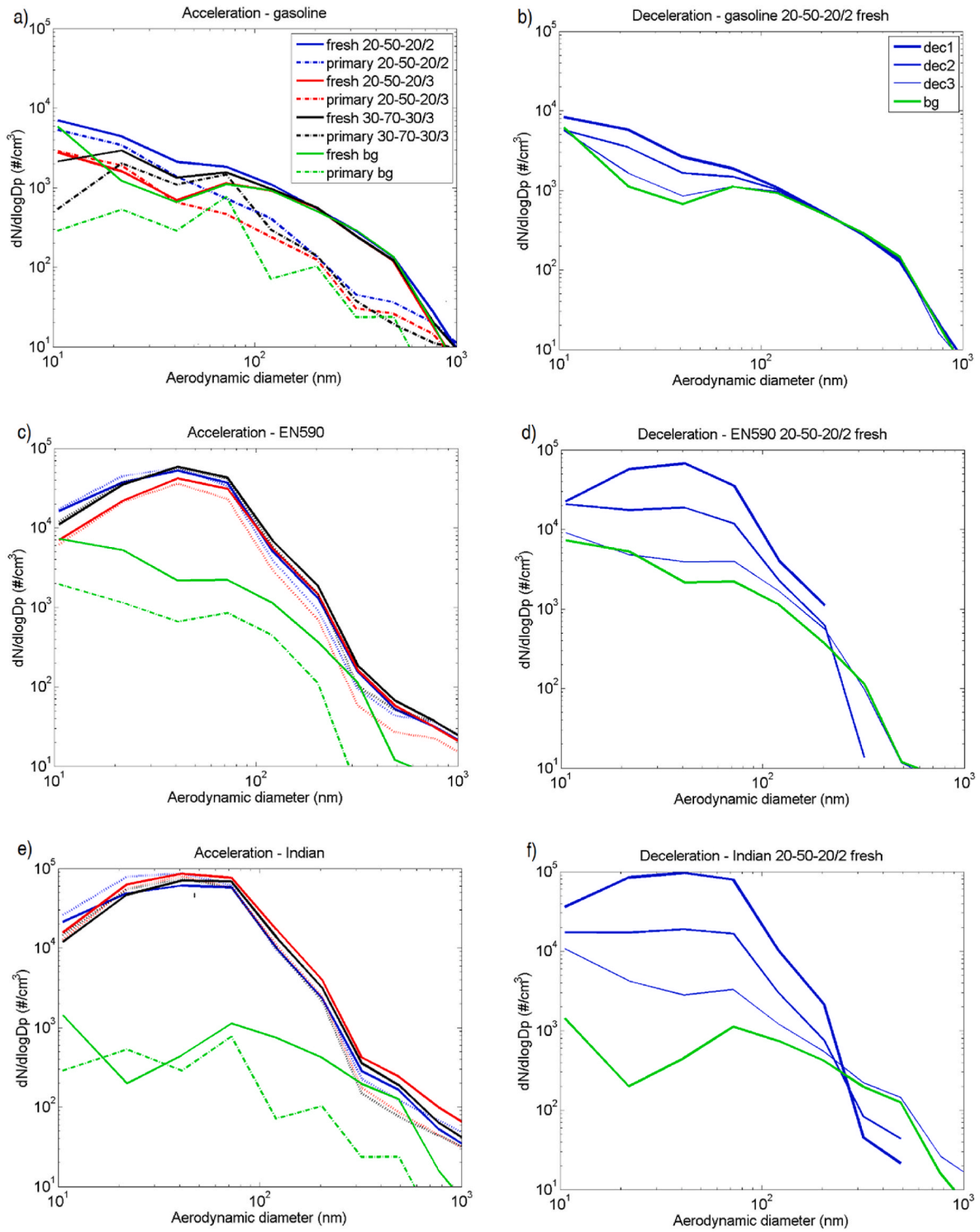

Fig. 3. Average exhaust plume particle number size distributions during accelerations for the gasoline car (a), diesel car with European diesel (EN590) (c) and diesel car with Indian diesel (e). The size distributions are shown for primary and fresh exhaust and for each studied driving cycle. Furthermore, shown are three single size distributions (dec1, dec2, dec3, see details in the text) for fresh exhaust particles emitted from gasoline (b), European (EN590) (d), and Indian (f) fuelled vehicles during decelerations for the 20-50-20 cycle with 2nd gear. Ambient background particles size distributions are shown as well.

were observed and these particles were smaller than the ones observed during acceleration. When comparing the number emissions from the diesel fuels measured by the ELPI and CPC, a large amount of 2.5–7 nm particles appeared in exhaust plume during decelerations as shown for example for Indian diesel (Fig. 4a). These particles consisted of semi-volatile compounds since the thermodenuder treatment reduced the concentration measured by the CPC closer to the parallel measurements by the ELPI (Fig. 4b). These semivolatile compounds are most likely originated from lubricant oil. Similar conclusions were reported by Karjalainen et al. (2016a) who studied emissions from two heavy duty diesel vehicles over a transient cycle and reported high numbers of emitted exhaust particles during engine motoring. Those particles were smaller than 40 nm and the majority of them were volatile. After the TD their sizes were smaller than 10 nm thus owing a small nonvolatile core,

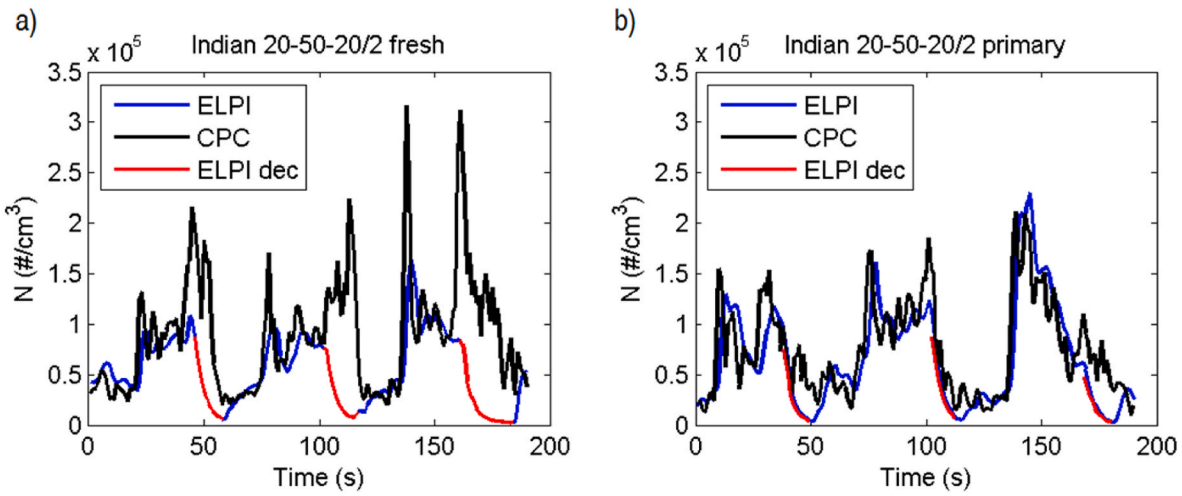

Fig. 4. Fresh (a) and primary (b) particle number concentrations for the Indian diesel during 20-50-20 cycle with 2nd gear measured by the ELPI and CPC. Also shown are the concentrations during engine braking (red color). Note that both the ELPI data and CPC data have been corrected by the same correction factor for the losses in the thermodenuder.

originated from lube oil. As seen from Figs. 2 and 3, right side panels, the particle emissions gradually drop during decelerations, and after the ~20 s engine braking period the size distributions are rather close to the background distributions. As mentioned earlier, no fuel is injected to cylinders during engine braking. On the other hand, the evaporation of lubricant oil compounds in the engine cylinder depends on wall and piston temperatures of the cylinder leading to consumption of oil and to semivolatile particulate emissions (Karjalainen et al., 2016a,b). During engine braking the temperature decreases with time, reducing oil evaporation and thus the source of semivolatile particulate matter. This explains the drop of particle emissions during deceleration.

3.3. Particle number emission factors

The number emissions factors (EF, #/km), shown in Table S2 for constant speed driving and in Table S3 for transient cycles for particles larger than 2.5 nm were calculated using the data from the CPC measurements. Due to a technical problem, the CPC data were not available for the EN590 diesel at 20 km/h constant speed driving. Therefore, the corresponding data for that driving situation were adopted from the corresponding parts of the transient cycles.

Over the steady state driving, the obtained particle EFs were systematically larger for the fresh emissions compared to the primary emissions (Table S2). Largest emission factors of 8.6×10^{13} #/km and 6.6×10^{13} #/km with European and Indian diesel fuels, respectively, appeared at a constant speed of 70 km/h. Importantly, the Indian diesel fuel was not observed to produce larger particle number emissions compared to the European diesel in spite of its larger sulphur content; thus, the improving of fuel quality in respect of its sulphur content may not directly decrease the primary and fresh exhaust particle number concentrations of traffic influenced areas. In this study, the reason for this observation is the lack of nucleation mode particles under these steady state driving conditions. However, it should be kept in mind that the fuel sulphur content has been observed to affect particle number emissions, especially in heavy duty diesel vehicles. Furthermore, the larger sulphur content might affect fresh particle mass concentrations due to higher condensation of sulphur compounds on the soot particles. The particle number emission factors for the gasoline vehicle were only 1–3% of the emissions factors of the diesel vehicle, both regarding fresh and primary particle emissions.

However, over the transient cycles the fresh and primary particle number emission factors (EF, #/km) were systematically highest for the Indian diesel, followed by the European diesel and more than a decade smaller for the gasoline fuelled vehicle (Table S3). This observation was independent of the cycle. As expected, based on the information above, the highest EFs for fresh and primary particles were obtained when driving with 2nd gear over the cycle 20-50-20 km/h; for example, EFs were 2.1×10^{12} #/km, 9.0×10^{13} #/km and 1.6×10^{14} #/km for fresh gasoline, European and Indian exhaust particles, respectively. The smallest EFs were determined with 3rd gear over the same speed cycle of 20-50-20 km/h.

In addition to emission factors using the unit #/km, Tables S2 and S3 present the particle emissions as an increase of exhaust plume particle number divided by the increase of exhaust plume CO_2 concentrations. The values show that, under the conditions studied here, the ratios dN/dCO_2 had large variation, both because of the changes in driving condition but also because of changes in fuel and vehicle. For instance, regarding fresh exhaust particles, the lowest ratios were observed for gasoline vehicle driving with constant speed, and the highest for diesel vehicle operating at transient conditions with Indian diesel fuel. Thus, the results demonstrate that, from the viewpoint of individual vehicles, the ratio between particle number and CO_2 is not constant and any universal ratios cannot be assumed to be observed in ambient studies. However, when studying the ambient aerosols in the vicinity of traffic routes, the differences between the individual vehicles are averaged over the local vehicle fleet, and the emission factors as well as the dN/dCO_2 ratios represent the average emissions of local traffic. To enable the determination of such emission factors also in the studies of ambient aerosols (e.g. Rönkkö et al., 2017), it is necessary to combine air quality measurements with simultaneous measurements of ambient CO_2 concentrations.

3.4. Chemical composition of particles and secondary aerosol formation potential of exhaust

BC concentrations of vehicle exhaust plume as a function of time, together with increases of exhaust plume CO_2 concentrations, are presented in Fig. 5. The average compositions of particulate matter for each driving situation are presented in Fig. 6. In general, the time series of BC had some similar features than particle number time series (Fig. 1); fresh BC concentrations of gasoline vehicle exhaust plume were very small, close to the detection limit of the measurement instrument, and those of diesel vehicle were peaking especially in accelerations. However, in contrast to particle number concentrations, BC was not peaking during decelerations. Because the BC formation takes place in combustion, resulting to similar concentration trends with exhaust plume CO_2

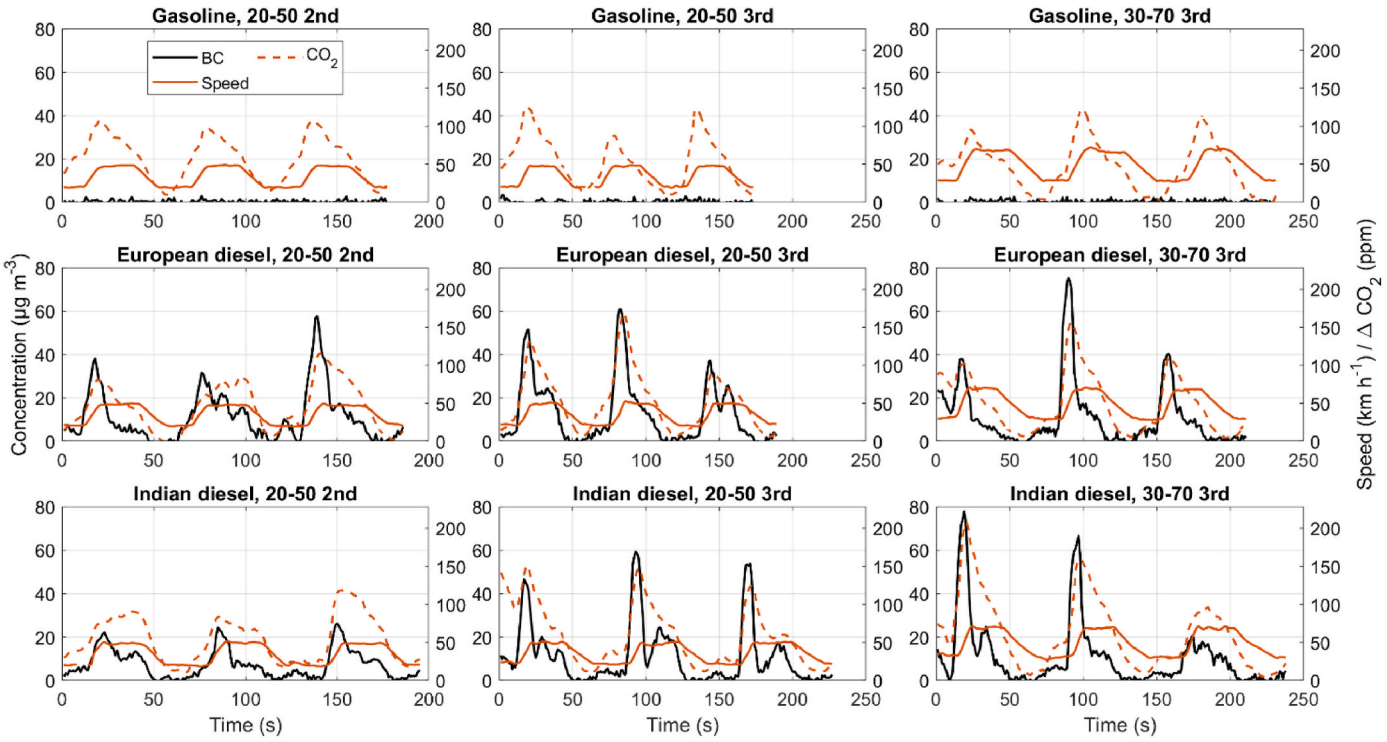

Fig. 5. Black carbon concentrations of fresh exhaust plumes of gasoline car and diesel car with two different fuels. Also the speed of test vehicle as well as increase of exhaust plume ΔCO_2 concentrations (background CO_2 was subtracted) are shown.

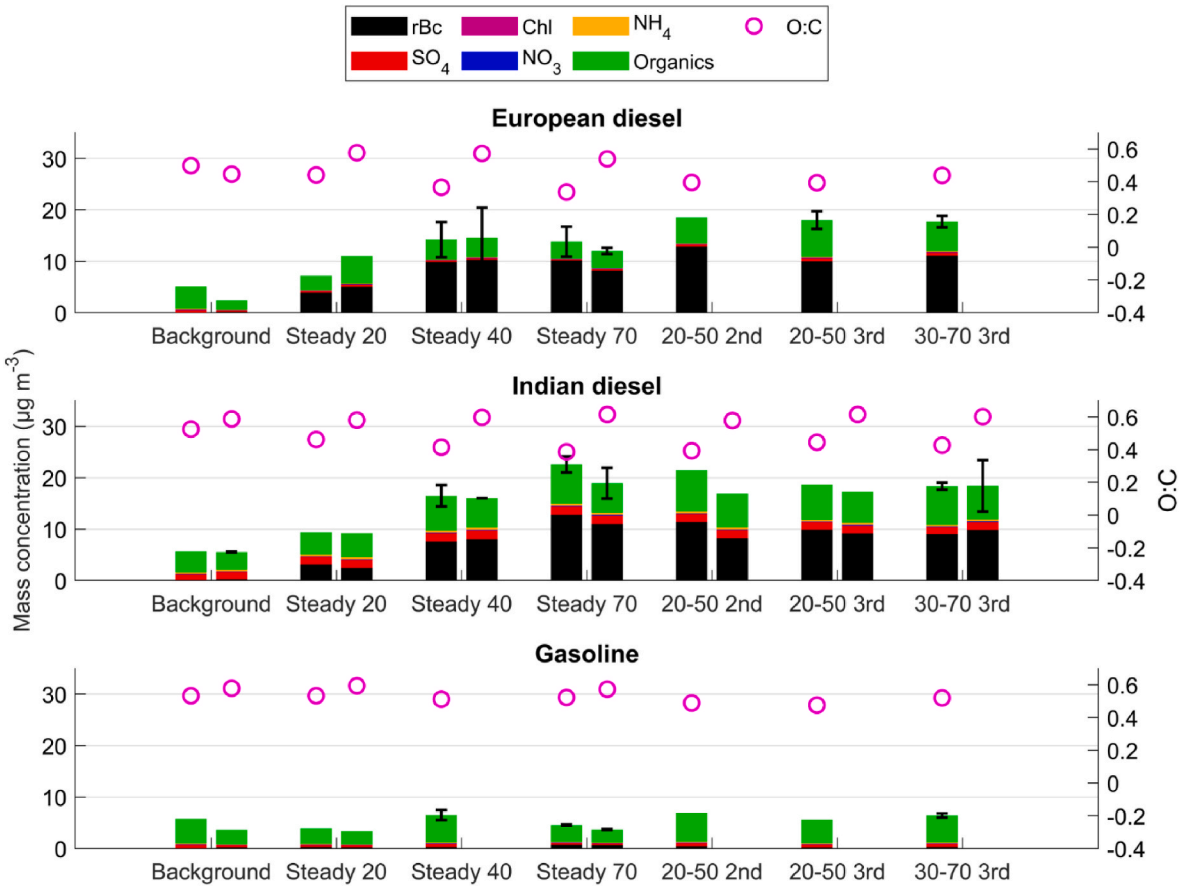

Fig. 6. Mass concentrations of the components of exhaust particles (left axis) and O:C ratio of particles (right axis). AE33 was used for the BC, other components and O:C were measured using the SP-AMS. Two bars are shown for each driving situation, left bar indicating fresh exhaust particles and the right-hand bar indicating aged exhaust particles.

(Fig. 5), this observation supports the discussion above that the elevated particle number emissions during deceleration are not originated from combustion process.

Fig. 6 shows the average composition of fresh and aged particulate matter of exhaust plumes of diesel car and gasoline car. Due to technical reasons affecting the data quality, the data for aged particulate matter at transient cycles of diesel car fuelled with European diesel and gasoline car are not presented. In addition, also the compositions of ambient background particles are shown, separately for each vehicle and each fuel investigated. Furthermore, Fig. 6 shows the O:C ratios of particles analysed from the SP-AMS data. Firstly, with the diesel car fuelled with Indian diesel and European diesel, the BC formed the most important fraction of the particulate mass. Secondly, the mass concentration of particulate organic compounds was higher in exhaust plume than in background aerosol measurements, and the share of organic compounds in particulate mass was higher with Indian fuel. Thus, it can be concluded that, in respect of particle composition, the role of organic compounds is significant which should be taken into account e.g. when evaluating the health impacts of the exhaust aerosol from these two types of diesel fuels. However, it should be noticed that the exhaust plume particle size distributions typically consisted only of soot mode, indicating that the exhaust originated organic compounds shown in Fig. 6 were mostly internally mixed with soot/BC particles. With all of the cars and fuels studied here, the mass of particulate sulphuric compounds in the exhaust plume was relatively close to the values measured for the background aerosol, indicating that the cars did not emit significantly sulphate. In principle, the higher fuel sulphur content of Indian diesel could lead to higher particulate sulphate concentrations and increased particle number concentrations in the exhaust plume. However, in this study we did not observe these.

Interestingly, the O:C ratios of organic compounds of fresh diesel car exhaust plume particles varied; the O:C ratio of exhaust plume particles gradually decreased from 0.5 (measured for the background aerosol) to approximately 0.3 (measured for the fresh exhaust aerosol at 70 km/h). This observation can be explained by higher contribution of less oxidized exhaust particles in the measured aerosol, since the O:C followed inversely the exhaust plume BC concentration. Thus, the O:C ratios of fresh exhaust plume particles are clearly lower than the O:C ratios of background air, giving one relatively simple way to differentiate fresh exhaust particulate matter from aged exhaust and e.g. urban background. Furthermore, Fig. 6 also shows the O:C ratios of aged exhaust for the situations when the functioning of TSAR was valid. All of those are slightly above the O:C ratios for the background and significantly higher than for the fresh exhaust aerosol. It should be noted that there are uncertainties in the concentrations of Fig. 6 because the measurements of each presented concentration bars were not simultaneous, and the measurements were affected e.g. by environmental parameters. However, the O:C ratios were always determined from simultaneously measured peaks of mass spectra, making their values more comparable than the ratios of the concentrations of exhaust plume particle compounds measured for fresh and aged exhaust and for different driving situations.

The oxidation state of fresh exhaust particles was further examined by subtracting the impact of background particles from the exhaust particles and plotting the average O:C and hydrogen to carbon ratios (H:C) for each car and measurement point (Fig. 7a). The particles from European diesel were least oxidized (smallest O:C for 20–50 2nd cycle) but the difference between Indian diesel and European diesel was small. Organics from the gasoline car were clearly more oxygenated than those from the diesel cars. By comparing steady and transient driving, organics from the constant speed measurement points were more oxygenated than those from transient cycles for Indian diesel and gasoline car, O:C ratio increasing with decreasing speed, however for the diesel car that trend was not visible.

The hydrocarbon content of exhaust particles was also different for different cars. Although the hydrocarbon pattern looked quite similar for every car in transient cycles, Indian diesel had relatively larger signal for saturated hydrocarbons (e.g. $C_3H_7^+$, $C_4H_9^+$ and $C_5H_{11}^+$ at m/z 43, 57 and 71) compared to corresponding unsaturated hydrocarbon fragments ($C_3H_5^+$, $C_4H_7^+$ and $C_5H_9^+$ at m/z 41, 55 and 69) than European diesel (Fig. S7). Gasoline car had nearly equal signal for the saturated and unsaturated hydrocarbons. Larger ratio of saturated to unsaturated hydrocarbons have been associated with the diesel fuel like organics whereas a lower ratio has been attributed to lubricating oil-like organics (Carbone et al., 2019). Based on this estimation, hydrocarbons from the gasoline car and European diesel car were located close to lubricating oil-like organics in $fC_4H_9^+$ vs $fC_4H_7^+$ plot ($fC_4H_9^+$ and fC_4H_{7+} denoted as the fraction of $C_4H_9^+$ and $C_4H_7^+$ in total hydrocarbons) while Indian diesel

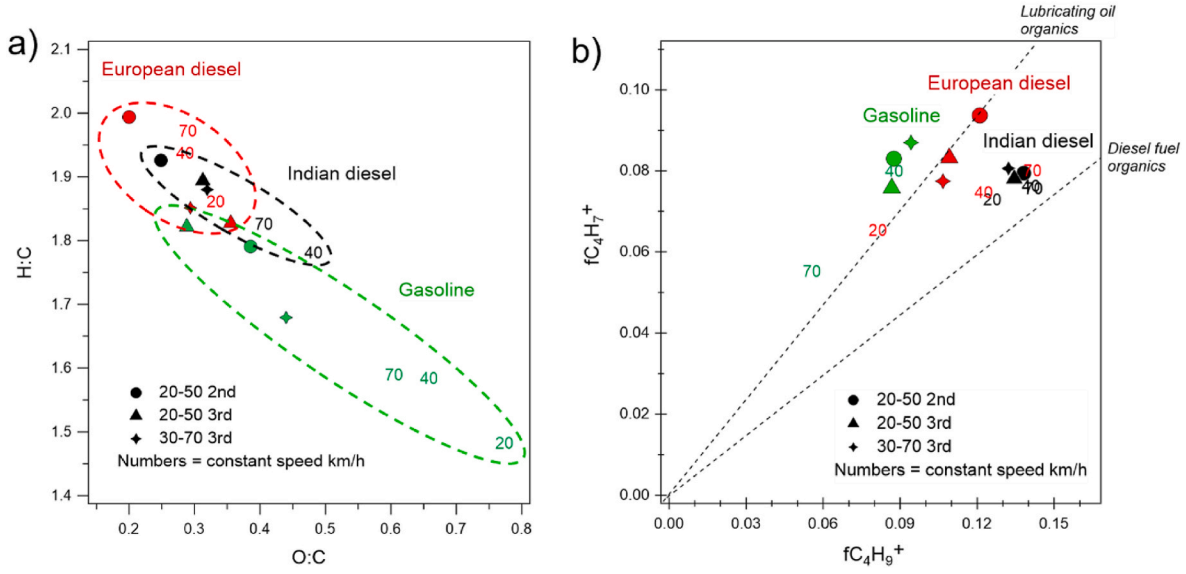

Fig. 7. Ratios of hydrogen-to-carbon (H:C) and oxygen-to-carbon (O:C) for organics (a), and the correlation of $fC_4H_7^+$ (at m/z 55) and $fC_4H_9^+$ (at m/z 57) for fresh gasoline, European diesel and Indian diesel particles (b). Dash lines in (b) are reference ratios for lubricating oil-like organics and diesel fuel-like organics from Carbone et al. (2019). The impact of background particles has been subtracted from the values. Constant speed measurement for Indian diesel at 20 km/h (a) and gasoline car at 20 km/h (b) were excluded from the figure as they were clear outliers.

particles were closer to diesel fuel-like organics (Fig. 7b) in transient cycles. However, when the constant speed points were examined, hydrocarbons from the European diesel car shifted close to Indian diesel at 40 and 70 km/h (close to pure diesel fuel organics) whereas at 20 km/h they were in line with the transient cycles. That finding is in line with the fraction of BC in particles (Fig. 6) as the contribution of BC was larger at constant speed of 40 and 70 km/h that at 20 km/h and transient cycles for European diesel. Hydrocarbon composition of Indian diesel was much less dependent on transient cycle or speed than that of gasoline and European diesel with all the measurement points at $fC_4H_9^+$-$fC_4H_7^+$ space being close to each other.

In terms of SOA formation, unsaturated hydrocarbon can be speculated to have larger SOA formation potential due to their larger reactivity. In this study, the comparison of fresh and aged exhaust composition indicates that the ageing of exhaust plume in the OFR did not significantly affect the mass of particles. Thus, the potential of exhaust to produce secondary aerosol mass was relatively low when compared to some previous studies of aged exhaust (Karjalainen et al., 2016b; Timonen et al., 2017). In principle, the result can be compared e.g. with Karjalainen et al. (2019) where the ratio of emission factors of aged and fresh particulate matter was low, approximately 1.1, for the diesel engine equipped with DOC and fuelled with fossil EN590 diesel fuel. The diesel car of this study was also equipped with DOC, and thus this real-world experiment confirms the previous laboratory experiments indicating relatively low secondary aerosol mass potential of the exhaust for diesel engines and vehicle with oxidizing exhaust after-treatment system. Thus, DOC can be seen as an efficient exhaust after-treatment device to mitigate the emissions of secondary aerosol precursors also in real-world driving conditions.

In this study the gasoline car had a multipoint fuel injection system which can be different in respect of secondary aerosol precursor emissions than the fuel injection systems in cars of previous studies. More importantly, these measurements were made when the three way catalyst (TWC) of the car was already warm; the TWC can significantly lower the SOA precursor emissions which has been seen in studies reporting the emissions during cold starts when the TWC is initially at ambient/room temperature and then start to warm during the emission testing (Pieber et al., 2018; Simonen et al., 2019). However, it should be noted that the real-world experiment and measuring from atmospheric exhaust plume can increase some measurement uncertainties, related to the effects of dilution, ambient background aerosols and environmental parameters such as temperature and humidity. Compared to the laboratory investigations, these parameters can have more variation between the individual measurements and even during each measurement. In addition, the exhaust is in real-world studies shortly exposed to atmospheric UV radiation before the measurement of potential secondary aerosol mass; however, the atmospheric lifetimes of the compounds proposed to be the most significant secondary aerosol precursors (BTEX compounds, see e.g. Timonen et al., 2017) are typically much longer (several days) than the time the exhaust is in the atmosphere between the emission and sampling (<1s).

4. Summary and conclusions

In general, passenger cars with internal combustion engines are significant sources of particle number emissions. Interestingly, the particle number emissions are contributed to also by very small particles, in addition to soot particles. Regarding the smallest particles, particle size range down to 1.5 nm was covered in this study, and we observed that especially with the diesel car, the deceleration conditions conducted with engine braking produced relatively high nanoparticle emissions.

The emission factors over the transient cycles varied in the range of (3.2–8.9)x10^{13} #/km and (3.9–8.7)x10^{13} #/km for fresh and primary particles larger than 2.5 nm, respectively, when the engine was fuelled with the European diesel. With the Indian diesel the corresponding emissions factors were (4.6–16)x10^{13} #/km and (4.1–9.8)x10^{13} #/km indicating slightly higher and more volatile particle emissions compared with the standard diesel. In the case of gasoline engine, the emission factors were in the range of (0.2–2.1)x10^{11} #/km. Consequently, our study highlights the need to include sub-10 nm particles in real world particle emissions studies.

Particle size distribution measurements showed that the particle number was mostly in ultrafine particle size range. In general, the particle number size distribution depended on driving situations and engine type, and it was significantly contributed by soot/black carbon particles.

Regarding the composition of particles, BC emission from gasoline car was very small while that from diesel cars was peaking during acceleration. In general, BC formed a significant fraction of particles from the diesel cars while gasoline car particles consisted mostly of organics. Additionally, the composition of organics was different for diesel and gasoline cars as organics from the gasoline car were more oxygenated while organics from diesel were largely hydrocarbons. Recent studies by Hakkarainen et al. (2022) showed that BC and related organic compounds can have significant impact on human alveolar cell toxicity.

With both vehicles investigated here in real-world driving conditions, the potential of exhaust to produce secondary aerosol mass was relatively low when compared to some previous laboratory studies of aged exhaust. This can be caused by exhaust after-treatment devices that mitigate efficiently the emissions of secondary aerosol precursors.

Credit author statement

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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

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References

Alam, A., Shi, J.P., Harrison, R.M., 2003. Observations of new particle formation in urban air. J. Geophys. Res. Atmos. 108 (3) https://doi.org/10.1029/2001jd001417. AAC 4-1 - AAC 4-15.

Alanen, J., Saukko, E., Lehtoranta, K., Murtonen, T., Timonen, H., Hillamo, R., Karjalainen, P., Kuuluvainen, H., Harra, J., Keskinen, J., Rönkkö, T., 2015. The formation and physical properties of the particle emissions from a natural gas engine. Fuel 162, 155e161. https://doi.org/10.1016/j.fuel.2015.09.003.

Arnold, F., Pirjola, L., Aufmhoff, H., Schuck, T., Lähde, T., Hämeri, K., 2006. First gaseous sulfuric acid measurements in automobile exhaust: implications for volatile nanoparticle formation. Atmos. Environ. 40, 7097–7105, 2006.

Arnold, F., Pirjola, L., Rönkkö, T., Reichl, U., Schlager, H., Lähde, T., Heikkila, J., Keskinen, J., 2012. First on-line measurements of sulphuric acid gas in modern heavy duty diesel engine exhaust: implications for nanoparticle formation. Environ. Sci. Technol. 46, 11227-11.

Bates, D.V., 2005. Ambient ozone and mortality. Epidemiology 16, 427–429. https://doi.org/10.1097/01.ede.0000165793.71278.ec.

Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., et al., 2013. Bounding the role of black carbon in the climate system: a scientific assessment. J. Geophys. Res. 118, 5380–5552.

Carbone, S., Timonen, H.J., Rostedt, A., Happonen, M., Rönkkö, T., Keskinen, J., Ristimäki, J., Korpi, H., Artaxo, P., Canagaratna, M., Worsnop, D., Canonaco, F., Prévôt, A.S.H., Hillamo, R., Saarikoski, S., 2019. Distinguishing fuel and lubricating oil combustion products in diesel engine exhaust particles. Aerosol. Sci. Technol. 53, 594–607. https://doi.org/10.1080/02786826.2019.1584389.

Charron, A., Harrison, R.M., 2003. Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere. Atmos. Environ. 37 (29), 4109–4119. https://doi.org/10.1016/S1352-2310(03)00510-7.

Chirico, R., DeCarlo, P.F., Heringa, M.F., Tritscher, T., Richter, R., Prévôt, A.S.H., et al., 2010. Impact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments. Atmos. Chem. Phys. 10, 11545–11563. https://doi.org/10.5194/acp-10-11545-2010.

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A.S.H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., Hansen, A.D.A., 2015. The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation. Atmos. Meas. Tech. 8, 1965–1979. https://doi.org/10.5194/amt-8-1965-2015.

Fu, B., Gasser, T., Li, B., Tao, S., Ciais, P., Piao, S., Balkanski, Y., Li, W., Yin, T., Han, L., Li, X., Han, Y., An, J., Peng, S., Xu, J., 2020. Short-lived climate forcers have long-term climate impacts via the carbon–climate feedback. Nat. Clim. Chang. 10, 851–855. https://doi.org/10.1038/s41558-020-0841-x.

Fushimi, A., Saitoh, K., Fujitani, Y., Hasegawa, S., Takahashi, K., Tanabe, K., Kobayashi, S., 2011. Organic-rich nanoparticles (diameter: 10-30 nm) in diesel exhaust: fuel and oil contribution based on chemical composition. Atmos. Environ. 45, 6326–6336.

Gordon, T.D., Pesto, A.A., Nguyen, N.T., Robertson, W.H., Na, K., Sahay, K.N., et al., 2014. Secondary organic aerosol production from diesel vehicle exhaust: impact of aftertreatment, fuel chemistry and driving cycle. Atmos. Chem. Phys. 14, 4643–4659. https://doi.org/10.5194/acp-14-4643-2014.

Hakkarainen, H., Salo, L., Mikkonen, S., Saarikoski, S., Aurela, M., Teinilä, M., et al., 2022. Black carbon toxicity dependence on particle coating: measurements with a novel cell exposure method. Sci. Total Environ. 838, 156543–156555. https://doi.org/10.1016/j.scitotenv.2022.156543.

Heikkilä, J., Rönkkö, T., Lähde, T., Lemmetty, M., Arffman, A., Virtanen, A., Keskinen, J., Pirjola, L., Rothe, D., 2009. Effect of open channel filter on particle emissions of modern diesel engine. J. Air Waste Manag. Assoc. 59, 1148–1154.

IARC, 2012. Diesel engine exhaust carcinogenic. Cent. Eur. J. Publ. Health 2012 Jun;20 (2):120, 138.

ICRP, 1994. Human respiratory tract model for radiological protection. ICRP Publication 66. Ann. ICRP 24 (1–3).

IPCC, 2018. Summary for Policymakers. In: Masson-Delmotte, V., Zhai, P., Pörtner, H.-O., Roberts, D., Skea, J., Shukla, P.R., Pirani, A., Moufouma-Okia, W., Péan, C., Pidcock, R., Connors, S., Matthews, J.B.R., Chen, Y., Zhou, X., Gomis, M.I., Lonnoy, E., Maycock, T., Tignor, M., Waterfield, T. (Eds.), Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. Cambridge University Press, UK and New York, NY, USA, pp. 3–24. https://doi.org/10.1017/9781009157940.001.

Janssen, N.A., Hoek, G., Simic-Lawson, M., Fischer, P., van Bree, L., ten Brink, H., Keuken, M., Atkinson, R.W., Anderson, H.R., Brunekreef, B., Cassee, F.R., 2011. Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2.5, 2011 Dec Environ. Health Perspect. 119 (12), 1691–1699. https://doi.org/10.1289/ehp.1003369. Epub 2011 Aug 2.PMID: 21810552.

Karjalainen, P., Pirjola, L., Heikkila, J., Lähde, T., Tzamkiozis, T., Ntziachristos, L., Keskinen, J., Rönkkö, T., 2014. Exhaust particles of modern gasoline vehicles: a laboratory and an on-road study. Atmos. Environ. 97, 262–270. https://doi.org/10.1016/j.atmosenv.2014.08.025.

Karjalainen, P., Ntziachristos, L., Murtonen, T., Wihersaari, H., Simonen, P., Myllari, F., Nylund, N.-O., Keskinen, J., Rönkkö, T., 2016a. Heavy duty diesel exhaust particles during engine motoring formed by lube oil consumption. Environ. Sci. Technol. 50, 12504–12511. https://doi.org/10.1021/acs.est.6b03284.

Karjalainen, P., Timonen, H., Saukko, E., Kuuluvainen, H., Saarikoski, S., AakkoSaksa, P., Murtonen, T., Dal Maso, M., Ahlberg, E., Svenningsson, B., Brune, W.H., Hillamo, R., Keskinen, J., Ronkkö, T., 2016b. Time-resolved characterization of primary and secondary particle emissions of a modern gasoline passenger car. Atmos. Chem. Phys. 16, 8559-8470.

Karjalainen, P., Rönkkö, T., Simonen, P., Ntziachristos, L., Juuti, P., Timonen, H., et al., 2019. Strategies to diminish the emissions of particles and secondary aerosol formation from diesel engines. Environ. Sci. Technol. 53, 10408–10416.

Keskinen, J., Pietarinen, K., Lehtimäki, M., 1992. Electrical low pressure impactor. J. Aerosol Sci. 23, 353–360.

Khalek, I.A., Spears, M., Charmley, W., 2003. Particle size distribution from heady duty diesel engine: steady-state and transient emission measurement using two dilution systems and two fuels. SAE Techical Paper 2003-01-0285.

Kittelson, D.B., 1998. Engines and nanoparticles: a review. J. Aerosol Sci. 29, 575–588.

Kroll, J.H., Smith, J.D., Worsnop, D.R., Wilson, K.R., 2012. Characterisation of lightly oxidised organic aerosol formed from the photochemical aging of diesel exhaust particles. Environ. Chem. 9, 211–220.

Kumar, P., Morawska, L., Birmili, W., Paasonen, P., Hu, M., Kulmala, M., Harrison, R.M., Norford, L., Britter, R., 2014. Ultrafine particles in cities. Environ. Int. 66, 1–10. https://doi.org/10.1016/j.envint.2014.01.013.

Lähde, T., Virtanen, A., Happonen, M., Söderström, C., Kytö, M., Keskinen, J., 2014. Heavy-duty, off-road diesel engine low-load particle number emissions and particle control. J. Air Waste Manage. 64, 1186–1194.

Maricq, M.M., 2007. Chemical characterization of particulate emissions from diesel engines: a review. J. Aerosol Sci. 38, 1079e1118 https://doi.org/10.1016/j.jaerosci.2007.08.001.

Maricq, M., Chase, R., Xu, N., Laing, P., 2002. The effects of the catalytic converter and fuel sulfur level on motor vehicle particulate matter emissions: light duty diesel vehicles. Environ. Sci. Technol. 36, 283–289.

Marjamäki, M., Ntziachristos, L., Virtanen, A., Ristimäki, J., Keskinen, J., Moisio, M., Palonen, M., Lappi, M., 2002. Electrical Filter Stage for the ELPI. Society of Automotive Engineers. SAE Technical Paper 2002-01-0055.

Martikainen, S., Salo, L., Kuuluvainen, H., Teinilä, K., Hooda, R.K., Datta, A., Sharma, V. P., Rahman, H., Subudhi, S., Kumar, P., Karjalainen, P., Keskinen, J., Timonen, H., Hyvärinen, A., Rönkkö, T., 2023. Reducing particle emissions of heavy-duty diesel vehicles in India: combined effects of diesel, biodiesel and lubricating oil. Atmos. Environ. X 17, 100202–100213.

Mathis, U., Mohr, M., Forss, A., 2005. Comprehensive particle characterization of modern gasoline and diesel passenger cars at low ambient temperatures. Atmos. Environ. 39, 107–117.

Monks, P.S., Archibald, A.T., Colette, A., Cooper, O., Coyle, M., Derwent, R., Fowler, D., Granier, C., Law, K.S., Mills, G.E., Stevenson, D.S., Tarasova, O., Thouret, V., von Schneidemesser, E., Sommariva, R., Wild, O., Williams, M.L., 2015. Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer. Atmos. Chem. Phys. 15, 8889–8973. https://doi.org/10.5194/acp-15-8889-2015.

Oberdörster, G., Oberdörster, E., Oberdörster, J., 2005. Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. Environ. Health Perspect. 113, 823e839 https://doi.org/10.1289/ehp.7339.

Onasch, T.B., Trimborn, A., Fortner, E.C., Jayne, J.T., Kok, G.L., Williams, L.R., Davidovits, P., Worsnop, D.R., 2012. Soot particle aerosol mass spectrometer: development, validation, and initial application. Aerosol Sci. Technol. 46, 804–817.

Pieber, S.M., Kumar, N.K., Klein, F., Comte, P., Bhattu, D., Dommen, J., Bruns, E.A., Kiluic, D., El Haddad, I., Keller, A., Czerwinski, J., Heeb, N., Baltensperger, U., Slowik, J.G., Prev ot, A.S.H., 2018. 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. 18, 9929e9954 https://doi.org/10.5194/acp-18-9929-2018.

Pirjola, L., Parviainen, H., Hussein, T., Valli, A., Hämeri, K., Aalto, P., Virtanen, A., Keskinen, J., Pakkanen, T., Mäkelä, T., Hillamo, R., 2004. "Sniffer" – a novel tool for chasing vehicles and measuring traffic pollutants. Atmos. Environ. 38, 3625–3635.

Pirjola, L., Karjalainen, P., Heikkilä, J., Saari, S., Tzamkiozis, T., Ntziachristos, L., Kulmala, K., Keskinen, J., Rönkkö, T., 2015. Effects of fresh lubricant oils on particle emissions emitted by a modern gasoline direct injection passenger car. Environ. Sci. Technol. 49, 3644–3652.

Pirjola, L., Dittrich, A., Niemi, J.V., Saarikoski, S., Timonen, H., Kuuluvainen, H., Järvinen, A., Kousa, A., Rönkkö, T., Hillamo, R., 2016. Physical and chemical characterization of real-world particle number and mass emissions from city buses in Finland. Environ. Sci. Technol. 50, 294–304.

Pirjola, L., Kuuluvainen, H., Timonen, H., Saarikoski, S., Teinilä, K., Salo, L., Datta, A., Simonen, P., Karjalainen, P., Kulmala, K., Rönkkö, T., 2019. Potential of renewable fuel to reduce diesel exhaust particle emissions. Appl. Energy 254, 113636–113647. https://doi.org/10.1016/j.apenergy.2019.113636.

Ravishankara, A.R., Davida, L.M., Pierceb, J.R., Venkataraman, C., 2020. Outdoor air pollution in India is not only an urban problem. Proc. Natl. Acad. Sci. USA 117 (46), 28640–28644. https://doi.org/10.1073/pnas.2007236117.

Raza, M., Chen, L., Leach, F., Ding, S., 2018. A review of particulate number (PN) emissions from gasoline direct injection (GDI) engines and their control techniques. Energies 11, 1417–1441.

Rönkkö, T., Timonen, H., 2019. Overview of sources and characteristics of nanoparticles in urban traffic-influenced areas. J. Alzheim. Dis. 72, 15–28. https://doi.org/10.3233/JAD-190170.

Rönkkö, T., Arffman, A., Karjalainen, P., Lähde, T., Heikkilä, J., Pirjola, L., Rothe, D., Keskinen, J., 2011. Diesel exhaust nanoparticle volatility studies by a new thermodenuder with low solid nanoparticle losses. In: Abstracts in the 15th ETH-Conference on Combustion Generated Nanoparticles. Zürich, Switzerland, pp. 26–29. June 2011.

Rönkkö, T., Lähde, T., Heikkilä, J., Pirjola, L., Bauchke, U., Arnold, F., Rothe, D., Yli-Ojanperä, J., Keskinen, J., 2013. Effects of gaseous sulphuric acid on diesel exhaust nanoparticle formation and characteristics. Environ. Sci. Technol. 47, 11882e11889.

Rönkkö, T., Pirjola, L., Ntziachristos, L., Heikkilä, J., Karjalainen, P., Hillamo, R., et al., 2014. Vehicle engines produce nanoparticles even when not fuelled. Environ. Sci. Technol. 48, 2043e2450.

Rönkkö, T., Saarikoski, S., Kuittinen, N., Karjalainen, P., Keskinen, H., Järvinen, A., Mylläri, F., Aakko-Saksa, P., Timonen, H., 2023. Review of black carbon emission factors from different anthropogenic sources. Environ. Res. Lett. 18, 033004 https://doi.org/10.1088/1748-9326/acbb1b.

Rönkkö, T., Kuuluvainen, H., Karjalainen, P., Keskinen, J., Hillamo, R., Niemi, J.V., Pirjola, L., Timonen, H., Saarikoski, S., Saukko, E., Järvinen, A., Silvennoinen, H., Rostedt, A., Olin, M., Yli-Ojanperä, J., Nousiainen, P., Kousa, A., Dal Maso, M., 2017. Traffic is a major source of atmospheric nanocluster aerosol. Proc. Natl. Acad. Sci. U. S.A. 114 (29), 7549–7554. https://doi.org/10.1073/pnas.1700830114.

Schneider, J., Hock, N., Weimer, S., Borrmann, S., Kirchner, U., Vogt, R., et al., 2005. Nucleation particles in diesel exhaust: composition inferred from in situ mass spectrometer analysis. Environ. Sci. Technol. 39, 6153–6161.

Seong, H., Choi, S., Lee, K., 2014. Examination of nanoparticles from gasoline direct injection (GDI) engines using transmission electron microscopy (TEM). Int. J. Automot. Technol. 15, 175–181.

Sgro, L.A., Borghese, A., Speranza, L., Barone, A.C., Minutolo, P., Bruno, A., D'Anna, A., D'Alessio, A., 2008. Measurements of nanoparticles of organic carbon and soot in flames and vehicle exhausts. Environ. Sci. Technol. 42, 859–863. https://doi.org/10.1021/es070485s.

Sgro, L.A., Sementa, P., Vaglieco, B.M., Rusciano, G., D'Anna, A., Minutolo, P., 2012. Investigating the origin of nuclei particles in GDI engine exhausts. Combust. Flame 159, 1687–1692.

Shi, J., Harrison, R., 1999. Investigation of ultrafine particle formation during diesel exhaust dilution. Environ. Sci. Technol. 33, 3730–3736.

Simonen, P., Saukko, E., Karjalainen, P., Timonen, H., Bloss, M., Aakko-Saksa, P., Ronkkö, T., Keskinen, J., Dal Maso, M., 2017. A new oxidation flow reactor for measuring secondary aerosol formation of rapidly changing emission sources. Atmos. Meas. Tech. 10, 1519–1537.

Simonen, P., Kalliokoski, J., Karjalainen, P., Rönkkö, T., Timonen, H., Saarikoski, S., Aurela, M., Bloss, M., Triantafyllopoulos, G., Kontses, A., Amanatidis, S., Dimaratos, A., Samaras, Z., Keskinen, J., Dal Maso, M., Ntziachristos, L., 2019. Characterization of laboratory and real driving emissions of individual Euro 6 light-duty vehicles – fresh particles and secondary aerosol formation. Environ. Pollut. 255, 113175 https://doi.org/10.1016/j.envpol.2019.113175, 2019.

Stohl, A., Wotawa, G., Seibert, P., Kromp-Kolb, H., 1995. Interpolation errors in wind fields as a function of spatial and temporal resolution and their impact on different types of kinematic trajectories. J. Appl. Meteorol. 34, 2149–2165.

Su, D.S., Serafino, A., Müller, J.O., Jentoft, R.E., Schlögl, R., Fiorito, S., 2008. Cytotoxicity and inflammatory potential of soot particles of low-emission diesel engines. Environ. Sci. Technol. 42, 1761–1765.

Timonen, H., Karjalainen, P., Saukko, E., Saarikoski, S., Aakko-Saksa, P., Simonen, P., Murtonen, T., Dal Maso, M., Kuuluvainen, H., Bloss, M., Ahlberg, E., Svenningsson, B., Pagels, J., Brune, W.H., Keskinen, J., Worsnop, D.R., Hillamo, R., Rönkkö, T., 2017. Influence of fuel ethanol content on primary emissions and secondary aerosol formation potential for a modern flex-fuel gasoline vehicle. Atmos. Chem. Phys. 17, 5311–5329. https://doi.org/10.5194/acp-17-5311-2017.

Tobias, H., Beving, D., Ziemann, P., Sakurai, H., Zuk, M., McMurry, P., Zarling, D., Watylonis, R., Kittelson, D., 2001. Chemical analysis of diesel engine nanoparticles using a nano-DMA/thermal desorption particle beam mass spectrometer. Environ. Sci. Technol. 35, 2233–2243.

Wihersaari, H., Pirjola, L., Karjalainen, P., Saukko, E., Kuuluvainen, H., Kulmala, K., Keskinen, J., Rönkkö, T., 2020. Particulate emissions of a modern diesel passenger car under laboratory and real-world transient driving conditions. Environ. Pollut. 265 https://doi.org/10.1016/j.envpol.2020.114948, 114948-114947.

World Health Organization, 2021. WHO Global Air Quality Guidelines: Particulate Matter (PM2.5 and PM10), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide. World Health Organization. https://apps.who.int/iris/handle/10665/345329. License: CC BY-NC-SA 3.0 IGO.

Yli-Ojanperä, J., Kannosto, J., Marjamäki, M., Keskinen, J., 2010. Improving the nanoparticle resolution of the ELPI. Aerosol Air. Qual. Res. 10, 360–366.