Characterization of the chemical composition of PM_{2.5} emitted from on-road China III and China IV diesel trucks in Beijing, China

Bobo Wu^a, Xianbao Shen^{a,b}, Xinyue Cao^a, Zhiliang Yao^{a,*}, Yunong Wu^a,

- a. School of Food and Chemical Engineering, Beijing Technology and Business University, Beijing 100048, China
- b. School of Environment, Tsinghua University, Beijing 100084, China

*Corresponding author.

E-mail address: yaozhl@th.btbu.edu.cn (Z. Yao).

ABSTRACT

The composition of diesel exhaust fine particulate matter (PM_{2.5}) is of growing interest because of its impacts on health and climatic factors and its application in source apportionment and aerosol modeling. We characterized the detailed chemical composition of the PM_{2.5}, including the organic carbon (OC), elemental carbon (EC), water-soluble ions (WSIs), and elemental contents, emitted from China III and China IV diesel trucks (nine each) based on real-world measurements in Beijing using a portable emissions measurement system (PEMS). Carbonaceous compounds were the dominant components (totaling approximately 87%) of the PM_{2.5}, similar to the results (greater than 80% of the PM_{2.5}) of our previous study of on-road China III diesel trucks. In general, the amounts of individual component groups (carbonaceous compounds, WSIs, and elements) and PM_{2.5} emissions for China IV diesel trucks were lower than those of China III diesel trucks of the same size, except for the WSIs and elements for the light- and medium-duty diesel trucks. The EC/OC mass ratios were strongly dependent on the emission standards, and the ratios of China IV diesel trucks were higher than those of China III trucks of the same size. The chemical species in the PM_{2.5} were significantly affected by the driving conditions. Overall, the emission factors (EFs) of the PM_{2.5} and OC under non-highway (NHW) driving conditions were higher than those under highway (HW) driving conditions, and the EC/OC mass ratios presented an increasing trend, with decreasing OC/PM_{2.5} and increasing EC/PM_{2.5} from NHW to HW driving conditions; similar trends were reported in our previous study. In addition, Pearson's correlation coefficients among the PM_{2.5} species were analyzed to determine the relationships among the various chemical components.

Key words: particulate matter, source profile, emission factor, PEMS.

Acronym list

CARB	California Air Resources Board	MPS	Micro-Proportional Sample System
CMB	chemical mass balance	MSAT	mobile source air toxic
DOC	diesel oxidation catalysts	NEDC	New European Driving Cycle
DPM	diesel particulate matter	NHW	non-highway
EC	elemental carbon	OC	organic carbon
EFs	emission factors	PAHs	polycyclic aromatic hydrocarbons
EGR	exhaust gas recirculation	PEMS	portable emissions measurement system
FTP	federal test procedure	PGE	platinum group elements
GVWs	gross vehicle weights	PM	particulate matter
HDDTs	heavy-duty diesel trucks	POC	particle oxidation catalysts
HHDDTs	heavy heavy-duty diesel trucks	R	Pearson's correlation coefficient
HW	highway	RSD	relative standard deviation
IC	ion-chromatography	SCR	selective catalytic reduction
ICP-MS	inductively coupled plasma-mass spectroscopy	TC	total carbon
LDDTs	light-duty diesel trucks	USEPA	United States Environmental Protection Agency
MDDTs	medium-duty diesel trucks	WSIs	water-soluble ions
MELs	mobile emission laboratory methods		

1. Introduction

Fine particulate matter (PM_{2.5}, particulate matter with an aerodynamic diameter less than 2.5 µm) emitted from diesel vehicles has been a focus of concern due to its adverse effects on human health, including its role in cardiopulmonary disease and cancer (Chio et al., 2014; Ema et al., 2013; Oravisjärvi et al., 2014; Ristovski et al., 2012; Sydbom et al., 2001; US-EPA, 2002), as well as environmental problems, such as urban air pollution and global climate change (Maricq, 2007; Robert et al., 2007). In China, diesel vehicles have significantly contributed to urban air pollution of PM_{2.5} (Huo et al., 2011; Wang et al., 2010; Wu et al., 2011). Chemical composition profiles of PM_{2.5} in diesel exhaust particles are important for the source apportionment of urban aerosols (Balachandran et al., 2013; Gross et al., 2005; Kim and Hopke, 2004; Toner et al., 2006) and provide supporting data for aerosol modeling (Cheng et al., 2013; Song et al., 2006; Watson et al., 1997; Yu et al., 2013). Primary PM_{2.5} emitted by diesel vehicles contains a variety of chemical constituents, such as elemental carbon (EC), organic carbon (OC), water-soluble ions

(WSIs), elemental compounds, and unidentified compounds that are important in the study of diesel exhaust (Biswas et al., 2009; Cheng et al., 2010; Cheung et al., 2010; Chiang et al., 2012). The EC of diesel particulate matter (DPM) is formed through the pyrolysis of unburned fuels at high temperatures. DPM can reduce visibility due to the absorption of direct light by EC and light scattering (Eidels-Dubovoi, 2002; Eldering and Cass, 1996). The OC of DPM is produced as a result of incomplete fuel combustion and lubricant oil (Kittelson et al., 2006; Li et al., 2014). WSIs are produced by inorganic contaminants in the fuel and lubricating oil and engine wear, which could play a role in diesel exhaust nucleation (Kleeman et al., 2000; Sakurai et al., 2003; Toner et al., 2006; Yu, 2001). Elements are important constituents of DPM, although they only account for a small fraction of the PM_{2.5} mass emissions (Lough et al., 2005).

Previously, tunnel testing, roadside tests and chassis dynamometer measurements were used to assess the particulate matter (PM) emitted from diesel vehicles (Biswas et al., 2008; Chellam et al., 2005; May et al., 2014; Ntziachristos et al., 2007; Kim Oanh et al., 2010; Park et al., 2003; Sharma et al., 2005). A number of studies have focused on the chemical composition of DPM using these methods. For example, Sharma et al. (2005) characterized particulate emissions in terms of the benzene soluble fraction and the metal and elemental and organic carbon contents from a mid-sized diesel engine operated under four different loads in India. Cheung et al. (2010) used a chassis dynamometer and assessed the chemical and oxidative potential of particulate exhaust emissions from a diesel vehicle with a three-stage oxidation system located in Greece. Chiang et al. (2012) measured the PM and its constituents, including the EC, OC, WSI species, elements and polycyclic aromatic hydrocarbons (PAHs) exhaust from six in-use, light-duty diesel vehicles by a chassis dynamometer following the driving pattern of the FTP-75 in Taiwan. Dallmann et al. (2014) measured the chemical composition of PM emitted by gasoline and diesel vehicles at a high temporal resolution through a highway tunnel in the San Francisco Bay area. In recent years, mobile emission laboratory methods (MELs) and a portable emissions measurement system (PEMS) have been developed. Mobile approaches have the potential to provide practical and highly effective methods of measuring emission characteristics directly from the tailpipe in real-world conditions (Cocker et al., 2004; Giechaskiel et al., 2014; Mamakos et al., 2013; Shah et al., 2004; Wang et al., 2012; Weiss et al., 2012). Shah et al. (2004) reported the EC, OC and PM emission rates of 11 heavy heavy-duty diesel trucks (HHDDTs) operating under real-world

conditions by following the speed trace from the CARB HHDDT cycle using a MEL in Coachella, CA. In China, PEMS are gradually being implemented to measure the emission factors (EFs) of vehicles on the road (Huo et al., 2012; Liu et al., 2009; Wang et al., 2012; Zheng et al., 2015). However, research on the chemical composition of PM_{2.5} emitted from on-road diesel trucks remains limited in China.

Recently, Zhang et al. (2015) characterized the chemical composition of PM_{2.5} emitted from on-road pre-China I and China I heavy-duty diesel trucks using PEMS. We characterized the OC and EC in PM_{2.5} emitted from on-road China III diesel trucks and investigated the influence of vehicle size and driving conditions according to distance and CO₂ emissions (Wu et al., 2015). However, the EFs for the detailed chemical components of PM_{2.5} emitted from diesel trucks were not studied, and the tested vehicles included only China III and not China IV diesel trucks. China IV emission standards for diesel trucks were adopted in Beijing in 2013 and were fully implemented in China in 2015. To attain the limits of the standard, exhaust gas recirculation (EGR), diesel oxidation catalysts (DOC), particle oxidation catalysts (POC), and selective catalytic reduction (SCR) were applied to China IV diesel trucks. Following our previous study, this study aims to characterize in greater detail the chemical composition of PM_{2.5} emitted from on-road China III and China IV diesel trucks, including the OC, EC, WSIs, and elemental contents, and to analyze the impact of new emission control technologies on the chemical components of PM_{2.5} emitted from diesel trucks. The EFs reported here can enrich the local database and be used for bottom-up emission inventories at urban and national scales where detailed fleet data are available.

2. Methodology

2.1 . Sampling system

A PEMS based on our previous on-board emission system was used to collect data and samples (Huo et al., 2012; Wu et al., 2015; Yao et al., 2007; Yao et al., 2014). This system consists of four main parts: the SEMTECH EFM-2 tube, the SEMTECH DS mobile emission analyzer, the SEMTECH MPS (Micro-Proportional Sample System; Sensors Inc., Ann Arbor, MI, USA), and the PM_{2.5} sampling system. The SEMTECH EFM-2 tube was used to measure the flow of diesel

exhaust, the SEMTECH DS was used to analyze the instantaneous concentration of gas emissions (CO₂, CO, HC, and NO_x), the SEMTECH MPS was used to dilute the diesel exhaust with clean air, and the PM_{2.5} sampling system was used to collect the samples. Additional detailed information on the system is provided in our previous study (Wu et al., 2015).

2.2 . Vehicle fleet and testing cycles

The primary PM_{2.5} emissions were measured from eighteen on-road diesel trucks in Beijing. The tested diesel trucks were divided into three groups based on their gross vehicle weights (GVWs): six light-duty diesel trucks (LDDTs, less than 4500 kg), six medium-duty diesel trucks (MDDTs, 4500-12,000 kg), and six heavy-duty diesel trucks (HDDTs, more than 12,000 kg). Half of the vehicles in each group were China III diesel trucks, and the other half were China IV diesel trucks. After-treatment devices for exhaust were not installed on the China III diesel trucks. For the China IV diesel trucks, POC, DOC, and EGR control devices were installed on the LDDTs and MDDTs, and SCR control devices were installed on the HDDTs. Detailed information on the tested vehicles is provided in **Table 1**. The fuel used for the tested diesel trucks in this study was commercially available diesel fuel (0#). The fuel met the 10 mg kg⁻¹ fuel sulfur limit of the Chinese phase V emission regulations for diesel vehicles in Beijing.

Based on the analysis of the traffic control measures and driving conditions of on-road diesel trucks in Beijing, two predesigned fixed routes were selected: one for the LDDTs and MDDTs and another for the HDDTs. Both of the test routes included highway (HW) and non-highway (NHW) roads to reflect the influence of driving patterns on the emissions. The total length of the test route for LDDTs and MDDTs was approximately 47 km in west Beijing and approximately 63 km for HDDTs in southwest Beijing. Detailed information on the test routes has been described by Yao et al. (2015). During the sampling, all of the tested diesel trucks were under hot stabilized conditions. An assistant remained in the trucks to monitor the emissions equipment to ensure that the system operated normally. The total weight of the emission measurement equipment was approximately 200 kg. The measurements were conducted in October 2014, during which the atmospheric temperature ranged from approximately 293 to 303 K. The temperature was measured by an atmospheric temperature device, which was mounted on the roof of the tested vehicles with a

measurement height of 2.9-3.8 m. In addition, the sampling time was adjusted (30-40 min) to ensure that the measurements of the chemical components analyzed in the laboratory were within the detection limits of the instruments.

Table 1 Characteristics of the tested diesel trucks

Test number	Vehicle size	Engine standard	Model year	Truck model	Engine model	GVW (kg)	Rate power (kW)	Engine displacement (L)	Odometer (km)
#1	LDDT	China III ^a	2011	BJ5040XXY13	4D26	4344	68	2.6	66494
#2			2012	BJ5049V8BEA	ISF3.8s3141	4490	105	3.8	71011
#3			2012	BJ5049V8BD6-FD	ISF2.8s3129T	4390	96	2.8	152059
#4		China IV ^b	2014	BJ5049XXY-AA	4J28TC	4330	81	2.8	867
#5			2014	HFC5048XXYP71K1C2	HFC4DA1-2C	4495	88	2.8	13625
#6			2014	HFC5048XXYP71K1C2	HFC4DA1-2C	4495	88	2.8	18621
#7	MDDT	China III ^a	2012	BJ5129VECEG	ISF3.8s3168	11995	125	3.8	62381
#8			2013	HFC5061XXYKT	CY4102-C3D	5665	80	3.9	68837
#9			2011	BJ5051VBBFA-S3	CY4102-C3C	5200	88	3.9	85348
#10		China IV ^b	2014	BJ5099XXY-FB	ISF3.8s4R154	5495	115	3.8	997
#11			2014	BJ5099VECED-FB	ISF3.8s4R154	9495	115	3.8	4199
#12			2014	BJ5099VECED-FB	ISF3.8s4R154	9495	115	3.8	31492
#13	HDDT	China III ^a	2009	BJ5253VMCHL-S	ISDe185-30	25000	136	6.7	140260
#14			2011	DFL5160XXYBX7	EQH160-30	15900	118	4.8	153997
#15			2009	BJ5253VMCHL-S	ISDe185-30	25000	136	6.7	327408
#16		China IV ^c	2014	DFL1120B18	EQH160-40	13580	118	4.8	23968
#17			2014	CA5168XXYPK2L2E4A80-3	BF4M2012-16E4	15800	121	4.0	24066
#18			2013	CA5168XXYPK2L2E4A80-3	BF4M2012-16E4	15800	121	4.0	63309

^a: without after-treatment; ^b: with EGR+DOC+POC after-treatment; ^c: with SCR after-treatment.

2.3 . Chemical constituent analysis of PM_{2.5}

PM_{2.5} was collected on a 47 mm Teflon filter (R2PJ047, PALL Corp., USA) with a pore size of 2 µm after dilution. The filter was conditioned for at least 24 h in a chamber controlled for humidity (RH: 30-40%) and temperature (25°C); the filter was then weighed using a microbalance (MT5, Mettler Toledo, Switzerland) until two measurements were obtained within 3 µg. The mass of the sample was determined by weighing the filter before and after each run. Quartz filters (47 mm, 2500QAT-UP, PALL Corp., USA) were pre-baked at 650°C for 8 h to eliminate organic pollutants and stored in baked aluminum foil before sampling. A 1 cm² punch was removed from the quartz filter after sampling to analyze the carbonaceous components (OC and EC) in PM_{2.5} using a Thermo/Optical Carbon Analyzer (DRI Model 2001A, Atmoslytic Inc., USA) according to

the NIOSH 5040 reference method. This method is often used when assessing the carbonaceous components of diesel-laden aerosols (Birch and Cary, 1996). The remaining quartz filters were ultrasonically extracted using distilled de-ionized water to determine the WSIs using ion-chromatography (IC; ICS2100, Thermo, USA). The detection limits of ions were 0.01-0.1 $\mu\text{g mL}^{-1}$ for anions with a relative standard deviation (RSD) < 3 and 0.01-0.02 $\mu\text{g mL}^{-1}$ for cations with an RSD < 1.5. After weighing, the entire Teflon filter was used to analyze the elements. The total $\text{PM}_{2.5}$ was digested in closed Teflon digestion vessels by a programmable microwave digestion unit (MARS5, CEM Corp., USA). The digested acid mixture was then analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS; X SERISII, Thermo-Fisher, USA). The detection limits for elements were as follows: 1 ppt to 1 ppb for In, Cs, Tl, Be, Li, Rb, Ga, Cd, Bi, Co, U, As, Ag, Cu, Mn, Ni, Pb, Sr, Se, Ba, V, and Al and 1-10 ppb for Hg, Cr, Fe, Ti, and Zn with an RSD < 3. Furthermore, two internal standards (Rh and Tb) were used to monitor the drift in the signal sensitivity over time during each set of analyses with the recovery ranging from 95% to 105%.

3. Results and discussion

3.1. EFs of the $\text{PM}_{2.5}$ chemical constituents

The average EFs for vehicles of the same size with different emission standards are presented in **Table S1 (Supplementary Material)**; these values are the weighted averages of the EFs of the two driving conditions (HW and NHW). The average EFs of the tested diesel trucks of different sizes and different emission standards are shown in **Table 2**. The average EF of $\text{PM}_{2.5}$ was 0.085 g km^{-1} (0.019-0.228 g km^{-1}). The average EF of the total carbon ($\text{TC} = \text{OC} + \text{EC}$) was 0.074 g km^{-1} (0.016-0.199 g km^{-1}). Total carbon was the dominant component and accounted for approximately 87% of the $\text{PM}_{2.5}$, whereas the OC and EC accounted for 32% and 55% of the $\text{PM}_{2.5}$, respectively, similar to the $\text{TC}/\text{PM}_{2.5}$ results (greater than 80%) in our previous study (Wu et al., 2015). The average EF of the total WSIs (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) was 2.74 mg km^{-1} (1.57-4.59 mg km^{-1}); total WSIs was the second largest group and contributed 3.2% of the $\text{PM}_{2.5}$. Finally, the average EF of the total elements (Li, Be, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, and U) was 486

$\mu\text{g km}^{-1}$ (299-600 $\mu\text{g km}^{-1}$), corresponding to 0.57% of the $\text{PM}_{2.5}$.

When we compared the results of the distance-based emission factors of the chemical components in $\text{PM}_{2.5}$ in this study with previous findings, detailed distance-based emission factors obtained under comparable conditions, such as the same method and tested vehicles, were lacking. A summary of the distance-based EFs of the chemical species in $\text{PM}_{2.5}$ emitted from diesel trucks from several studies that adopted PEMS and the use of a chassis dynamometer is presented in **Table 2**. The proportions of the chemical groups in $\text{PM}_{2.5}$ in our study were within the ranges of those reported in related studies (Cheung et al., 2010; Chiang et al., 2012; Kim Oanh et al., 2010). Similar results were also presented in other studies. For example, the United States Environmental Protection Agency (USEPA) concluded that diesel exhaust particles are typically composed of 75% EC (as high as 90%), 20% OC (as low as 7%), and small amounts of sulfate, nitrate, elements, water, and unidentified compounds (McClellan et al., 2012), and Jin et al. (2014) reported that total carbon accounted for $82 \pm 9\%$ of the total DPM mass followed by 15 inorganic elements ($6.3 \pm 1.4\%$) for a heavy-duty diesel engine. However, the wide range of EFs of the chemical constituents of $\text{PM}_{2.5}$ reported in various studies may reflect study differences in test methods, vehicle model and year, driving cycle, fuel quality, and other factors. The results of this study are of significance for the development of local EFs.

Table 2 Average EFs of the chemical species in $\text{PM}_{2.5}$ in this and related studies

Species	This study		Related studies			
			Chiang et al., 2012	Kim Oanh et al., 2010	Cheung et al., 2010	
	Diesel trucks		LDDTs	Diesel trucks	LDDTs	
	Range	Average EFs	Average EFs	Average EFs	Honda	Golf
$\text{PM}_{2.5}^a$	(0.019-0.228)	0.085	0.151	0.995	0.027	0.072
OC ^a	(0.003-0.105)	0.027	0.037	0.192	0.005	0.024
EC ^a	(0.013-0.095)	0.047	0.072	0.467	0.02	0.039
WSIs ^b	(1.57-4.59)	2.74	2.35	40.2	0.07	0.14
Cl ⁻	(0.07-0.45)	0.21	0.003	2.2	—	—
NO ₂ ⁻	(0-0.09)	0.07	0.217	—	—	—
NO ₃ ⁻	(0.27-0.80)	0.45	0.819	3.4	—	—
SO ₄ ²⁻	(0.12-1.14)	0.45	0.687	18.7	0.07	0.14
Na ⁺	(0.17-1.27)	0.57	0.048	2.8	—	—
NH ₄ ⁺	(0.09-0.22)	0.16	0.412	1.3	—	—
K ⁺	(0.09-0.18)	0.14	0.038	1.3	—	—
Mg ²⁺	(0.07-0.18)	0.1	0.01	2.4	—	—
Ca ²⁺	(0.43-0.79)	0.6	0.113	8.1	—	—
Elements ^c	(299-600)	486	2812	4840	8.007	25.43
Li	(0.03-0.10)	0.07	— ^d	10	—	—
Be	(0.005-0.021)	0.016	—	10	—	—
Al	(27-79)	45	1239	1020	0.148	1.16
Ti	(79-177)	123	—	20	—	—
V	(0-1.33)	0.59	12	10	0.038	0.027
Cr	(2.26-12.8)	9.41	43	270	0.341	0.245
Mn	(1.08-2.82)	1.68	89	50	0.124	0.426
Fe	(72-295)	210	900	1980	0.005	0.618
Co	(0.07-0.25)	0.16	14	40	0.006	0.023
Ni	(0.46-2.79)	1.63	88	60	0.16	0.196
Cu	(1.48-5.56)	3.27	44	560	—	—

Zn	(25-159)	65	178	610	7.02	22.3
Ga	(0-0.05)	0.02	—	—	—	—
As	(1.02-1.62)	1.28	12	—	—	—
Se	(0.54-1.65)	1.24	10	—	—	—
Rb	(0-0.08)	0.03	—	—	—	—
Sr	(0.13-6.87)	3.18	5	30	—	—
Ag	(0-0.29)	0.06	—	—	—	—
Cd	(0-0.30)	0.11	6	10	0.005	0.006
In	(0-0.0022)	0.0004	—	—	—	—
Cs	(0-0.014)	0.005	—	—	—	—
Ba	(0.35-2.81)	1.66	97	—	0.142	0.185
Hg	(0-42)	14	—	—	—	—
Tl	(0-0.0022)	0.0008	—	—	—	—
Pb	(0-13.70)	4.36	75	160	0.018	0.247
Bi	(0-0.04)	0.01	—	—	—	—
U	(0.01-0.03)	0.02	—	—	—	—
OC/PM _{2.5}		32%	25%	19%	19%	33%
EC/PM _{2.5}		55%	48%	47%	74%	54%
WSIs/PM _{2.5}		3.2%	1.6%	4.0%	0.26%	0.19%
Elements/PM _{2.5}		0.57%	1.9%	0.49%	0.03%	0.04%
Method		PEMS		Chassis dynamometer		

^a The unit g km⁻¹ was used to represent the carbonaceous composition and PM_{2.5}.

^b The unit mg km⁻¹ was used to represent the WSIs.

^c The unit µg km⁻¹ was used to represent the elements.

^d Data not available.

3.2. Chemical characterization of PM_{2.5} from China III and China IV diesel trucks

The PM_{2.5} chemical composition characterizations are shown as stacked columns in **Fig. 1**. PM_{2.5} emissions, except for LDDTs, were significantly reduced under more stringent emission standards. The PM_{2.5} emissions were reduced by 51% for MDDTs and 45% for HDDTs in China IV diesel vehicles relative to China III diesel vehicles, which was mainly due to the reduction of OC emissions (81% for MDDTs and 86% for HDDTs). With the use of SCR for HDDTs, the reductions observed for OC may have been due to the decrease in the generation of gaseous organic emissions before they could be absorbed by the primary EC particles (Liu et al., 2009). The proportions of OC components in the PM_{2.5} were also significantly reduced, and the proportions of EC in the PM_{2.5} were increased for MDDTs and HDDTs with the change from China III to China IV emission standards. Cheng et al. (2015) reported that the use of DOC promoted moderate reductions of EC (a reduction of 36%) and more significant reductions of OC (a reduction of 53%) for a heavy-duty diesel engine (HDDE). Similar results were shown in our study: the use of DOC + POC + EGR for MDDTs promoted moderate reductions of EC (a reduction of 28%) and more significant reductions of OC (a reduction of 81%). However, China IV LDDTs that were equipped with the same control device as the MDDTs did not show decreases in PM_{2.5} emissions. Rather, the PM_{2.5} emissions increased by 66%, with the EC emissions doubling and OC emissions increasing slightly (an increase of 8%) when changing from the China III to the China IV emission standard. This anomalous result may have been

caused by a number of potential factors (such as the type of after-treatment, the engine power, and the diesel truck manufacturer). Cheng et al. (2015) reported that the after-treatment promotes changes in the OC/EC ratio and indicated that the effectiveness of DOC catalytic oxidation is revealed in the OC/EC ratio. Upon closer examination, we found that the average EC/OC mass ratios of China IV LDDTs (4.25) and China IV MDDTs (4.73) were similar. Additionally, the EC/OC mass ratios were also similar to the EC/OC mass ratio (3.98) of a light-duty diesel vehicle equipped with a three-stage oxidation system that includes a closed-coupled oxidation catalyst, EGR, and a main underbody oxidation catalyst, thus meeting the “Euro 4” emission standard reported by Cheung et al. (2010). This result demonstrates that high PM may not be caused by the after-treatment without oxidation and indicates that a poorly working engine may produce a large amount of particulate matter for China IV LDDTs. Additional samples and in-depth studies are required to explain this result for LDDTs, and after-treatment device inspections should be improved to avoid devices that do not function well.

The EC/OC mass ratios of the 18 diesel trucks varied widely (0.20-6.94), with the EC/OC mass ratios ranging from 0.20 to 3.06 for the China III diesel trucks and from 2.52 to 6.94 for the China IV diesel trucks, as shown in **Fig. 1**. This variation might reflect differences among vehicles in engine type/power, GVW, model year, and manufacturer (Shah et al., 2004). However, the EC/OC mass ratios were strongly dependent on the emission standards. The average EC/OC mass ratios of the China IV diesel trucks were 4.25 for the LDDTs, 4.73 for the MDDTs, and 5.81 for the HDDTs, and these values were higher than the corresponding values of the China III diesel trucks (2.16, 1.09, and 1.56, respectively). The analysis of the EC/OC mass ratios suggested that the trends in the EC/OC mass ratios for the same sized diesel vehicles with different emission standards are related to the OC/PM_{2.5} and EC/PM_{2.5} mass ratios. For the tested China III LDDTs, MDDTs, and HDDTs, the OC/PM_{2.5} mass ratios were 29%, 44%, and 46%, and the EC/PM_{2.5} mass ratios were 57%, 46%, and 41%, respectively. The mass ratios of the OC/PM_{2.5} were 19%, 18%, 12%, and the EC/PM_{2.5} were 68%, 67%, 77% for the China IV LDDTs, MDDTs, HDDTs, respectively. Cheng et al. (2015) reported that the effectiveness of the DOC to preferentially remove the OC fraction via oxidation is demonstrated by its small OC/EC mass ratio.

Fig. 1. Distance-based EFs of the chemical constituents of $PM_{2.5}$ and EC/OC mass ratios of 18 diesel trucks. The numbers (i.e., #1, #2, ..., #18) beside the circles represent the test vehicle identification numbers.

The characterized WSIs in the $PM_{2.5}$, including Ca^{2+} , NO_3^- , Na^+ , SO_4^{2-} , K^+ , Mg^{2+} , Cl^- , NO_2^- , and NH_4^+ , are shown as stacked columns in **Fig. 2**. For the same sized vehicles, the amount of WSIs decreased from the China III to China IV emission standards, and the average EFs of WSIs were reduced by 2% for LDDTs, 31% for MDDTs, and 17% for HDDTs. The large differences in the quantities of the WSI species for the tested diesel trucks may be due to several reasons (e.g., engine power/type, fuel quality, emission standard, model year, and odometer reading). For the LDDTs, Ca^{2+} and NO_3^- were the most abundant ions, contributing 25% and 34% of the WSIs for the China III diesel trucks, respectively, and accounting for 34% and 27% of the WSIs for the China IV diesel trucks, respectively. For the MDDTs, Na^+ , Ca^{2+} , and SO_4^{2-} contributed 24%, 22%, and 19% of the WSIs for the China III diesel trucks, respectively, whereas Ca^{2+} and NO_3^- contributed 28% and 17% of the WSIs for the China IV diesel trucks. Na^+ , Ca^{2+} , and SO_4^{2-} were also abundant WSIs for the HDDTs, with the combination of compounds contributing 71% and 62% of the WSIs for the China III and China IV HDDTs, respectively. The average EFs of SO_4^{2-} decreased from the China III to China IV diesel trucks for the same sized vehicles and were reduced by 28% for LDDTs, 70% for MDDTs, and 45% for HDDTs.

Fig. 2. Ion fraction characterization in the PM_{2.5} from diesel trucks

The utilization of organometallic additives in lubricating oil, the presence of elements in the fuel, and the wear and corrosion of the engine and exhaust system are potential sources of various elements measured in the diesel exhaust (Vouitsis et al., 2009; Wang et al., 2003). Although the elements show an insignificant contribution to the PM_{2.5} emissions, some elements are important source markers, even at low concentrations. A range of elements found in PM_{2.5} can also serve as markers for currently used fuel additives and lubricant oil (Kim Oanh et al., 2010). The EFs (average and standard deviation) for individual elements emitted from the same sized vehicles for different emission standards are presented in Fig. 3. The amount of the elements tested in our study accounted for 1.42% and 0.74% of the PM_{2.5} for China III and IV LDDTs, respectively, 0.91% and 2.86% for China III and IV MDDTs, respectively, and 0.31% and 0.27% for China III and IV HDDTs, respectively. The EFs of the elements for the China III LDDTs were higher than those for the China IV LDDTs except for the individual elements Fe, Cr, Hg, Se, Bi, and Ag, as shown in Fig. 3a. For the China III HDDTs, the EFs of trace elements were higher than those for the China IV HDDTs except for the individual elements Ti, Cr, Co, Sr, Li, Rb, and Cs, as shown in Fig. 3c. The total element EFs were reduced by 13% for LDDTs and 53% for HDDTs with the change from the China III to China IV emission standards. However, the EFs of elements for the China IV MDDTs were higher than those for the China III MDDTs

except for the individual elements Ti, Pb, As, Cd, Li, Cs, Tl, and In, as shown in **Fig. 3b**, with the total elements increasing by 53% from the China III to the China IV. The differences in the results for the individual elements may be affected by many factors, such as differences in the engine rate power, GVW, complex reactions in the engine and the after-treatment. [Hu et al. \(2009\)](#) classified the total elements in PM into the following groups: oil additives (Ca and Zn), Fe, Cu, platinum group elements (PGE: Pt, Pd, and Rh), V, Ti, mobile source air toxic (MSAT) metals (As, Cr, Pb, Mn, and Ni), and other metals. The EFs of the tested elements in this study were less than 1 mg km^{-1} , and the abundant elements Fe, Ti, Zn, and Al for the tested diesel trucks ranged from 10^{-5} to $10^{-3} \text{ g km}^{-1}$. Fe is typically one of the most abundant elements in diesel vehicle exhaust ([Geller et al., 2006](#); [Okada et al., 2003](#)) and is derived from wearing of the exhaust manifold, abrasion of the engine block, and fuel oil; Fe is also a known redox agent. The MSAT metals ranged from 0.001 to 0.01 mg km^{-1} . The PGEs were not tested in our study. [Ravindra et al. \(2004\)](#) reported that there is incontrovertible evidence of increasing levels of PGEs in the environment since the introduction of the catalytic converter into cars. Except for sulfur, elements were not selectively removed in comparison to bulk PM with the change from China III to China IV diesel vehicles. Because there are many types of elements in $\text{PM}_{2.5}$, and most of them have adverse health effects, more stringent control technology and improved fuel quality should be developed to reduce the emissions of total elements.

Fig. 3. Characterization of individual elements from the diesel trucks

3.3. Chemical characterization of PM_{2.5} under HW and NHW driving conditions

The carbonaceous composition of the PM_{2.5} EFs, the mass ratios of OC/PM_{2.5}, EC/PM_{2.5}, and EC/OC, and the average speeds of two driving conditions for the same sized vehicles and emission standards are presented in **Fig. 4**. The average speed was greater than 60 km h⁻¹ for HW driving conditions and between 20 and 30 km h⁻¹ for NHW driving conditions. In general, the EFs of PM_{2.5} under NHW driving conditions were higher than those under HW driving conditions with the exception of the China IV LDDTs and HDDTs. The OC EFs under NHW driving conditions were higher than those under HW driving conditions for the same sized and standard vehicles with the exception of the China IV HDDTs. During NHW driving conditions, the fuel consumed per kilometer was greater than that under HW driving conditions, and high

1 fuel consumption was the main factor resulting in the high EFs of $PM_{2.5}$. The tested diesel
2 vehicles used under NHW driving conditions at low speeds with a low combustion temperature
3 presented lower fuel pyrolysis, and lubricant oil contributed more to OC emissions during NHW
4 conditions than HW driving conditions. The mass ratios of EC/OC, OC/ $PM_{2.5}$ and EC/ $PM_{2.5}$
5 showed that the driving conditions had a significant impact on the carbonaceous components.
6 For vehicles of the same size and with the same emission standards, the EC/OC mass ratios
7 increased from the NHW to HW driving conditions with the exception of the China IV HDDTs
8 (a decreasing trend). We found that the increased EC/OC mass ratios were caused by the
9 decreased OC/ $PM_{2.5}$ mass ratio and increased EC/ $PM_{2.5}$ mass ratio from the NHW to HW driving
10 conditions. The OC/ $PM_{2.5}$ mass ratios were higher during NHW driving conditions because of
11 the low vehicle speeds and long idling times, whereas the EC/ $PM_{2.5}$ mass ratios were higher
12 during HW driving conditions because of higher vehicle speeds, lower air/fuel ratios and higher
13 pressure and temperatures (Cocker et al., 2004; Hildemann et al., 1991; Li et al., 2014; Yang et
14 al., 2015). For the China IV HDDTs, the decreased EC/OC mass ratio was caused by the
15 increased OC/ $PM_{2.5}$ mass ratio and decreased EC/ $PM_{2.5}$ mass ratio from the NHW to HW driving
16 conditions. Complex internal reactions in the China IV heavy-duty diesel engines as well as the
17 SCR after-treatment device may be the primary factors leading to the abnormal results under the
18 real-world driving conditions. These results include a number of inherent uncertainties due to
19 factors such as engine conditions, a limited sample size, and the use of offline analyses.
20 Therefore, additional samples and more detailed experimental designs that test for these and
21 other factors are necessary in future studies.
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Fig. 4. Carbonaceous composition of the $PM_{2.5}$ and average speeds for the diesel trucks under HW and NHW driving conditions

The EFs of the WSIs with individual species under HW and NHW driving conditions and according to the vehicle size and emission standard are presented as stacked columns in **Fig. 5**. It is obvious that driving conditions affected the amount of WSIs. Under HW driving conditions, the WSIs were significantly lower relative to the NHW driving conditions for the same sized vehicles with the same emission standards. The WSIs were reduced by 23-39% from NHW to HW driving conditions except for the China III LDDTs and China IV HDDTs, and the WSI levels under NHW and HW driving conditions were approximate equal for China III LDDTs and China IV HDDTs, respectively. The amount of WSIs emissions may have been affected by individual ions, such as SO_4^{2-} . In general, the EFs of SO_4^{2-} presented a decreasing trend from NHW to HW driving conditions (reduced by 14-61%) for the same sized vehicles with the same emission standards except for the China III LDDTs (increased by 26%) and China IV HDDTs (increased by 55%). NH_4^+ presented a decreasing trend (reduced by 15-69%) for the same sized vehicles with the same emission standards, although the trend increased by 6% and 42% for the China III and China IV HDDTs from NHW to HW driving conditions, respectively. Except for

the China IV MDDTs, the NO_2^- EFs were higher (8-437%) under HW than under NHW driving conditions for the same sized vehicles with the same emission standards, especially the China IV HDDTs (an increase of 437%). The NO_3^- EFs were mainly reduced (7-79%) from NHW to HW driving conditions, although the China IV MDDTs increased by 74%. Overall, the emissions of Cl^- , Mg^{2+} , K^+ , and Ca^{2+} presented a decreasing trend and Na^+ presented an increasing trend from NHW to HW driving conditions for diesel trucks of the same size and emission standard.

Fig. 5. WSIs EFs according to driving conditions

The individual element EFs under NHW and HW driving conditions for the same sized vehicles with the same emission standards are presented as stacked columns in **Fig. 6**. Fe, Ti, Zn, and Al were the primary tested elements, and they accounted for 81% to 97% of the total tested elements. For the tested diesel trucks, all of the tested elements were significantly affected by driving conditions. For the China III LDDTs, the total element emissions were reduced by 55%, and there were reductions in all of the tested individual elements from NHW to HW driving conditions. [Vouitsis et al. \(2009\)](#) reported that the effect of the driving cycle is significant for the emission rates of all elements. Increased element emissions under NHW driving conditions are likely associated with the accumulation mode of the particles, which could provide a more active

surface area for the absorption of metallic compounds (Hu et al., 2009). For the China IV MDDTs and HDDTs, the average total element EFs decreased significantly (36% for MDDTs and 22% for HDDTs) from NHW to HW driving conditions. However, for the China IV LDDTs, the total elements emission increased by 26% from NHW to HW driving conditions. For the MDDTs and HDDTs with the China III emission standard, the average EFs of the total elements did not present a significant increase (5% for MDDTs and 3% for HDDTs) from NHW to HW driving conditions. Several species of the tested elements that presented higher amounts under HW driving conditions for the diesel trucks with after-treatment devices may be associated with higher engine loads, which would result in high exhaust temperatures and less variable power consumption, and an emission control system.

Fig. 6. Individual element EFs under NHW and HW driving conditions

3.4 Correlations among $PM_{2.5}$ species

Statistical tests, such as Pearson's correlation analysis, for chemical species in the PM of vehicle exhaust have been conducted in previous studies (Chellam et al., 2005; Cheung et al., 2009; Cheung et al., 2010; Jin et al., 2014; Mkoma et al., 2014; Thiruvengadam et al., 2014).

Table S2 (Supplementary Material) lists the Pearson's correlation coefficients (R-values) and significance levels observed for the individual chemical species in the PM_{2.5} from the China III and China IV diesel trucks. For the China III and China IV diesel trucks, strong correlations were observed among the carbonaceous contents of the PM_{2.5}. The PM_{2.5} and OC contents showed strong correlations, with an R-value of 0.89 for the China III diesel trucks and 0.88 for the China IV vehicles, and the PM_{2.5} and EC contents showed strong correlations of 0.73 and 0.99 for the China III and China IV diesel trucks, respectively. For the China III diesel trucks, the OC and EC contents were not strongly correlated, although they were strongly correlated for the China IV diesel trucks, with an R-value of 0.86. SO₄²⁻ is used as a tracer for vehicle emissions, and it was strongly correlated with Cl⁻ and Na⁺, with $0.92 < R < 0.97$ for the China III diesel trucks and $0.66 < R < 0.88$ for the China IV diesel trucks. Fuel burning is an important source of SO₄²⁻ and Cl⁻ in PM_{2.5}. Fe was negatively correlated with SO₄²⁻, Cl⁻, and Na⁺, with $-0.52 < R < -0.59$ for the China IV diesel trucks. Most of the elements tested in our study were well correlated, including Ti, V, Cr, Mn, Co, Ni, Cu, Ga, As, Sr, Pb, and U. For the China III diesel trucks, Pb was strongly correlated with Sr (R = 0.93) and Cd (R = 0.99). The MSAT elements presented significant correlations of $0.52 < R < 0.99$ at the p = 0.01 level for the China III diesel trucks, although the correlations between Pb and Mn and between Cd and each of Mn, As, and Ni were weak. For the China IV diesel trucks, the MSAT elements presented significant correlations of $0.54 < R < 0.86$ at the p = 0.01 level, although some correlations between individual elements had low R-values.

4. Conclusions

In this study, the detailed chemical composition of $PM_{2.5}$ emitted from nine China III and nine China IV diesel trucks of three sizes (LDDTs, MDDTs, and HDDTs) on actual roads in Beijing was investigated using a PEMS. The samples represented actual emissions from diesel trucks. The highest proportion of $PM_{2.5}$ was contributed by carbonaceous compounds and was approximately 87% of the $PM_{2.5}$, which is similar to the result (greater than 80%) of our previous study (Wu et al., 2015). WSIs accounted for 3.2% of the $PM_{2.5}$, and the total elements tested accounted for approximately 0.57% of the $PM_{2.5}$. In general, the $PM_{2.5}$ emissions were reduced in the China IV diesel trucks relative to the China III diesel trucks with the exception of the LDDTs. The EC/OC mass ratios were strongly dependent on the emission standards, with those of the China IV diesel trucks higher than those of the China III diesel trucks for the same sized vehicles. The amount of WSIs and elements presented a decreasing trend from the China III to China IV diesel trucks for the same sized vehicles except for the total element content of MDDTs. The chemical species of the $PM_{2.5}$ were significantly affected by the driving conditions. Overall, the EC/OC mass ratios presented an increasing trend with a decrease in OC/ $PM_{2.5}$ and an increase in EC/ $PM_{2.5}$ mass ratios from NHW to HW driving conditions; these trends are similar to those of our previous study (Wu et al., 2015). The vast majority of WSIs and some element emissions were lower under HW driving conditions. To understand the relationships between the various chemical components, Pearson's correlation coefficients among the $PM_{2.5}$ species were analyzed. Some chemical species were strongly correlated, such as the carbonaceous contents of $PM_{2.5}$; SO_4^{2-} , Cl^- , and Na^+ ; and Ti, V, Cr, Mn, Co, Ni, Cu, Ga, As, Sr, Pb, and U.

Measurements of the diesel truck emissions were obtained through the use of the PEMS. However, uncertainty is present in the EF results due to uncontrolled factors such as operating conditions, fuel quality and engine type. Therefore, to assess these and other key factors, future investigations must include more rigorous designs and larger sample sizes. The chemical constituents of PM (carbonaceous, WSI, and elemental) play important roles in $PM_{2.5}$ toxicity studies. The $PM_{2.5}$ EFs presented in our study provide a concrete basis for studying the health

and climatic impacts of PM as well as source apportionment and aerosol modeling in China and other developing countries.

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