



## Are standardized diesel exhaust particles (DEP) representative of ambient particles in air pollution toxicological studies?



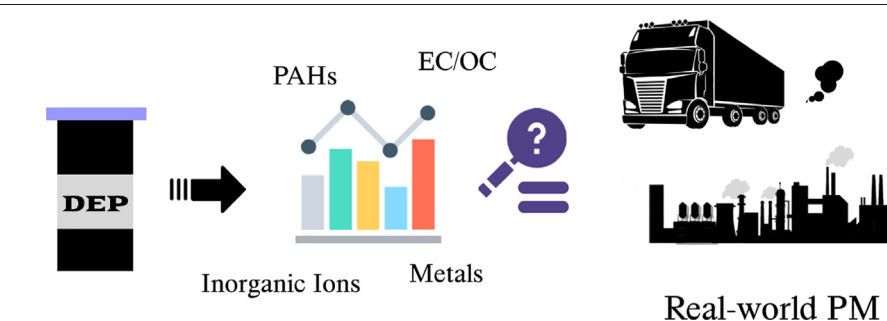
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### HIGHLIGHTS

- Chemical characteristic of a standardized diesel exhaust particle (DEP) was analyzed.
- EC contribution to the DEP is notably higher than that of typical traffic conditions.
- Unlike real-world PM, content of inorganic ions and SOAs is negligible in the DEP.
- The DEP was almost entirely devoid of several high molecular weight PAHs.
- Standardized DEP cannot represent typical ambient PM nor traffic emissions.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 30 March 2021

Received in revised form 14 May 2021

Accepted 15 May 2021

Available online 20 May 2021

Editor: Pavlos Kassomenos

#### Keywords:

Diesel exhaust particles (DEPs)

Standard material

Particulate matter

Toxicological studies

Health impacts

### ABSTRACT

In this study, we investigated the chemical characteristics of standardized diesel exhaust particles (DEP) and compared them to those of real-world particulate matter (PM) collected in different urban settings to evaluate the extent to which standardized DEPs can represent ambient particles for use in toxicological studies. Standard reference material SRM-2975 was obtained from the National Institute of Standards and Technology (NIST) and was chemically analyzed for the content of elemental carbon (EC), organic carbon (OC), polycyclic aromatic hydrocarbons (PAHs), inorganic ions, and several metals and trace elements. The analysis on the filter-collected DEP sample revealed very high levels of EC (i.e., ~397 ng/ $\mu$ g PM) which were comparable to the OC content (~405 ng/ $\mu$ g PM). This is in contrast with the carbonaceous content in the emitted particles from typical filter-equipped diesel-powered vehicles, in which low levels of EC emissions were observed. Furthermore, the EC mass fraction of the DEP sample did not match the observed levels in the ambient PM of multiple US urban areas, including Los Angeles (8%), Houston (~14%), Pittsburgh (~12%), and New York (~17%). Our results illustrated the lack of several high molecular weight carcinogenic PAHs in the DEP samples, unlike our measurements in major freeways of Los Angeles. Negligible levels of inorganic ions were observed in the sample and the DEP did not contain toxic secondary organic aerosols (SOAs) formed through synchronized reactions in the atmosphere. Lastly, the analysis of redox-active metals and trace elements demonstrated that the levels of many species including vehicle emission tracers (e.g., Ba, Ti, Mn, Fe) on Los Angeles roadways were almost 20 times greater than those in the DEP sample. Based on the abovementioned inconsistencies between the chemical composition of the DEP sample and those of real-world PM measured and recorded in different conditions, we conclude that the standardized DEPs are not suitable representatives of traffic emissions nor typical ambient PM to be used in toxicological studies.

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## 1. Introduction

Rapid urbanization and the resulting surge in anthropogenic emissions have made air pollution a major environmental and public health concern. Previous studies have extensively investigated the severe effects of air pollution on the human health such as cardiovascular diseases, lung cancer, neurodegenerative disorders, and premature mortality (Apte et al., 2018; Delfino et al., 2009; Brook et al., 2010). Particulate matter (PM), as a criteria air pollutant, has been the focus of a wide range of in vivo and in vitro health studies (Hazlehurst et al., 2021; Kim et al., 2015; Stanek et al., 2011). The latest study of the global burden of diseases has linked 4 million annual deaths worldwide to exposure to ambient PM (Cohen et al., 2017).

Traffic emissions are one of the most significant sources of ambient PM in various metropolitan areas with notable contributions to ambient PM concentrations (Pant and Harrison, 2013; Saraga et al., 2019; Taghvaei et al., 2018). Approximately, 25–35% of annual  $PM_{2.5}$  concentration (i.e., particles with aerodynamic diameter less than  $2.5 \mu m$ ) has been attributed to vehicular primary emissions in the Los Angeles basin (CARB et al., 2013; Hasheminassab et al., 2014; Altuwayjiri et al., 2020). The chemical composition of PM originating from traffic activities depends on the age and type of engine, fuel composition, load characteristics, lube oil compounds, and efficiency of after-treatment emission control technologies (Rosenkranz, 1996; Mauderly, 2001; Singh et al., 2004; Pakbin et al., 2009; Thiruvengadam et al., 2014). The complex nature of physiochemical properties of PM makes it difficult to reproduce in the laboratory (Taghvaei et al., 2019; Bladt et al., 2012; Filep et al., 2016; Jacoby et al., 2011; Keskinen and Rönkkö, 2010). Therefore, it is vital to employ real-world PM in controlled toxicological studies in order to improve our understanding of the identified associations between PM and adverse effects. However, direct use of ambient PM in the lab is not always a viable alternative, because ambient PM concentrations are generally not sufficiently high to induce acute adverse health effects in toxicological studies (Jung et al., 2010; Liu et al., 2008; Pirhadi et al., 2019).

Diesel exhaust particles (DEPs) have been linked to various human health risks, including increased carcinogenicity (Benbrahim-Tallaa et al., 2012), potentiation of autoimmune disorders (Yoshino and Sagai, 1999), pulmonary inflammation (Jeong et al., 2021), heart impairment (Nawrot et al., 2011), mental disorders (Power et al., 2011), asthma and allergic reactions (Sydbom et al., 2001). DEP is a mixture of various chemical components including elemental carbon (EC) and organic carbon (OC) which constitute the carbon core, metals and trace elements, and organic compounds such as n-alkanes, branched alkanes, alkyl-cycloalkanes, alkyl-benzenes, polycyclic aromatic hydrocarbons (PAHs) and various cyclic aromatics.

Recently, the use of standardized DEPs collected under controlled conditions has been extended in toxicological studies. The protocol for generation and collection of DEPs has been developed by the National Institute of Standards and Technology (NIST); DEPs are available as standard reference material (SRM) used in analytical methods to evaluate complex diesel mixtures. For instance, standard reference material

SRM-2975 (NIST, US) is a commonly used standardized DEP sample and has been employed in multiple health effect studies of air pollution (Mundandhara et al., 2006; Szwedzińska et al., 2017). For example, van den Brule et al. (2021) used DEP SRM-2975 (NIST) to investigate the effect of diesel particles on the profile and function of the gut microbiota in the mice. Robinson et al. (2018) conducted a health study to identify the mechanisms involved in activation of airway sensory afferents by DEPs, in which SRM-2975 (NIST) was considered a representative of the real-world environmental exposure. Similarly, human bronchial epithelial cells were exposed to SRM-2975 (NIST) by Smyth et al. (2020) and changes in barrier function were monitored to determine the effect of diesel exhaust exposure on airway epithelial barrier function. Lawal et al. (2015) used human microvascular endothelial cells to examine the toxic effects of DEPs on endothelial cells and their role in inducing heme oxygenase-1 (HO-1). Enhancement in ROS production, cellular toxicity/inflammatory, and cellular adhesion were linked to SRM 2975 (NIST) transfection. Rychlik et al. (2019) explored the effects of in utero UFP exposure on young pulmonary immune response in mice, using SRM 2975 (obtained from NIST).

Considering the widespread use of DEPs in the field of air pollution and its health effects, it is essential for the air pollution research communities and policymakers to evaluate the extent to which the standardized DEP represents typical ambient PM as well as PM originated from traffic emissions. In this study, we conducted a comprehensive investigation of the representativeness of DEP samples by analyzing the chemical composition of DEP SRM-2975 (NIST) and comparing it with that of real-world PM collected and analyzed in different urban settings.

## 2. Methodology

### 2.1. DEP type and sampling

We used SRM-2975 (NIST) as a reference for the chemical and toxicological constituents of the standardized DEPs. The DEP sample is generated by a diesel-powered industrial forklift and collected by a particular filtering system designed for diesel forklifts under “hot” conditions, without a dilution tunnel (Singh et al., 2004; Wright et al., 1991). The DEP sample employed in our study was purchased from NIST and processed for chemical analysis in a multi-stage procedure discussed in detail below.

Fig. 1 illustrates the schematic of our laboratory setup. First, DEP suspension was prepared by dissolving 20 mg of the sample in 100 ml of ultrapure Milli-Q water (Millipore A-10, EMD Millipore, Billerica, MA, US). The solution was then sonicated for 30 min by means of an ultrasonic bath (3510R-MT, Branson Ultrasonics Corp., US) to achieve a homogeneous slurry with a concentration of approximately  $200 \mu g/ml$ . The DEP slurry was re-aerosolized using the aerosol generation system elaborately discussed in Taghvaei et al. (2019). In summary, the prepared slurry is atomized into small aerosol droplets, using a HOPE nebulizer (Model 11,310, B&B Medical Technologies, US). The re-aerosolized stream is then mixed with the HEPA-filtered clean air, followed by passing through a diffusion dryer (Model 3620, TSI Inc., US) filled with silica gel to remove excess water from the airborne particles. Subsequently,

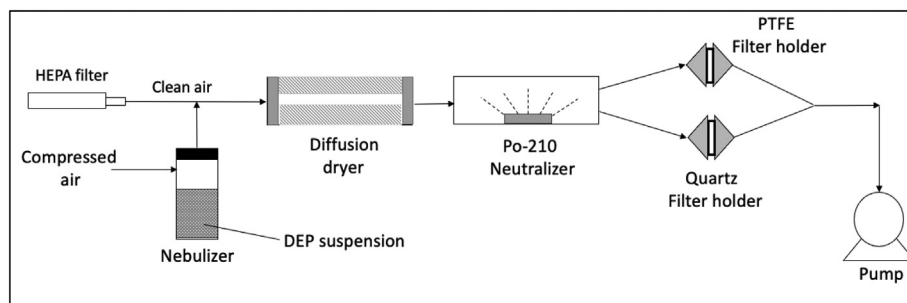


Fig. 1. Schematic of the laboratory setup.

the aerosol stream passes through a column filled with Po-210 neutralizers (Model 2 U500, NRD Inc., US) to remove electrical charges from the particles. The re-aerosolized PM was collected simultaneously on a 37-mm PTFE filter (2- $\mu\text{m}$  pore, Pall Corp., Life Sciences, US) and a pre-baked quartz filter (Pall Corp., Life Sciences, US) to compare their chemical composition to the corresponding values of the real-world particles collected in different urban environments.

## 2.2. Chemical analysis of DEP

The DEP sample was chemically analyzed for the content of EC/OC, PAHs, inorganic ions, metals and trace elements at the Wisconsin State Laboratory of Hygiene (WSLH). The EC and OC concentration of the samples were determined by following the Thermal Optical Transmission (TOT) protocol of the National Institute for Occupational Safety and Health (NIOSH) (Birch and Cary, 1996). A punch of the quartz filter was directly extracted and then analyzed by the semi-continuous EC/OC field analyzer (Sunset Laboratory Inc., US). The mass content of anions (sulfate, nitrate, chloride and phosphate) and cations (sodium, ammonium, potassium) was determined by applying ion chromatography (IC) on the filtered water extract of a part of the PTFE filter. The metals and trace element constituents of DEP were quantified by the inductively coupled plasma mass spectrometer (ICP-MS), using a microwave-aided mixed-acid (Lough et al., 2005). A punch of the PTFE filter was digested with a mixture of ultrahigh-purity nitric acid and ultrahigh-purity hydrochloric acid. Lastly, to determine the content of PAHs, a section of the PTFE filter was extracted and analyzed by means of the Gas Chromatography/Mass Spectrometry (GC/MS) (Schauer et al., 1999).

## 2.3. Comparisons with real-world PM

The quantified chemical components of the DEP SRM-2975 (NIST), including EC/OC, PAHs, inorganic ions, and metals and trace elements were compared to the corresponding ambient values in major US metropolitan areas.

The annual average of ambient  $\text{PM}_{2.5}$  chemical composition at four major urban areas of the US, including Los Angeles, Houston, Pittsburgh, and New York city, were retrieved through the Air Quality System (AQS) from chemical speciation network (CNS) database recorded by the US Environmental Protection Agency (US EPA). Further details regarding the CSN database has been elaborated elsewhere (Solomon et al., 2014). The data on the mass concentration of OC, EC, sulfate, nitrate, ammonium, and total metals and elements were extracted for year 2019, which was the most recent year for which the annual data were available. Moreover, these four areas were selected to cover a wide range of geographical locations in the US.

We evaluated the EC and OC profile of the DEP sample by comparing it to the corresponding values in the heavy-duty diesel vehicles (HDDV) exhaust tests under different aftertreatment configurations, conducted earlier by our group (Biswas et al., 2009). The recorded values included measurements on HDDVs with six various configurations of vehicles with advanced emission control technologies: 1) a 1998 Kenworth truck HDDV without aftertreatment as the baseline. 2) the same HDDV with a continuously regenerating technology [CRT], 3) the HDDV with a CRT in combination with a vanadium-based selective catalytic reduction system [V-SCRT], 4) the HDVV with a CRT in combination with a zeolite-based selective catalytic reduction system [Z-SCRT], 5) a Caltrans truck with an Engelhard DPX filter, and 6) a school bus equipped with a Claire electric particle filter [Horizon].

Several components of the ambient PM, including metals and trace elements as well as insoluble organic species (i.e., PAHs) have been widely associated with the PM toxicity and oxidative potential (Bates et al., 2019; Chen and Lippmann, 2009; Cho et al., 2005; Gao et al., 2020; Li et al., 2009; Pirhadi et al., 2020;). We compared the mass fraction of individual metals and elements as well as PAHs in the DEP sample to the real-world ambient data measured on major freeways in Los

Angeles to assess if the standardized DEP can capture the complex nature of the ambient particles originated from traffic emissions. The measurements were conducted on the main campus of the University of Southern California (USC), which was used as a reference urban background site, as well as three roadways in the Los Angeles basin including the I-110 freeway, I-710 freeway, and the Wilshire/Sunset boulevard (Shirmohammadi et al., 2017). A 2014 Toyota Prius C hybrid car equipped with six battery-operated Leland Legacy pumps (SKC Inc., Eighty-Four, PA) was used to perform the on-road sampling. Each pump was connected to a Sioutas Personal Cascade Impactor Sampler (PCIS) (SKC Inc., Eighty-Four, PA) and the flow rate for each PCIS was set to be 9 lpm (Misra et al., 2002). The PAH species analyzed included: phenanthrene, fluoranthene, acephenanthrylene, pyrene benzo(ghi)fluoranthene, benzo(a)anthracene, Chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, and coronene. The investigated metals and elements were Mg, Al, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sb, Ba, and Pb.

Particles generated from traffic emissions, especially tailpipe emissions, are mostly in the quasi-ultrafine range (i.e.,  $\text{PM}_{0.25}$ , particles less than 0.25  $\mu\text{m}$  in diameter) (Habre et al., 2021; Hasheminassab et al., 2013). To further investigate the relevance of the standardized DEP sample, its chemical composition was compared to that of the ambient  $\text{PM}_{0.25}$  concentrations measured earlier by our group in the Los Angeles basin (Saffari et al., 2013). The ambient  $\text{PM}_{0.25}$  were collected at ten distinct locations across the Los Angeles South Coast air basin, using two parallel Sioutas PCIS which were operating simultaneously with a flow rate of 9 lpm. The total metallic and elemental composition of the samples were analyzed using a high-resolution magnetic sector inductively coupled plasma sector field mass spectrometry (ICP-SFMS, Thermo-Finnigan Element 2) (Herner et al., 2006).

## 3. Results and discussion

### 3.1. Chemical profiles of standardized DEP

Fig. 2 shows the PM mass fraction of the measured chemical compounds in the standardized DEP sample. According to Fig. 2(a), the EC concentration ( $\sim 397 \text{ ng}/\mu\text{g PM}$ ) is high and almost comparable to OC ( $\sim 405 \text{ ng}/\mu\text{g PM}$ ). This observation is not consistent with the measured EC and OC values in many studies conducted on the real-world PM, which observed significantly low EC emissions. This inconsistency will be further elaborated in Section 3.2.1. As shown in Fig. 2(b), the content of inorganic ions (e.g., ammonium, sulfate and nitrate) in the DEP sample is negligible. The quantified mass fractions for ammonium, sulfate and nitrate are 2.77, 7.97 and 1.5  $\text{ng}/\mu\text{g PM}$ , respectively, which is almost 40 times smaller than those of OC and EC. The inorganic content of the sample will be discussed in detail in Section 3.2.2. The PAHs mass fraction profiles measured in the DEP sample are illustrated in Fig. 2(c). While the DEP sample was missing some low molecular weight PAHs (e.g., anthracene, acephenanthrylene, cyclopenta(cd)pyrene), it was almost entirely devoid of several high molecular weight PAHs (e.g., benzo(a)pyrene, benzo(j)fluoranthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, dibenzo(a,e)pyrene, perylene, and picene). Thus, DEP contained mostly low molecular weight PAHs (e.g., phenanthrene, fluoranthene, pyrene, benzo(ghi)fluoranthene, benz(a)anthracene, chrysene) with low-to-moderate mass fractions. This observation is in contrast with the PM chemical profile in the typical ambient conditions, where the combined contribution of medium and high molecular weight PAHs was 52.2% (Pakbin et al., 2009). Additionally, other studies have reported high levels of three and four-ring PAHs (anthracene, phenanthrene, and pyrene) in HDDV exhaust which is not consistent with the recorded values in the SRM-2975 (NIST) powder (Liu et al., 2008; Riddle et al., 2007; Marr et al., 1999). This inconsistency will be elaborated further in Section 3.2.3. Fig. 2(d) shows the PM mass fraction of metals and

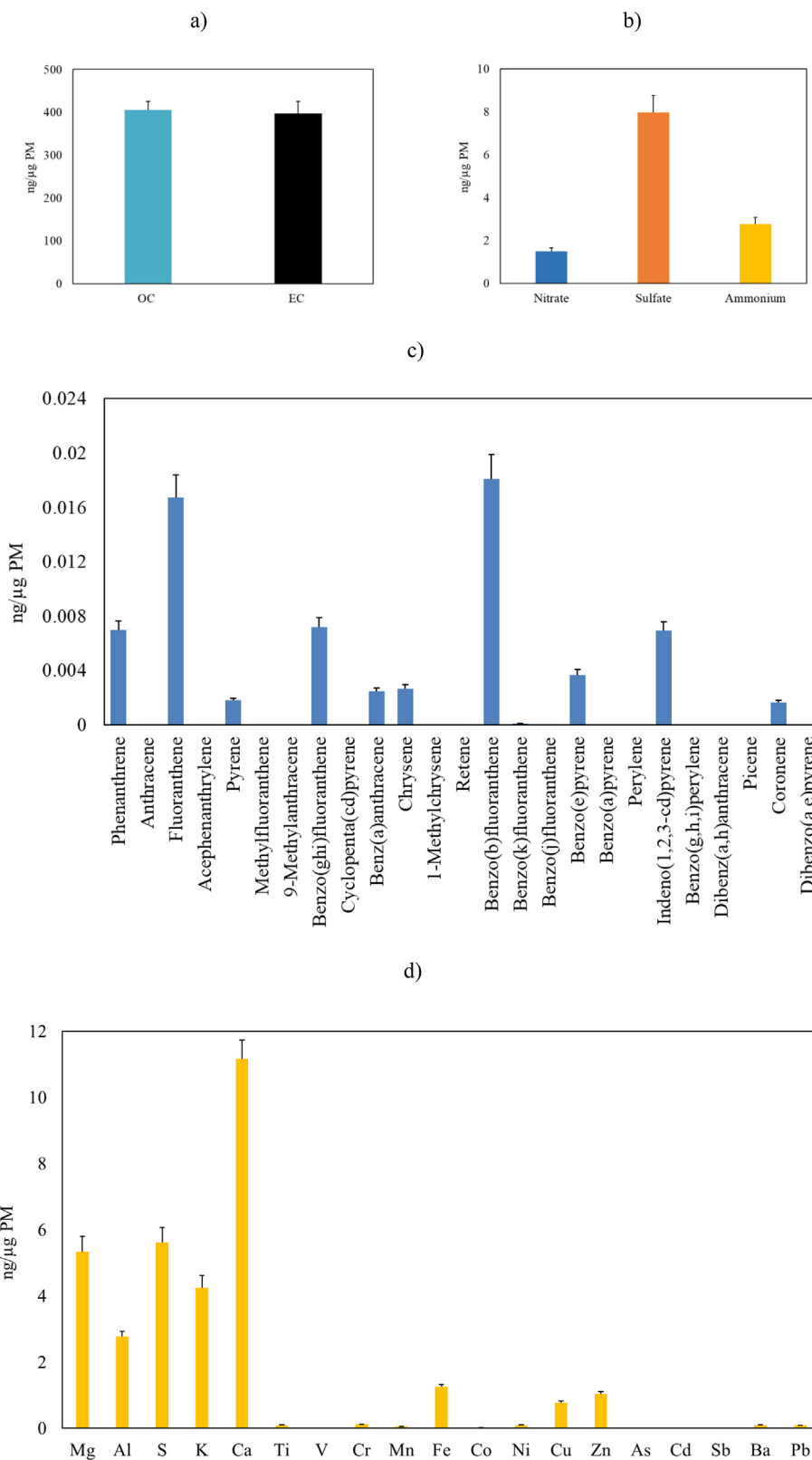


Fig. 2. The mass fraction of a) EC and OC, b) inorganic ions, c) PAHs, and d) metals and elements in the standardized DEP sample.

trace elements in the standardized DEP particles. The metal and trace elements levels range from 0.0003 ng/μg PM (Cd) to 11.17 ng/μg PM (Ca). The sample's metallic content will be further investigated and compared to the corresponding ambient values in Section 3.2.4.

### 3.2. Comparison between DEP and real-world PM

#### 3.2.1. EC/OC

Carbonaceous compounds constitute a large portion of vehicle exhaust emissions, and EC has been extensively used as surrogate of diesel

particulate matter (Schauer, 2003). As discussed earlier, the chemical analysis of carbonaceous compounds in the standardized DEP shows high levels of EC (of almost 40% by mass), resulting in the EC/OC ratio of almost 1. Investigation of EC emissions from diesel-powered vehicles in earlier studies conducted mostly in 1990s and early 2000s show comparable or even higher levels of EC contribution compared to OC (Lowenthal et al., 1994; Watson et al., 2004), similar to those found in the DEP sample. However, it is imperative to consider the impact of the emission control regulations implemented in various countries in recent years, leading to significant alterations in the EC and OC content of tailpipe emissions. Starting in 2007, a number of stringent regulations were implemented in state of California to mitigate the tailpipe emissions including: (i) Low emission vehicles II (LEV II) program (2007), requiring vehicles to meet the newly-developed emission standards on non-methane organic gases (NMOG), PM, NO<sub>x</sub>, and CO defined for various vehicle groups; (ii) Low carbon fuel standards (LCFS) program (2013), which encouraged California's car manufactures to use low-carbon fuel to decrease the petroleum-related emissions; and (iii) Cleaner port truck (CPT) program (2007), which was implemented to limit the diesel emissions from drayage company's trucks working at the ports of Los Angeles and Long Beach. Comparing the EC/OC ratios pre- and post- 2007 clearly shows the impact of the abovementioned regulations on carbonaceous content of diesel particulate matter. For instance, in a study on gasoline and diesel vehicle engine emissions in San Francisco Bay area, Ban-Weiss et al. (2008) have reported the EC/OC ratio of near 0.7 and 2 for light duty and diesel-powered trucks, respectively. Similar studies in the past have measured the EC/OC ratios in the 0.8–1.8 range, depending on the vehicle engine (Watson et al., 1990, 1994, 2004). The adopted regulations and standards resulted in the development of novel after-treatment emission control technologies which have altered the chemical composition in vehicle exhaust PM. In a study conducted earlier by our group (Biswas et al., 2009), the EC/OC profiles of PM emitted from a diesel exhaust with a wide range of retrofitted diesel vehicle configurations (i.e., CRT, V-SCRT, Z-SCRT, DPX, Horizon) and a diesel exhaust without after-treatment (baseline) were investigated over steady state cruise (50 mph) and transient EPA urban dynamometer driving schedule (UDDS) cycles, the results of which are shown in Fig. 4. The EC emissions in the baseline are significantly reduced after employing different common retrofitted configurations in cruise and transient cycles. According to the figure, the mass fraction of EC is less than 5% of OC in most retrofitted configurations. This observation is not consistent with the EC and OC content of the standardized DEP sample (Fig. 2(a)). The difference in the EC content of diesel exhaust emissions and that of the DEP sample suggest that the high EC content of standardized DEP particles cannot be considered representative of the emissions from most of the recent diesel-powered vehicles.

Furthermore, we compared the carbonaceous content of DEP sample to that of real-world mass fractions in Los Angeles area (Shirmohammadi et al., 2017). Fig. 5 shows the measured mass fraction of EC and OC in three major roadways of Los Angeles county, including I-110, I-710, and Wilshire/Sunset Blvd. as well as the University of Southern California (USC) sampling site. The three selected roadways are among the most trafficked routes in Los Angeles, representing an urban area heavily impacted by vehicle engine emissions. The main campus of USC served as the urban reference site. According to the figure, the EC fraction of PM did not exceed levels of  $0.13 \pm 0.04 \mu\text{g}/\mu\text{g}$  PM, with the average of almost  $0.1 \mu\text{g}/\mu\text{g}$  PM in all sampling sites. The higher EC levels on freeways have been attributed to the significant number of HDVs, as one of the major EC emission sources, on these routes (Shirmohammadi et al., 2017; Schauer, 2003). According to Fig. 3, which demonstrates the annual chemical composition of ambient PM<sub>2.5</sub> in multiple cities across the US, the EC fraction of ambient PM<sub>2.5</sub> in Los Angeles, Houston, Pittsburgh and New York was around 8%, 14%, 12% and 17%, respectively. This observation further illustrates that not only standardized DEP particles do

not have the same EC and OC profile of the particles emitted from typical vehicles exhaust, but they also are not representatives of real-world ambient PM to which most of the people are exposed in typical urban areas.

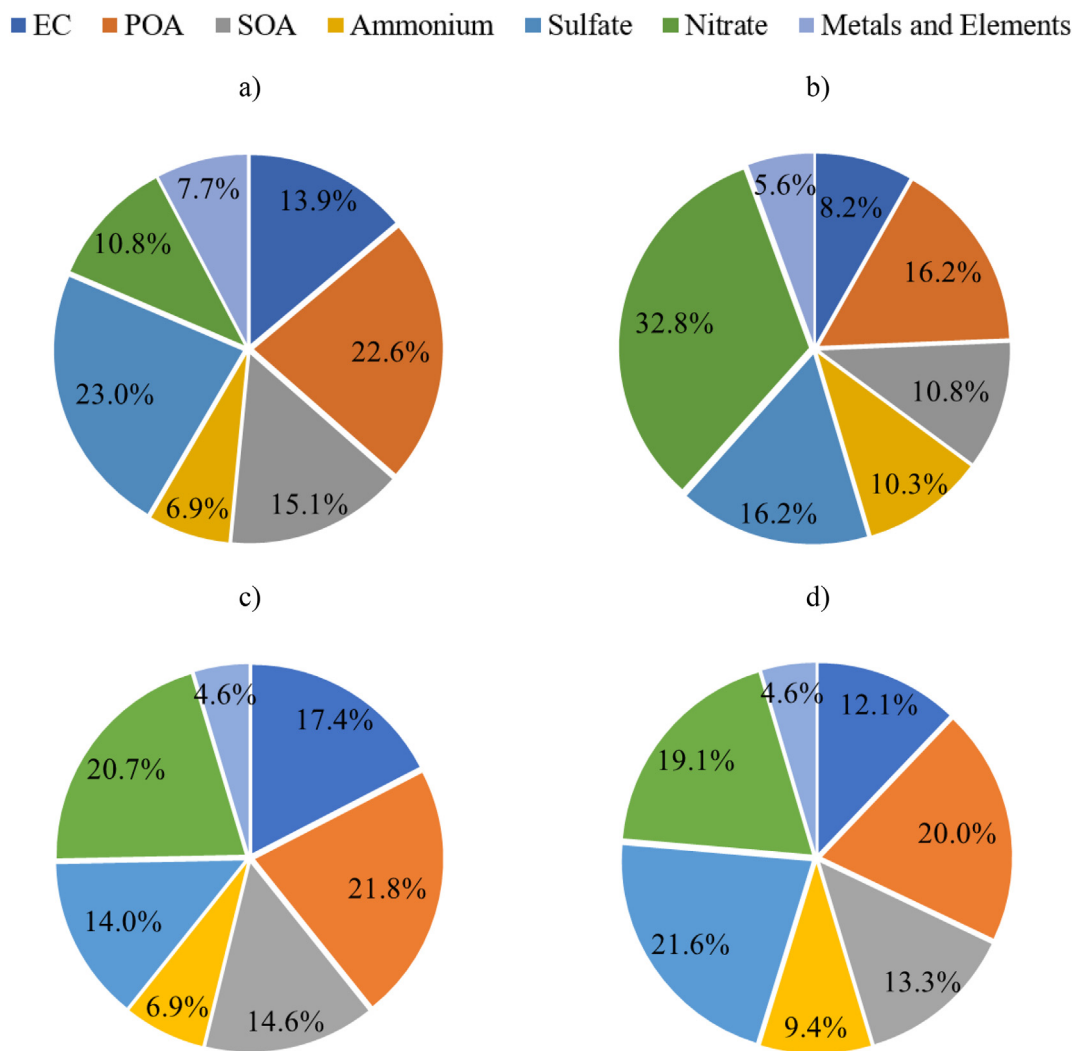
### 3.2.2. Inorganic ions and SOAs

As shown in Fig. 2(b), nitrate, sulfate and ammonium constitute a small fraction of the DEP mass concentration. Mass fractions of inorganic ions in typical ambient conditions of multiple cities across the US are illustrated in Fig. 3. According to the figure, inorganic ions have a large contribution to ambient PM<sub>2.5</sub> concentrations. Combined contribution of nitrate, sulfate and ammonium to ambient PM<sub>2.5</sub> mass in Los Angeles, New York, Houston and Pittsburgh were 59.3%, 41.5%, 40.7% and 50.1%, respectively, which is not consistent with the observed values in the DEP sample.

Secondary organic aerosols (SOAs) are formed from photochemical reactions of species emitted by combustion sources in the atmosphere (Huang et al., 2014), and have been extensively linked to adverse health effects (Chowdhury et al., 2018; Kramer et al., 2016; Lodovici and Bigagli, 2011; Lund et al., 2013; McDonald et al., 2010). Recent studies have corroborated the significant role of SOAs in underlying mechanisms leading to PM oxidative potential and toxicity (Chu et al., 2014; Daumit et al., 2016; Tuet et al., 2017). SOAs constitute a considerable fraction of ambient PM mass in different urban environments. The SOA in Los Angeles ambient air has been reported to be about 40–45% of total OC (Altwayjiri et al., 2020; Polidori et al., 2007). Consistent with this observation, the ambient SOA values in Atlanta, Claremont, CA and Pittsburgh have been estimated to be around 44%, 40% and 38% of total OC, respectively (Cabada et al., 2004; Lim and Turpin, 2002; Turpin and Huntzicker, 1995). The DEP sample is devoid of secondary aerosols since DEP samples are collected from freshly emitted particles immediately after the exhaust and do not have sufficient time to undergo different atmospheric processes. The lack of SOA components in the DEP sample further weakens its relevance in PM toxicological studies.

### 3.2.3. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are organic compounds that are products of incomplete fossil fuel combustion in industries, vehicle emissions and biomass burning (Alves et al., 2015; Galarneau, 2008; Guo et al., 2003; Harvey, 1998; Lima et al., 2005; Miller et al., 2010). Table 1 compares the concentrations of multiple PAHs per PM mass in the DEP sample and their corresponding values measured in the different sampling sites of Los Angeles as mentioned earlier (i.e., I-110, I-710, Wilshire/Sunset, and USC). According to the literature, vehicle emissions (e.g., gasoline- and diesel-fueled) are one of the main contributors to the ambient PAHs concentrations in the Los Angeles basin, which is consistent with the higher values observed on freeways compared to other sites. Combined concentrations of PAHs on I-110 ( $0.16 \pm 0.01 \text{ ng}/\mu\text{g}$  PM) and I-710 ( $0.15 \pm 0.01 \text{ ng}/\mu\text{g}$  PM) were 3 and 3.3-fold greater than that of Wilshire/Sunset Blvd. and USC, respectively (Shirmohammadi et al., 2017). The cumulative mass fraction of PAHs in the DEP sample was  $0.068 \pm 0.005 \text{ ng}/\mu\text{g}$  PM which is significantly lower than the levels exhibited in Los Angeles roadways. According to the table, this difference largely stems from the lack of several high molecular weight PAHs (i.e., PAHs having four or more rings) in the standardized DEP particles, including benzo(j)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and benzo(k)fluoranthene. High molecular weight PAHs are characterized by having four or more rings and are mostly found in particulate phase due to their low vapor pressure (Baek et al., 1991; Park et al., 2002; Rezaian et al., 2016; Taghvaei et al., 2018). While PAHs can be formed from the combustion of both diesel fuel and lubrication oil, higher levels of high molecular weight PAHs have been reported in the used lubricating oil (Pakbin et al., 2009). Due to their mutagenic characteristics, the higher molecular weight PAHs are often more carcinogenic according to the International Agency for Research on Cancer (IARC). Thus, the absence of several heavy PAHs in



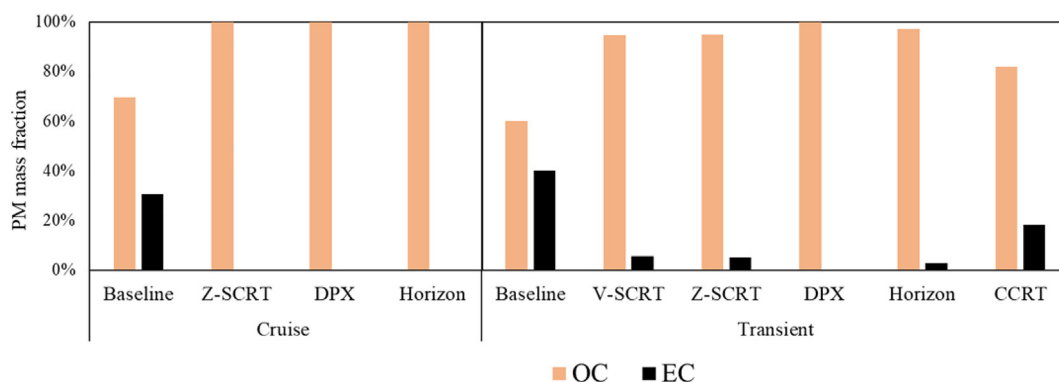
**Fig. 3.** Ambient PM<sub>2.5</sub> chemical composition during year 2019 in a) Houston, b) Los Angeles, c) New York, and d) Pittsburgh obtained from the Chemical Speciation Network (CSN) database provided by the US Environmental Protection Agency (US EPA). SOAs have been estimated to be 40% of total OC according to the literature in these cities.

the chemical compounds of the standardized DEP questions the relevance of its application in toxicological studies.

3.2.4. Metals and trace elements

Table 2 shows the mass fraction of metals and trace elements in the DEP sample in comparison with the ambient measured values in various sampling sites in Los Angeles. The content of several redox-active species (e.g., Ti, V, Mn, Fe, As, Cd, Sb, Ba) in the DEP sample are significantly

lower those of ambient PM<sub>2.5</sub> in different locations. Ba, Ti, and Mn are documented tracers of vehicle emission (Farahani et al., 2021; Jain et al., 2018; Lim et al., 2010; Taghvaei et al., 2018). While Fe has been treated as a marker of mineral dust in previous studies (Almeida et al., 2005), this species has been also attributed to vehicular emissions in the PM<sub>2.5</sub> range as well in Los Angeles (Mousavi et al., 2018). The sum of vehicle emission tracers (e.g., Ba, Ti, Mn, and Fe) found in the DEP sample was  $1.47 \pm 0.58$  ng/mg PM. In contrast, the cumulative mass



**Fig. 4.** PM mass fraction of EC and OC at cruise and transient urban dynamometer driving schedule (UDDS) cycles.

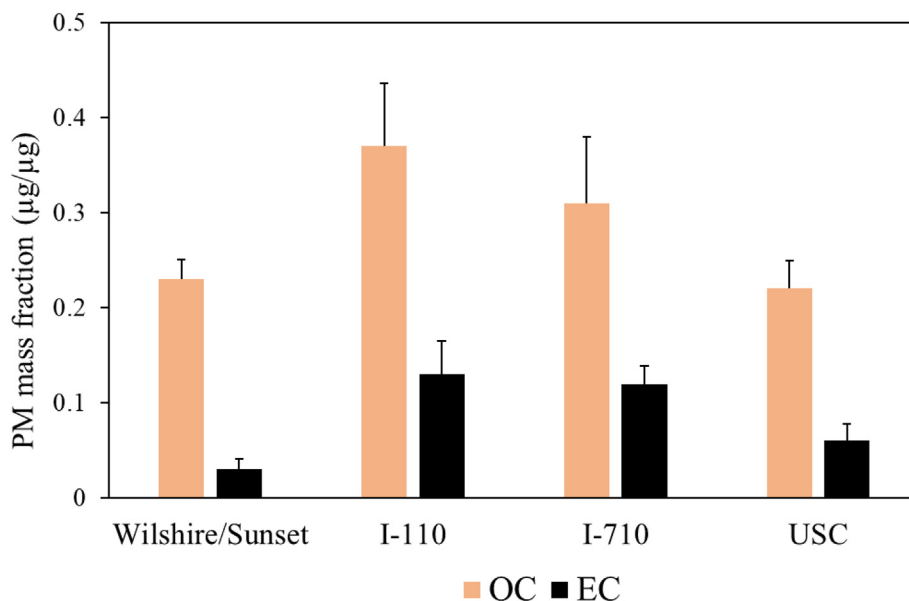


Fig. 5. PM mass fraction of EC and OC at Interstate 110 (I-110), Interstate 710 (I-710), Wilshire/Sunset Blvd., and USC sampling site.

Table 1

Mass fraction of PAHs in DEP sample and PM<sub>2.5</sub> sampling sites (I-110 freeway, I-710 freeway, Wilshire/Sunset Blvd., and USC). All values are in units of ng/µg PM.

Species	DEP	I-710	I-110	Wilshire/sunset	USC
Phenanthrene	0.0070	0.0164	0.0038	0.0017	0.0058
Fluoranthene	0.0167	0.0246	0.0007	0.0034	0.0020
Pyrene	0.0018	0.0246	0.0033	0.0016	0.0044
Benzo( <i>ghi</i> )fluoranthene	0.0072	0.0038	0.0011	0.0014	0.0048
Benz( <i>a</i> )anthracene	0.0025	0.0113	0.0079	0.0014	0.0010
Chrysene	0.0027	0.0038	0.0061	0.0034	0.0055
Benzo( <i>b</i> )fluoranthene	0.0181	0.0318	0.0307	0.0089	0.0044
Benzo( <i>e</i> )pyrene	0.0037	0.0068	0.0154	0.0020	0.0034
Indeno(1,2,3- <i>cd</i> )pyrene	0.0069	0.0010	0.0102	0.0027	0.0014
Coronene	0.0016	0.0017	0.0020	0.0058	0.0027
Acephenanthrylene	–	0.0010	0.0311	0.0044	0.0003
Benzo( <i>j</i> )fluoranthene	–	0.0010	0.0003	0.0007	0.0020
Benzo( <i>a</i> )pyrene	–	0.0003	0.0116	0.0007	0.0007
Benzo( <i>g,h,i</i> )perylene	0.0000	0.0102	0.0225	0.0085	0.0048
Benzo( <i>k</i> )fluoranthene	0.0001	0.0061	0.0099	0.0034	0.0020

fractions of the mentioned redox-active metals measured on I-110, I-710, and Wilshire/Sunset were  $49.82 \pm 20.38$ ,  $46.37 \pm 19.27$ , and  $11.82 \pm 4.97$  ng/mg PM, respectively. On average, the concentrations of vehicle emission tracers on roadways were 21-fold greater than those in the DEP sample. These observations are further corroborated by the annual average PM<sub>0.25</sub> mass fraction of metals and trace elements in several urban areas spread across the Los Angeles basin: Long Beach, Los Angeles, Riverside and Lancaster, as shown in Table 2. The content of several elemental and metallic constituents in the DEP sample are considerably smaller than the respective values measured in ambient quasi-ultrafine particles. Compared to the DEP, the average content of V, Fe, Cd, Sb in ambient PM<sub>0.25</sub> in all monitoring stations is higher by 217, 11.2, 16.4, 25.1-fold, respectively, even though vehicle emissions are dominant emission sources in the PM<sub>0.25</sub> range (Habre et al., 2021). This observation further suggests that standardized DEP particles are not representative of traffic emissions nor of typical ambient PM in major metropolitan areas like Los Angeles.

Table 2

Mass fraction of metals and elements in the DEP sample, PM<sub>2.5</sub> sampling sites (I-110 freeway, I-710 freeway, Wilshire/Sunset Blvd., and USC), and PM<sub>0.25</sub> sampling sites (Long Beach (LB), Los Angeles (LA), Riverside, and Lancaster). All values are in units of ng/µg PM.

Species	DEP	PM <sub>2.5</sub>				PM <sub>0.25</sub>			
		I-710	I-110	Wilshire	USC	LB	LA	Riverside	Lancaster
Mg	5.33	2.37	1.65	1.15	1.87	1.89	1.29	2.77	2.93
Al	2.78	7.03	3.97	3.85	6.42	7.84	5.08	9.64	11.10
S	5.62	12.48	10.10	7.47	9.80	32.87	31.69	23.60	21.18
K	4.25	4.75	4.47	2.04	3.85	5.32	4.67	8.01	8.72
Ca	11.17	10.41	8.95	4.09	8.18	7.29	4.79	9.91	7.56
Ti	0.09	2.10	2.60	0.67	1.38	0.97	0.74	0.96	1.34
V	0.00	0.08	0.09	0.03	0.05	0.74	0.41	0.21	0.08
Cr	0.12	0.22	0.11	0.16	0.09	0.12	0.13	0.13	0.08
Mn	0.05	0.51	0.53	0.15	0.26	0.27	0.19	0.34	0.34
Fe	1.25	40.46	42.97	10.41	13.25	12.87	12.13	14.23	16.83
Co	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ni	0.09	0.23	0.21	0.16	0.04	0.21	0.15	0.11	0.04
Cu	0.78	2.04	3.31	0.58	0.65	0.51	0.99	0.80	0.45
Zn	1.04	1.38	1.60	0.45	0.85	1.48	0.88	0.90	0.66
As	0.00	0.03	0.02	0.01	0.01	0.02	0.02	0.02	0.01
Cd	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00
Sb	0.00	0.43	0.65	0.09	0.14	0.08	0.13	0.10	0.06
Ba	0.08	3.31	3.73	0.59	0.88	0.56	0.68	0.49	0.55
Pb	0.09	0.20	0.19	0.05	0.12	0.17	0.20	0.23	0.11

#### 4. Summary and conclusions

In this study, we analyzed the chemical constituents of a standardized DEP sample and compared the content of EC, OC, PAHs, inorganic ions, metals, and trace elements to those of real-world PM measured and recorded in different conditions. The ratio of EC/OC in the DEP sample was almost 1. While earlier studies have recorded EC/OC ratios between 0.8 and 1.5 in the emissions from diesel powered vehicles, the recent filter-equipped diesel vehicles have significantly lower levels of EC emissions. Similarly, the EC mass fraction in the typical ambient PM of selected cities (e.g., Houston, Los Angeles, Pittsburgh and New York) across the US did not exceed ~17.4%. The analysis of PAH compounds in the standardized DEP demonstrated lack of high molecular weight PAHs observed in many ambient environments. **The content of inorganic ions in the sample was not comparable to the ambient values.** While SOAs, one of the notable drivers of ambient PM toxicity, constitute a significant fraction of ambient PM mass, **DEPs do not contain SOAs since they are collected from freshly emitted particles immediately after the exhaust.** Moreover, the concentrations of many redox-active metals and elements in the standardized DEP were significantly lower than those of ambient PM. The cumulative levels of vehicle emission tracers (e.g., Ba, Ti, Mn, Fe) in the sample was  $1.47 \pm 0.58$  ng/ $\mu$ g PM, which was considerably lower than the measured values on major Los Angeles roadways, including I-110 ( $49.82 \pm 20.38$  ng/ $\mu$ g PM), I-710 ( $49.82 \pm 20.38$  ng/ $\mu$ g PM) and Wilshire/Sunset ( $11.82 \pm 4.97$  ng/ $\mu$ g PM). The abovementioned discrepancies between the chemical content of the standardized DEP and the measured ambient values lead us to the conclusion that standardized DEP samples are not accurate representatives of neither traffic emissions nor typical ambient PM.

#### CRedit authorship contribution statement

**Vahid Jalali Farahani:** Conceptualization, Methodology, Data curation, Writing – original draft. **Milad Pirhadi:** Data curation, Methodology, Validation, Writing – review & editing. **Constantinos Sioutas:** Conceptualization, Project administration, Supervision, Writing – review & editing.

#### Declaration of competing interest

The authors of this paper declare that there is no conflict of interest.

#### Acknowledgements

This study was supported by the National Institutes of Health (NIH) (grant number: 1P01AG055367-01A1). We would also like to acknowledge the support of the PhD fellowship award from the USC Viterbi School of Engineering.

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