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Chemical composition of $PM_{2.5}$ from two tunnels with different vehicular fleet characteristics

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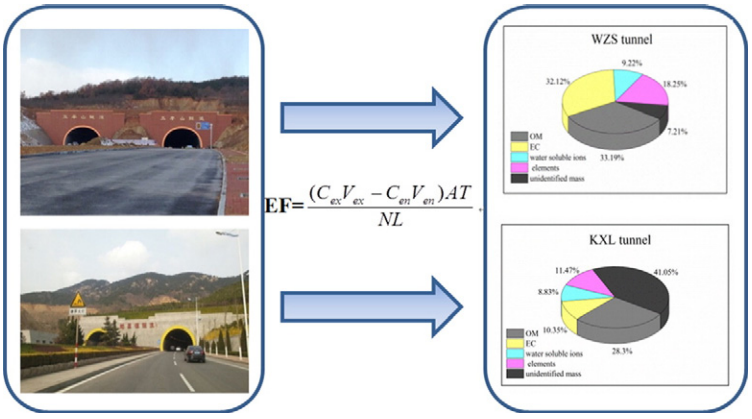
HIGHLIGHTS

- Composition profiles of $PM_{2.5}$ were obtained in smaller city, Yantai.
- Characteristics of $PM_{2.5}$ were changed by emission standards and fuel policy.
- Source profiles of $PM_{2.5}$ for gasoline vehicles and diesel vehicles were given.
- The diesel vehicles play a major role in $PM_{2.5}$ emissions in Yantai.

GRAPHICAL ABSTRACT



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ABSTRACT

The chemical compositions of $PM_{2.5}$ including OC, EC, water soluble ions, elements, and organic components such as polycyclic aromatic hydrocarbons (PAHs), hopanes, and steranes, emitted in Wuzushan (WZS) and Kuixinglou (KXL) tunnels were determined. WZS tunnel is a major route for diesel vehicles traveling, while KXL tunnel has limited to diesel vehicles. The results showed that the proportions of the different constituents of $PM_{2.5}$ in the Wuzushan (WZS) tunnel were OC (27.7%), EC (32.1%), elements (13.9%), and water soluble ions (9.2%). Whereas the chemical profile of $PM_{2.5}$ in the Kuixinglou (KXL) tunnel was OC (17.7%), EC (10.4%), elements (8.90%), and water soluble ions (8.87%). The emission factors (EFs) of $PM_{2.5}$ and proportions of SO_4^{2-} and Pb were decreased by vehicle emission standards and fuel quality policy in China, and the higher molecular weight PAHs (4 + 5 + 6 rings) were more abundant than the lower molecular weight PAHs (2 + 3 rings) in the two tunnels. The proportions of 17A(H)-21B(H)-30-Norhopane and 17A(H)-21B(H)-Hopane in the hopane and sterane were not dependent on the vehicles types. In addition, specific composition profiles for $PM_{2.5}$ from gasoline-fueled vehicles (GV)

Abbreviations: OC, organic carbon; EC, elemental carbon; GV, gasoline-fueled vehicles; DV, diesel-fueled vehicles; EFs, emission factors; PAHs, polycyclic aromatic hydrocarbons; WZS, Wuzushan; KXL, Kuixinglou; HMW, higher molecular weight; LMW, lower molecular weight; LDV, light-duty vehicles; HDV, heavy-duty vehicles.

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Gasoline-fueled vehicles
Diesel-fueled vehicles

and diesel-fueled vehicles (DV) emissions were drafted, which indicated that OC (0.974 mg·veh^{-1}·km^{-1}) was the most abundant component in $PM_{2.5}$, followed by Fe, Cl^-, and Mg for GV. The relative proportions of the different constituents in the $PM_{2.5}$ for DV were EC (35.9%), OC (27.2%), elements (12.8%), and water soluble ions (11.7%). Both the $PM_{2.5}$ EFs and EC proportions in DV were higher than those in GV, and the HMW PAHs were the dominant PAHs for both GV and DV. The $PM_{2.5}$ emissions from the vehicles in Yantai were 581 ± 513 tons to 1353 ± 1197 tons for GV, and 19,627 ± 2477 tons to 23,042 ± 2887 tons for DV, respectively.

1. Introduction

Increasingly, attention is being given to fine particle ($PM_{2.5}$) pollution in China because of its significant influence on public health (Cheng et al., 2010; Shen et al., 2014). Health studies have proved that $PM_{2.5}$ has a close relationship with the incidence of human heart diseases, and mortality because of lung cancer (Adar et al., 2007; Liu et al., 2015b; Pope et al., 1995). Because of the rapid increase in the number of motor vehicles in China, in recent years, vehicle exhaust has been considered a main source of $PM_{2.5}$ emissions in the country. For example, Che (2010) has reported that 8.3 million tons and 6.7 million tons of PM_{10} and $PM_{2.5}$, respectively, were emitted by vehicles in the Pearl River Delta during 2006. More recently, it was calculated that vehicle exhaust has contributed 31.1% and 15.0% of $PM_{2.5}$ in Beijing (Bureau BMEP, 2014) and Jinan, respectively, during 2014 (Bureau JEP, 2014).

It's hard to evaluate the contribution of vehicle emission to air pollution, due to lacking of specific vehicle emission data in China, although growing attentions have been paid to vehicle pollution. For example, contributions of vehicles exhausts to atmospheric pollutants in source apportionment result by PMF model in Guangzhou were different (Gao et al., 2013; Gao et al., 2015). In addition, the emission factors of $PM_{2.5}$ used in various published emission inventories were mostly simulated using the International Vehicle Emission (IVE) model (Huo et al., 2011) and MOBILE-China (Wu et al., 2011), and modified by local features. Large uncertainties for emission inventories would exist by using those estimated emission factors. Zheng et al. (2009) claimed that uncertainties were from −60% to +70% for particle pollutants in vehicle emission inventory. Lacking of the specific characterization of $PM_{2.5}$ from vehicle emission is the major reason for the difference and uncertainties, in China. Vehicles are classified as GV or DV based on the type of fuel they use. Although DV are considered to emit higher amount of PM than GV, the debate about which emission of PM (GV or DV) is more harmful to human health has continued for many years, as some studies have found that GV might emit more fine particulate matter than DV (Sandhu et al., 2014; Shen et al., 2014) China had implemented vehicle emission standards for both types of vehicle before 2000 and the standards have since been tightened every few years. The emission standards for both types of vehicle were stipulated in China I to China V (Yue et al., 2015), however, because the implementation of the regulations on fuel quality has been postponed, the emission standards could not be met (Yue et al., 2015). For that reason, the EFs and chemical compositions of GV and DV might have changed throughout these years and should update constantly.

Several different approaches have been employed to investigate vehicle emissions, including the engine dynamometer test (Na et al., 2015; Pietikainen et al., 2015), on-road test (Durbin et al., 2008; Frey et al., 2008) and tunnel test (Ho et al., 2009; Pio et al., 2013). Tunnels are usually constructed to ease traffic congestion, and because of the confined space, there is an increase in the concentrations of the emissions and prolonged exposure to the pollutants emitted by the vehicles (El-Fadel and Hashisho, 2001). Therefore, the tunnel test has become the most popular method for studying vehicle emissions, as real traffic emissions are reflected, including pollutants from vehicle exhaust, as well as related emissions (e.g., tire and brake friction and road dust) (Handler et al., 2008).

Various tunnel studies have been conducted in megacities (first-tier cities) in China, with fewer studies having been conducted in smaller cities, such as Yantai, a coastal city because of the perceived better air quality of the smaller cities. However, in 2014, the eco-compensation policy (Seasonal average concentrations of $PM_{2.5}$, PM_{10}, SO_2 and NO_2 were used to evaluate air quality) was implemented in Shandong Province, and the worst result was found in Yantai (Zhou et al., 2014). Therefore, more attention has to be paid to air pollutants in the second-tier cities such as Yantai (the secondary air quality standards was 75 μgm^{-3}), a city with a population of 6.5 million and the licensed vehicle number up to 1.8 million in 2013. Moreover, many tunnel studies published in China were just focusing on characteristics of emissions for mixed vehicles. For example, Zhang et al. (2014) reported EFs of $PM_{2.5}$, carbonaceous aerosols and gaseous pollutants for mixed vehicles in Pearl River Delta region. However, only a few tunnel studies about the emission factors for GV and DV were carried out in China. To our best knowledge, He et al. (2008) estimated the EFs of $PM_{2.5}$, OC and EC for GV and DV in Zhujiang tunnel in Guangzhou. In addition, Most of researches on vehicle emissions by tunnel test were mainly focusing on EFs of inorganic matters (Cheng et al., 2006; Chiang and Huang, 2009, Zhang Yanli et al., 2015), with very few studies concerning about the characteristics of organic matters (2013). Due to some organic matters (hopanes and steranes) having been used as makers of mobile source emissions and some of them being known to be carcinogenic and mutagenic (PAHs) (Chen et al., 2013), we should pay more attention for those matters. The tunnel tests could provide bottom-up emissions for vehicles as long as having vehicle activity data in each city. However, the method evaluated emissions from vehicles was neglected in almost all of the tunnel studies.

This study has three main objectives, namely to (1) investigate the chemical-speciated characteristics of $PM_{2.5}$ emitted in the different tunnels, (2) calculate the EFs of $PM_{2.5}$ and the related components emitted by GV and DV, and (3) estimate the $PM_{2.5}$ emissions by GV and DV in Yantai city. Improved knowledge on chemical-speciated $PM_{2.5}$ from the emission source would be beneficial to improving $PM_{2.5}$ and associated chemical-component emission inventories and the source apportionment models.

2. Experimental methods

2.1. Tunnels

$PM_{2.5}$ sampling was conducted in two tunnels, the WZS and the KXL tunnels, located in the urban district of Yantai. The WZS tunnel (1150 m long) is situated in Zhenda Road, which connects the Wolong economic zone and the city center area. The tunnel has two bores, with, three lanes each, and there is a sidewalk on the right-hand side of each bore of the tunnel. The diameter of each bore is 14.75 m. The KXL tunnel is located in the East Hongqi Road, and it connects the Laishan and the Zhifu districts. This tunnel is 1023 m long, with two independent bores, and two lanes per bore. The diameter of each bore is 11.5 m. In the KXL tunnel, restrictions are in place on medium- and heavy-duty trucks from 6:00 am to 22:00 pm. The longitudinal ventilation system within the tunnel was not in operation during the sampling periods.

2.2. Sampling and instruments

A high volume sampler (Tisch) with a $PM_{2.5}$ cut was placed at the entrance (80 cm and 50 cm from the entrances for KXL and WZS tunnels, respectively) or the exit of the tunnels (85 cm and 60 cm from the exits for KXL and WZS tunnels, respectively), respectively, as shown in Fig. S1. The high volume sampler was about 50 cm from the tunnels wall, and 100 cm from the tunnels ground. The operating flow rate of the sampler was 1.13 $m^3 \cdot min^{-1}$. In addition, a camera was placed at the side of the tunnel to record the vehicles crossing the tunnel during the sampling periods. The sampling was done for the period November 12–20 of November 2014, in both tunnels, including weekdays and weekends. The daily sampling at the exit was from 7:00 am to 9:00 am and 17:00 pm to 19:00 pm, while it was from 11:30 am to 13:30 pm at the entrance. Vehicles pass through the two tunnels without congesting, and the vehicles were divided into three categories, namely, diesel-fueled vehicles (buses and trucks), gasoline-fueled vehicles (passenger, light commercial vehicles and taxies), and motorcycles during the sampling times. The fine particulate matter ($PM_{2.5}$) was collected on 8 × 10-inch quartz-fiber filters (Whatman). The filters were pre-heated at 450 °C for 6 h to reduce the carbonaceous species. Before sampling, the filters were balanced under conditions of 25 °C and 41% relative humidity conditions for 24 h. The filter samples were stored in a refrigerator at −20 °C after sampling and before further chemical analysis.

2.3. Chemical analysis

One quartz-fiber filter was cut into pieces for various measurements in each test. The quartz-fiber filters were weighed before and after sampling to determine the mass concentrations of $PM_{2.5}$. OC and EC were measured by the Desert Research Institute (DRI) Model 2001 thermal/optical reflectance (TOR) Carbon analyzer (Atmoslytic Inc., Calabasas, CA) following the Interagency Monitoring of Protected Visual Environment (IMPROVE) protocol, with additional information being obtained from Zong et al. (2015). Water soluble ions (Cl^-, NH_4^+, NO_3^- and SO_4^{2-}) were analyzed by ion chromatograph (Dionex ICS3000, Dionex Ltd., America) following the method of Zhang et al. (2014). Before analysis, 47 mm filters were ultrasonically extracted three times, for 15 min each time, with 10 ml deionized water. Finally, the volume in each vial was adjusted to 45 ml exactly with the deionized water. The elements (Na, Mg, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, La and Pb) were analyzed by using inductively coupled plasma coupled with mass spectrometer (ICP-MS of the ELAN DRC II type, Perkin Elmer Ltd., Hong Kong). The filters were digested with 5 ml HNO_3 for 10 h, and subsequently adjusted to 45 ml. The resolution of the ICP-MS ranged from 0.3 to 3.0 amu, with a detection limit below 0.01 ng ml^{-1}.

Sub quartz-filter samples, spiked with internal standards, including acenaphthene-d10, benz[a]anthracene-d12, pyrene-d10, coronene-d12, and cholestane-d4 were ultrasonically extracted twice, for 10 min each time, in 30 ml of a 1:1 mixture of hexane and dichloromethane. The extracts of each sampler were combined, filtered, and concentrated to ~0.5 ml.

The PAHs, hopane and sterane were subsequently analyzed, using the GC–MS (Agilent 7890A GC-5975C MS), equipped with a DB-5MS column (length 30 m × i.d. 0.25 mm × thickness 0.25 μm). The GC operating program was as follows: 60 °C for 4 min, 5 °C·min^{-1} to 150 °C for 2 min, 3 °C·min^{-1} to 306 °C for 20 min. The GC conditions were as follows: the injector temperature was 290 °C, the volume of the injector was 2 μl, the carrier gas was helium, and the flow rate of the gas was 1.2 ml·min^{-1}. The electron impact (EI) mode of 70 eV and the selected-ion-monitoring (SIM) mode were selected to determine the PAHs, hopane and sterane.

Sixteen USEPA priority PAHs, hopane and sterane were analyzed. The abbreviations of the sixteen priority PAHs are as follows: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), ben[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA) and benzo[ghi]perylene (BghiP).

2.4. Quality assurance and control (QA/QC)

Rigorous quality assurance and control measures were maintained during the whole experiment. Filter blanks, reagent blanks, and duplicate samples were analyzed for quality control. The duplicate samples were examined after analyzing a batch of 10 samples for OC and EC, which ensured that the error was within 5%. The results of each sample for water-soluble ions and elements were subtracted from the filter blanks results. The average recoveries of the five surrogates ranged from 66.7% to 128%. The final concentrations of organic matters were not corrected for the recoveries.

2.5. Emission factors

The emission factors of $PM_{2.5}$ from the vehicles in the two tunnels were calculated by the following Eq. (1) (Ameur-Bouddabbous et al., 2012; Chen et al., 2013):

$$EF_i = \frac{(C_{iex}V_{ex} - C_{ien}V_{en})AT}{NL} \quad (1)$$

where EF_i (mg·veh^{-1}·km^{-1}) is the average emission factor for species *i*. C_{iex} and C_{ien} (mg·m^{-3}) are the mass concentrations of species i at the exit and the entrance of the tunnel, respectively. V_{ex} (m·s^{-1}) is the wind speed at exit of the tunnel, and V_{en} (m·s^{-1}) is the wind speed at the entrance of the tunnel. *N* (veh) is the number of vehicles crossing the tunnel during the sampling period. *L* (km) is the distance from the entrance to the exit. *A* (m^2) is the cross-section area of the tunnel, and *T* (s) is the sampling duration.

The EFs of GV and DV could be calculated based on the following equation described by He and co-workers (He et al., 2008).

$$EF_{i,j} = EF_{GV}X_{GVj} + EF_{DV}X_{DVj} \quad (j \geq 2) \quad (2)$$

where $EF_{i,j}$ (mg·veh^{-1}·km^{-1}) is the EFs of the mixed vehicle fleet in test j for species *i*; EF_{GV} and EF_{DV} (mg·veh^{-1}·km^{-1}) are the EFs of gasoline vehicles and diesel vehicles, respectively, X_{GVj} and X_{DVj} (%) are the proportions of the gasoline and the diesel vehicles of the total vehicles, respectively.

The total $PM_{2.5}$ emission from the vehicles in Yantai was calculated by Eq. (3) as follows:

$$Q_{i,j} = EF_j \cdot VKT_{i,j} \cdot P_{i,j} \quad (3)$$

where *j* is the vehicle type (e.g. GV and DV), $Q_{i,j}$ (ton) is the total $PM_{2.5}$ emission of vehicle *j* in *i* year, $VKT_{i,j}$ (km) is the kilometers traveled per year by vehicle type vehicle *j* in *i* year (Supporting information), $P_{i,j}$ (veh) is the vehicle population of vehicle *j* in *i* year (Table S2), EF_j (mg·veh^{-1}·km^{-1}) is the $PM_{2.5}$ EFs of vehicle *j* calculated in this study (Table S3).

3. Results and discussion

3.1. Vehicle fleet

Vehicles passing through the two tunnels during the sampling times were divided into three categories, namely, diesel-fueled vehicles (buses and trucks), gasoline-fueled vehicles (passenger, light commercial vehicles and taxis), and motorcycles. The vehicle flows and the composition in the tunnels during the sampling periods are shown in Fig. 1. The average vehicle flow in the WZS tunnel was 1080 veh·h^{-1}, with the

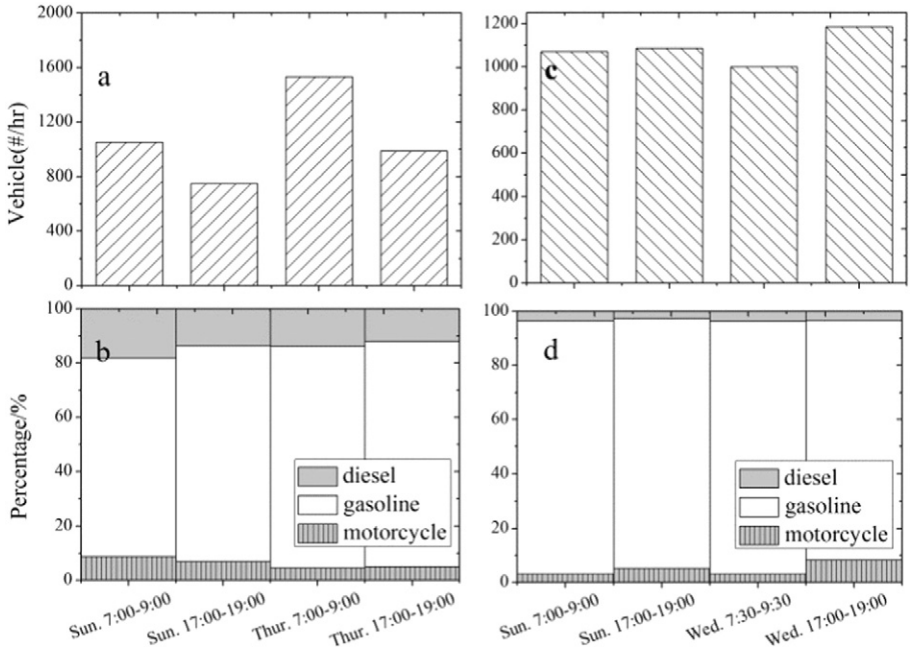

Fig. 1. Vehicle flow and composition of different sampling periods: (a) Total vehicle flows in WZS tunnel during sampling periods; (b)vehicle types in WZS tunnel during sampling periods; (c) total vehicle flows in KXL tunnel during sampling durations; (d) vehicle types in KXL tunnel during sampling periods.

average vehicle flow on weekdays being 1260 veh·h^{-1} and that over weekends 901 veh·h^{-1}. The average vehicle flow in the KXL tunnel was 1086 veh·h^{-1}, with the average vehicle flows on weekdays being 1093 veh·h^{-1} and that over weekend 1079 veh·h^{-1}. The vehicle flows during the week were higher than those were over the weekend in WZS tunnel, while this trend wasn't obviously in KXL tunnel. In the KXL tunnel, light-duty trucks are not allowed from 7:00 am to 8:30 am and from 16:30 pm to 18:30 pm every day; therefore, GV represented 91.5% of the total vehicles in the KXL tunnel, with the remaining 3.4% being DV and 5.1% being motorcycles. The only route connecting the South Tongshi Road and the S302 Road runs through the WZS tunnel and diesel trucks are therefore allowed to use in the tunnel. The average proportion of diesel vehicles in the WZS tunnel during the sampling period was 14.4%, which was four times as much as that of the KXL tunnel. The average flows of the motorcycles in the WZS and KXL tunnels were 66 veh·h^{-1} and 56 veh·h^{-1}, respectively, indicating little difference between the two tunnels in this respect.

A multiple linear regression Eq. (4) was established by using the SPSS 16.0 software to represent the relationship between the $PM_{2.5}$ concentrations (Table S4) and the vehicle flows of the different vehicle types (motorcycles, GV and DV) as follows:

$$Y = 0.55X_1 + 0.034X_2 + 1.212X_3 \quad (P<0.01,\ R = 0.99) \tag{4}$$

where Y (μg·m^{-3}) is the mass concentrations of $PM_{2.5}$, while X_1, X_2, and X_3 (veh·h^{-1}) represent the vehicle flows of motorcycles, GV, and DV, respectively.

In order to distinguishing the each vehicle contribution of the three types of vehicles on $PM_{2.5}$ concentration, a regression Equation is obtained by using standardization dataset (eliminate the influence of the traffic flow), as follows:

$$Y' = 0.176X_1' + 0.157X_2' + 0.700X_3' \tag{5}$$

where Y', X_1', X_2' and X_3' represent the standardized data of Y, X_1, X_2 and X_3 (non-dimensional).

Multiple linear regression analysis showed that the $PM_{2.5}$ concentrations in the two tunnels were influenced significantly by the DV flows, and each vehicle contributions of GV and motorcycles were 15.7% and 17.6%. As vehicle flows of the motorcycles were negligible (66 veh·h^{-1} and 56 veh·h^{-1}), and motorcycles were therefore excluded from the following discussion.

3.2. Emission factors of $PM_{2.5}$ and comparison with that from other tunnels

The EFs of $PM_{2.5}$ in the two tunnels were calculated based on Eq. (1) and, are shown in Table 1 and Table S5. As shown in Table 1, the EFs of $PM_{2.5}$ in the WZS tunnel was 70.1 ± 15.9 mg·veh^{-1}·km^{-1}, whereas it was 22.2 ± 6.52 mg·veh^{-1}·km^{-1} in the KXL tunnel.; It is known that, the $PM_{2.5}$ EFs of vehicles could be influenced by many factors, such as vehicle type (Cheng et al., 2010; He et al., 2008), fuel quality (Yue et al., 2015), model year of the vehicles (Liu et al., 2009; Shah et al., 2006), vehicle speed (Gillies et al., 2001), and the features of the road (Pio et al., 2013). EFs of $PM_{2.5}$ in this study were compared with those from other tunnel studies in China (Table 1). EF of $PM_{2.5}$ in KXL tunnel was lower than those in other tunnels listed in Table 1. Results based on Eqs. (4) and (5) indicated that the DV flow had a significant influence on the $PM_{2.5}$ concentration. The main reason for this could be ascribed to the lowest proportion of diesel vehicles in KXL tunnel. EF of $PM_{2.5}$ in WZS tunnel (70.1 ± 15.9 mg·veh^{-1}·km^{-1}, 14% diesel, gasoline: China 4, diesel: China 3) was lower than that in Zhujiang tunnel (110 ± 4.00 mg·veh^{-1}·km^{-1}, 20% diesel, gasoline: China 1, diesel: China 1) (He et al., 2008) and Shing Mun tunnel (131 ± 36.9 mg·veh^{-1}·km^{-1}, 50% diesel, GV: China 1, DV: China 1) (Cheng et al., 2010). Fleet compositions in the three tunnels were similar, but, the emission standards were different. It indicated that $PM_{2.5}$ EF decreased when the emission control strategies were enforced by Chinese government. As shown in Table 1, there is a decreasing trend of EFs of $PM_{2.5}$ in Zhujiang tunnel from 110 ± 4.00 mg·veh^{-1}·km^{-1} in 2004 (He et al., 2008), 92.4 ± 8.9 mg·veh^{-1}·km^{-1} in 2013 (Dai et al., 2015) and 82.7 ± 28.3 mg·veh^{-1}·km^{-1} in 2014 (Zhang et al., 2014). That is, the EFs of $PM_{2.5}$ would decrease 20.4% during implementing emission standard of China 1 to China 4.

3.3. Chemical composition of the $PM_{2.5}$ in two tunnels

Chemical compositions in $PM_{2.5}$ emitted by the mixed vehicles in different tunnels were shown in Table 2. Proportions of different

Table 1
$PM_{2.5}$ EF comparison between the WZS, KXL and other tunnel studies.

Tunnel	Vehicle type	Test year	Emission standards	*EF* ($mg \cdot veh^{-1} \cdot km^{-1}$)
Zhujiang tunnel Guangzhou (Yanli et al., 2015)	12% HDV 61% LDV 27% LPG	2014	GV: China 4 DV: China 3	82.7 ± 28.3
Zhujiang tunnel Guangzhou (Dai et al., 2015)	14% HDV 60% LDV 26% LPG	2013	GV: China 4 DV: China 3	92.4 ± 8.9
Zhujiang tunnel Guangzhou (He et al., 2008)	20% diesel	2004	GV: China 1 DV: China 1	110 ± 4.00
Yan'an east road tunnel Shanghai (Liu et al., 2015a)	5.5% diesel	2012	GV: China 4 DV: China 3	56.7 ± 69.4
Shing Mun tunnel Hong Kong (Cheng et al., 2010)	50% diesel 41% gasoline 9% LPG	2003	GV: China 1 DV: China 1	131 ± 36.9
Sepulveda tunnel Los Angeles (Gillies et al., 2001)	2.6% HDV	1996	Euro 2	52.0 ± 27.0
KXL tunnel Yantai This study	3.4% diesel	2014	GV: China 4 DV: China 3	22.2 ± 6.52
WZS tunnel Yantai This study	14% diesel	2014	GV: China 4 DV: China 3	70.1 ± 15.9

constituents in $PM_{2.5}$ in the WZS tunnel were OC (27.7%), EC (32.1%), elements (13.9%), and water soluble ions (9.2%). Chemical profile in $PM_{2.5}$ in the KXL tunnel was OC (17.7%), EC (10.4%), elements (8.90%), and water soluble ions (8.87%). Proportions of different species in WZS and KXL tunnels were similar to those in Zhujiang tunnel (Dai et al., 2015), in which chemical profile of $PM_{2.5}$ were OC (18.1%), EC (17.7%), elements (11.4%) and water-soluble ions (5.36%).

3.3.1. OC and EC

EF of OC and EC for mixed vehicles was 19.4 ± 8.56, and 22.5 ± 7.02 $mg \cdot veh^{-1} \cdot km^{-1}$ in WZS tunnel, respectively (Table 1), while it was 3.93 ± 1.34 and 2.30 ± 1.11 $mg \cdot veh^{-1} \cdot km^{-1}$ in KXL tunnel. A series dynamometer tests had proved that the OC/EC ratio was a good indicator to separate diesel vehicle emission from gasoline vehicle emission. When OC/EC was in the range of 0.3–0.9, $PM_{2.5}$ was mainly derived from the diesel vehicle, and when OC/EC is larger than 2.0, $PM_{2.5}$ was primarily from gasoline car (Cadle et al., 1999; Liu et al., 2012). OC/EC in WZS tunnel ranged from 0.48 to 1.45 with an average value of 0.86. Emission factors of OC and EC in WZS tunnel were similar to those reported in Sepulveda tunnel (Gillies et al., 2001).

3.3.2. Water soluble ions

Table 2 showed that EFs of water soluble ions including SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ in WZS tunnel were 2.60 ± 1.65, 2.30 ± 1.90, 0.96 ± 0.64 and 0.61 ± 1.09 $mg \cdot veh^{-1} \cdot km^{-1}$ respectively. And it was 0.81 ± 0.53 $mg \cdot veh^{-1} \cdot km^{-1}$ (NO_3^-), 0.67 ± 0.17 $mg \cdot veh^{-1} \cdot km^{-1}$ (SO_4^{2-}), 0.46 ± 0.35 $mg \cdot veh^{-1} \cdot km^{-1}$ (Cl^-), and 0.03 ± 0.03 $mg \cdot veh^{-1} \cdot km^{-1}$ (NH_4^+) in KXL tunnel. In KXL tunnel, emissions of SO_4^{2+} and NO_3^- were lower than those in the WZS tunnel, as the predominant emissions in the KXL tunnel did not derive from diesel engines. EFs of water soluble

Table 2
Emission factors of $PM_{2.5}$ compositions for mixed vehicles in several tunnels ($mg \cdot veh^{-1} \cdot km^{-1}$).

Tunnel	WZS	KXL	Sepulveda	Zhujiang	Chung-Liao	Shing Mun	Zhujiang
Year	2014	2014	1996	2004	2005	2003	2013
Vehicle type	14.4% diesel	3.4% diesel	2.6% HD	19.8% HD	/	50% diesel	14% HD
References	This study	This study	Gillies et al. (2001)	He et al. (2008)	Chiang and Huang (2009)	Cheng et al. (2010)	Dai et al. (2015)
OC	19.4 ± 8.56	3.93 ± 1.34	19.3 ± 8.46	24.3 ± 0.930	4.67 ± 1.49	35.7 ± 11.7	16.7 ± 1.9
EC	22.5 ± 7.02	2.30 ± 1.11	25.5 ± 4.98	49.6 ± 1.90	15.1 ± 4.46	65.8 ± 18.4	16.4 ± 2.1
Cl^-	0.960 ± 0.640	0.460 ± 0.350	0.670 ± 0.990	0.980 ± 0.160	0.09 ± 0.081	0.590 ± 0.510	4.17 ± 0.9
NO_3^-	2.30 ± 1.90	0.810 ± 0.530	3.27 ± 1.17	1.37 ± 0.590	0.374 ± 0.047	1.10 ± 0.860	0.1 ± 0.03
$SO4^{2-}$	2.60 ± 1.65	0.670 ± 0.170	1.77 ± 2.06	3.87 ± 0.610	0.917 ± 0.042	7.10 ± 3.30	0.61 ± 0.1
NH_4^+	0.610 ± 1.09	0.030 ± 0.030	1.61 ± 1.06	0.800 ± 0.250	0.151 ± 0.108	2.80 ± 0.880	0.17 ± 0.06
Na	0.260 ± 0.280	0.070 ± 0.050	0.350 ± 0.160	0.370 ± 0.070	1.05 ± 1.31	1.00 ± 1.20	3.53 ± 0.4
Mg	1.41 ± 1.15	0.250 ± 0.170	0.260 ± 0.290	0.220 ± 0.020	0.112 ± 0.158	0.350 ± 0.210	0.50 ± 0.08
K	0.680 ± 0.460	0.130 ± 0.070	0.100 ± 0.080	0.140 ± 0.040	0.379 ± 0.050	0.290 ± 0.420	0.34 ± 0.04
Ca	3.80 ± 2.15	0.470 ± 0.300	0.300 ± 0.070	0.640 ± 0.090	0.428 ± 0.561	0.550 ± 0.480	1.93 ± 0.3
Ti	0.150 ± 0.100	0.020 ± 0.010	0.090 ± 0.500			0.084 ± 0.099	
V	0.006 ± 0.003	0.001 ± 0.0004	0.050 ± 0.210		0.013 ± 0.014	0.012 ± 0.007	0.007 ± 0.0004
Cr	0.010 ± 0.005	0.030 ± 0.010	0.020 ± 0.050		0.072 ± 0.047	0.013 ± 0.018	0.01 ± 0.0008
Mn	0.060 ± 0.040	0.020 ± 0.010	0.020 ± 0.030	0.019 ± 0.001	0.152 ± 0.210	0.020 ± 0.020	0.08 ± 0.02
Fe	3.22 ± 2.09	0.930 ± 0.310	2.79 ± 0.290	1.12 ± 0.090	0.582 ± 0.423	0.950 ± 0.760	3.91 ± 0.2
Co	0.001 ± 0.001	0.0002 ± 0.0001	0.000 ± 0.100	0.0001 ± 0.00004	0.015 ± 0.020	0.013 ± 0.009	0.002 ± 0.003
Cu	0.030 ± 0.017	0.024 ± 0.017	0.170 ± 0.020		0.037 ± 0.046	0.048 ± 0.023	0.09 ± 0.01
Zn	0.120 ± 0.040	0.024 ± 0.024	0.140 ± 0.020		0.149 ± 0.018	0.200 ± 0.093	0.16 ± 0.02
As	0.002 ± 0.001	0.0005 ± 0.0004	0.000 ± 0.050	0.002 ± 0.001	0.015 ± 0.021		0.005 ± 0.001
La	0.004 ± 0.003	0.0005 ± 0.0004	0.000 ± 1.83				
Pb	0.010 ± 0.007	0.006 ± 0.004		0.014 ± 0.003	0.292 ± 0.398	0.024 ± 0.026	0.01 ± 0.001

ions in WZS and Zhujiang tunnels (He et al., 2008) were in the same order (of magnitude). However, as shown in Table 2, EF of SO_4^{2-} in Zhujiang tunnel (3.87 ± 0.610 mg·veh^{-1}·km^{-1}) was higher compared to WZS tunnel and KXL tunnel. It was suggested that the content of SO_4^{2-} emitted by vehicles was correlated with the sulfur content in fuel, especially in diesel fuel (Lowenthal et al., 1994). Limits of the sulfur content in gasoline and diesel quality standards issued in 2003, around which year Zhujiang tunnel test was conducted, were 800 ppm and 1000 ppm, respectively (Yue et al., 2015), which were higher than those issued in 2014 (50 ppm for gasoline, and 350 ppm for diesel) (Yue et al., 2015), when WZS and KXL tunnel test were conducted. Therefore, the fuel quality policy enforced by the Chinese government could affect the EF of SO_4^{2-}.

3.3.3. Elements

EF of Ca was the highest (3.80 ± 2.15 mg·veh^{-1}·km^{-1}) compared with the other elements in WZS tunnel, followed by Fe, Mg, K and Na (see Table 2). These five elements accounted for 96.0% of the total mass of elements. However, EF of Fe was the highest (0.93 ± 0.31 mg·veh^{-1}·km^{-1}) in KXL tunnel, followed by Ca, Mg, and K (see Table 2). These five elements accounted for 91.7% of the total mass of elements. The sum of the elements accounted for 13.9% and 8.9% of the $PM_{2.5}$ mass in WZS and KXL tunnels, respectively. Table 2 showed that EFs of the elements in WZS tunnel were higher than those in KXL tunnel. This might be ascribed to the rougher road surface in WZS tunnel. Trucks with cargo crossing the WZS could release more mineral elements. Table 2 showed the EF of elements in different tunnels such as species of Fe, Ca, Mg, K and Na which constituted the majority of elements in different tunnels (Cheng et al., 2010; Chiang and Huang, 2009; Dai et al., 2015; He et al., 2008). Proportions of elements in $PM_{2.5}$ in WZS and KXL tunnels were consistent with that found in Zhujiang tunnel in 2013 (Dai et al., 2015). Due to the implement of unleaded gasoline policy since 2000, it is clear to see from Table 2 that the proportion (3.36%) of Pb in elements obtained after year 2013 was decreased compared to those (0.17%) calculated before year 2005.

3.3.4. Organic compounds

The EF of the sixteen USEPA priority pollutants was averaged as 0.149 mg·veh^{-1}·km^{-1}, with the individual PAHs varying from 0.001 mg·veh^{-1}·km^{-1} (for Flu) to 0.033 mg·veh^{-1}·km^{-1} (for BghiP). The EFs of BghiP, Pyr, Fluo and Chry were higher than were the other PAHs in the WZS tunnel. He et al. (2008) have indicated that the PAHs EF in the Zhujiang tunnel was 51.2 μg·veh^{-1}·km^{-1}, which was lower than was that in the WZS tunnel. The highest EF among the PAHs was that of BghiP in the Zhujiang tunnel, which was similar to the WZS tunnel. However, the range of PAHs EFs in the KXL tunnel was 0.00003 mg·veh^{-1}·km^{-1} (DahA) to 0.005 mg·veh^{-1}·km^{-1} (BghiP), among which the EFs of BghiP, Pyr, BbF and Fluo were the highest (Fig. 2). The PAH EFs in the KXL tunnel were higher than were those found by a study conducted in the Yan'an east Road tunnel (Shanghai) of 19.61 μg·veh^{-1}·km^{-1} (Liu et al., 2015a). The vehicle profiles in the Yan'an east road tunnel were similar to those of the KXL tunnel, the difference could probably be ascribed to Shanghai having its own local gasoline standard. This standard requires higher quality oil in comparison with the national standard (Yue et al., 2015). Furthermore, Fraser et al. (1998) have reported that the EFs of BghiP, Chry and BbF were higher than were the other PAHs in the Van Nuys tunnel, which was consistent with the content of PAHs in the KXL tunnel. It is known that the HMW PAHs (4 + 5 + 6 rings) are more abundant in the particle phase than are the LMW PAHs (2 + 3 rings) (Chen et al., 2013). Accordingly, the HMW PAHs (4 + 5 + 6 rings) percentages in the WZS and the KXL tunnels were 82.5% and 81.9%, respectively.

Fig. 3 shows the EFs for hopane and sterane in the WZS and KXL tunnels. The dominant hopanes and steranes in both tunnels were 17A(H)-21B(H)-30-Norhopane and 17A(H)-21B(H)-Hopane, in total, accounting for the majority mass of PAHs (WZS: 76.8%, KXL: 74.8%), which is consistent with the result of He et al. (2008). In addition, Simoneit (1985) has reported that the proportions of 17A(H)-21B(H)-30-Norhopane and 17A(H)-21B(H)-Hopane were predominant and unchanged, irrespective of the vehicle types (GV or DV). Hopane and sterane are considered as coming from the emissions of lubricating oil,

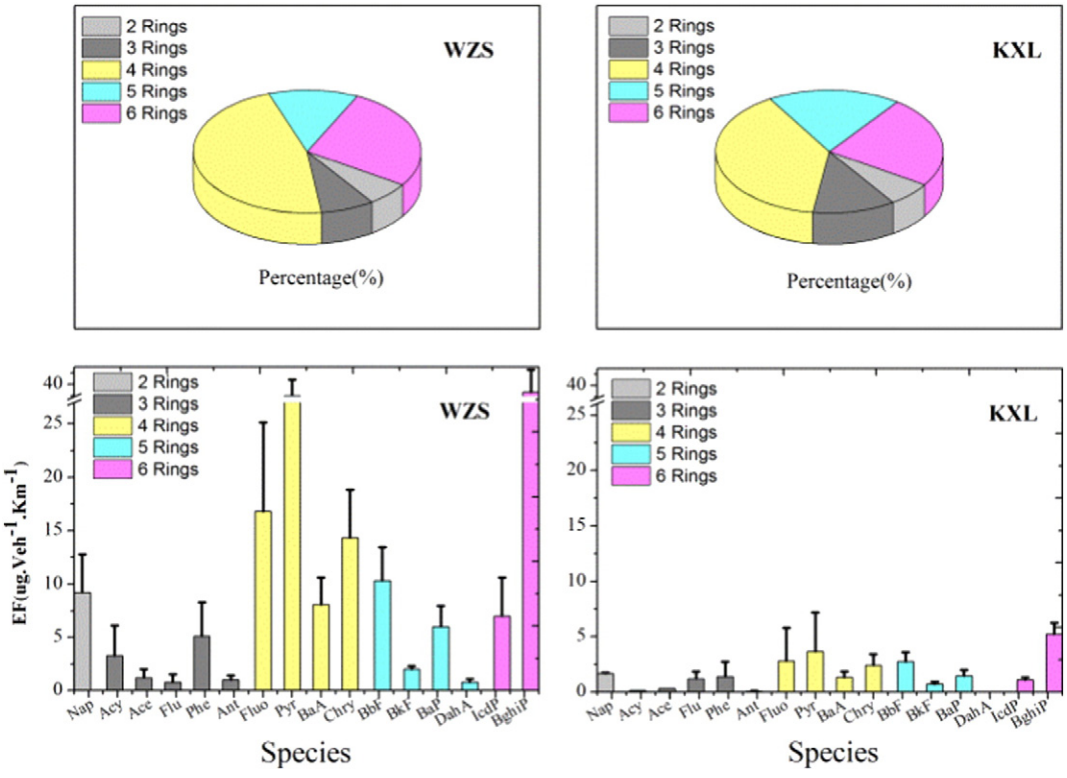

Fig. 2. PAHs emission factors and relative contributions of different rings to PAHs emission factors in KZS and KXL tunnel.

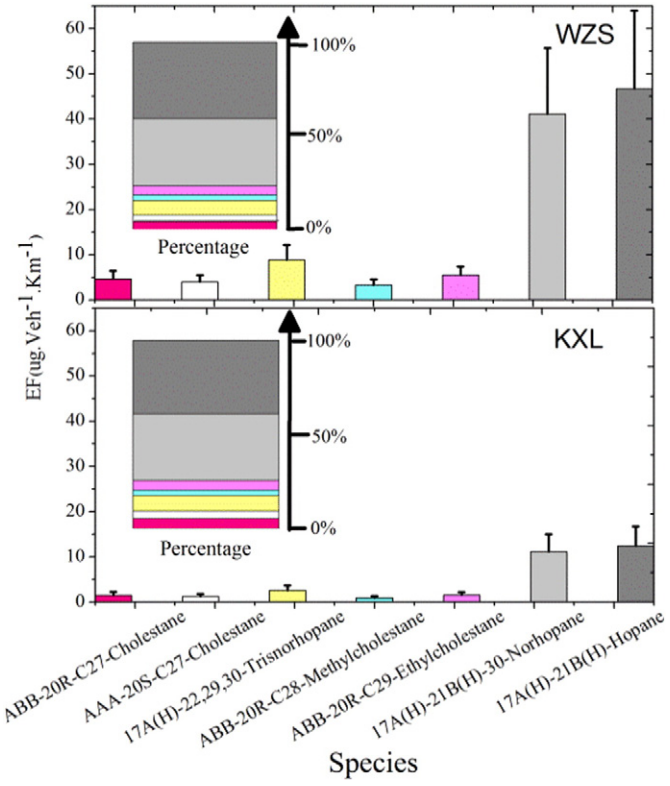

Fig. 3. Emission factors of hopane and sterane in WZS and KXL tunnel.

rather than from fossil fuel combustion (Liacos et al., 2012; Pakbin et al., 2009). Therefore, the proportions of 17A(H)-21B(H)-30-Norhopane and 17A(H)-21B(H)-Hopane in the hopane and sterane were constant in this study, and could be used as indicators of the vehicle exhaust emissions.

3.4. Speciated emission factors of $PM_{2.5}$ for GV and DV

The speciated emission factors of $PM_{2.5}$ for GV and DV are summarized in Table 3. The emission factor of $PM_{2.5}$ for GV was 7.36 mg·veh^{-1}·km^{-1}, and it is clear that OC (0.974 mg·veh^{-1}·km^{-1}) was the most abundant component in $PM_{2.5}$, followed by Fe (0.672 mg·veh^{-1}·km^{-1}), Cl^- (0.322 mg·veh^{-1}·km^{-1}) and Mg (0.173 mg·veh^{-1}·km^{-1}). The EF of $PM_{2.5}$ for DV was 415 mg·veh^{-1}·km^{-1} and the relative proportions of the different constituents in the $PM_{2.5}$ for DV were EC (35.9%), OC (27.2%), elements (12.8%), and water soluble ions (11.7%). The EF for $PM_{2.5}$ of DV was 56 times higher than that in GV. Furthermore, the emission factor for the $PM_{2.5}$ of GV was lower than was that found in the Shing Mun tunnel (Cheng et al., 2010) (Table 3). This finding is mainly attributed to the emission standards of GV in 2014 being more stringent than they were in 2003. The chemical composition for the $PM_{2.5}$ of DV was similar to that found in the Shing Mun tunnel (Cheng et al., 2010), excluding the percentages of the elements. The other proportions for DV were 26.5%, 51.1%, and 11.7% for OC, EC, and the water soluble ions, respectively.

For GV, the PAHs, hopane and sterane accounted for 0.5% and 0.2% of OC, while the EF of Flu (0.002 mg·veh^{-1}·km^{-1}) had the highest value in the PAHs. For DV, the PAHs, hopane and sterane accounted for approximately 0.9%, and 0.7% of OC, while BghiP (0.002 mg·veh^{-1}·km^{-1}) had the highest value in the PAHs, followed by Pyr (0.215 mg·veh^{-1}·km^{-1}), Fluo (0.113 mg·veh^{-1}·km^{-1}) and Chry (0.102 mg·veh^{-1}·km^{-1}). The result obtained from the roadway tunnel (Phuleria et al., 2006) for LDV was similar to that of the diesel vehicles, that is, that BghiP was the most abundant of the PAHs, followed by BaP, and Chry. It is known that the LMW PAHs are mostly associated with diesel engines, while the HMW PAHs are associated with gasoline engine (Chen et al., 2013). As is shown in Table 3, the HMW PAHs were higher for the gasoline vehicles than were the LMW PAHs. However, the proportion of LMW PAHs to the total PAHs in diesel vehicles (12.2%) was lower than that found by other studies on diesel vehicles (90.2%) (Tavares et al., 2004). This finding implies that the PAHs for both gasoline- and diesel-fueled vehicles in this test mainly derived from pyrogenic sources. Furthermore, we found that the trend of the LMW PAHs for diesel vehicles was similar to that indicated by a study in the Fu Gui-shan tunnel (Chen et al., 2013). Some diagnostic ratios of PAHs were obtained for diesel vehicles in this test, namely, BaA/(BaA + Chry) and IcdP/(IcdP + BghiP), of which the ratios were 0.36 and 0.17, respectively. The values of the diagnostic ratios of PAHs for diesel vehicles obtained from this test were different from those obtained by other studies. According to these other studies, the BaA/(BaA + Chry) ratios were 0.38–0.65 for DV, and the IcdP/(IcdP + BghiP) ratio was 0.37 for DV (Ravindra et al., 2008). Therefore, it seems that obtaining the diagnostic ratio of PAHs was not a valid way to distinguish gasoline and diesel vehicles in the tunnels, especially when the pyrogenic source was dominant in the diesel vehicles. Furthermore, the most abundant hopane and sterane in the diesel vehicles were 17A(H)-21B(H)-Hopane (0.310 mg·veh^{-1}·km^{-1}) and 17A(H)-21B(H)-30-Norhopane (0.270 mg·veh^{-1}·km^{-1}), These figures are, similar to the results for the mixed vehicles.

3.5. Comparison of emission factors with that from other methods

Comparisons of the speciated EFs in this study with those published in previous studies have been conducted and shown in Table 3, including comparisons of speciated EFs between LDV and HDV in this study and previous studies based on chassis dynamometer (Oanh et al., 2010) and on-road studies (Kam et al., 2012). The $PM_{2.5}$ EFs of LDV and HDV obtained from Oanh et al. (2010) were 230 mg·veh^{-1}·km^{-1} and 1761 mg·veh^{-1}·km^{-1}. Carbonaceous constitutes (OC and EC) accounted for 66.7% and 63.0% of the total $PM_{2.5}$ for LDV and HDV, while the contribution of water soluble ions (0.26% for LDV, 2.05% for HDV) and elements (0.37% for LDV, 0.24% for HDV) was slight. It should be noted that the dynamometer testing is not related to real emissions, compared with the tunnel studies, while the on-road studies and tunnel studies reflect real world emission characteristics. Kam et al. (2012) studied the vehicle emission characteristics in Los Angeles by on-road testing and confirmed that BghiP was the most abundant species of the PAHs, followed by Chry, and Pry. Additionally, the 17A(H)-21B(H)-Hopane and 17A(H)-21B(H)-30-Norhopane EFs were found to be the largest of the hopanes and steranes. These results are similar to those obtained for GV in the Yantai tunnels. The elements contributed 9.8% to the $PM_{2.5}$ in the Los Angeles on-road testing, which was lower than was the test-result in Yantai (13.8% for GV, 12.8% for DV). It should be noted that the samples collected in the tunnel studies could also impact by other sources besides exhaust emissions (Mancilla and Mendoza, 2012; Sternbeck et al., 2002). Consequently, there are still uncertainties with regard to the tunnel studies.

3.6. Estimation of total $PM_{2.5}$ emission from vehicles

Fig 4 showed the $PM_{2.5}$ emissions for GV and DV in Yantai during 2008 to 2013. The maximum $PM_{2.5}$ emissions for GV and DV were 1353 tons in 2010 and 23,042 tons in 2013, respectively. Overall, the $PM_{2.5}$ emissions for DV were higher than those for GV, approximately 14.6 to 36.0 times as much as those for GV. The total $PM_{2.5}$ emission from vehicles in Yantai in 2012 was 22,400 tons, which was higher than those in the urban of Chongqing in 2012 (8000 tons) (Wang, 2013). As indicated by Fig 4, the increment rates of $PM_{2.5}$ for gasoline vehicles have obviously decreased (−57.1%) in 2011, which might cause by improving gasoline quality in this year. The some trend was happened for DV in 2010 in which sulfur content in diesel was decreasing from 500 ppm to 350 ppm. The average increment rate of $PM_{2.5}$ was

Table 3
Emission factors of $PM_{2.5}$ and compositions for gasoline-fueled and diesel-fueled vehicles in several tunnels ($mg \cdot veh^{-1} \cdot km^{-1}$).

Vehicle type	Gasoline vehicle	Diesel vehicle	Gasoline vehicle	Diesel vehicle	LDV	HDV	LDV	HDV	LDV
Sample period	2014	2014	2003	2003	2010	2010	2004	2004	2011
Sampling location	Yantai	Yantai	Hong Kong	Hong Kong	Taiwan	Taiwan	California	California	Los Angeles
Methods	Tunnel	Tunnel	Tunnel	Tunnel	Dynanonmeter	Dynanonmeter	Tunnel	Tunnel	On-road test
Reference	This study	This study	Cheng et al. (2010)		Oanh et al. (2010)		Phuleria et al. (2006)		Kam et al. (2012)
PM	7.36 ± 6.51	415 ± 52.0	16.6 ± 28.5	256 ± 31.3	230 ± 121	1,761 ± 803			162 ± 135
OC	0.974 ± 5.19	113 ± 41.4	8.50 ± 9.30	67.9 ± 10.2	46.5 ± 13.8	229 ± 115			59.4 ± 8.17
EC	ND	164 ± 25.4	3.20 ± 13.3	131.0 ± 14.1	107 ± 27.8	845 ± 145			5.29 ± 4.09
Cl^-	0.322 ± 0.383	4.39 ± 3.06		0.000 ± 0.001	0.557 ± 0.973	1.99 ± 38.5			
NO_3^-	ND	15.8 ± 7.95		3.60 ± 1.10	0.860 ± 1.32	2.78 ± 6.17			
$SO4^{2-}$	ND	19.9 ± 5.13		21.9 ± 7.00	4.36 ± 3.52	30.66 ± 23.97			
NH_4^+	ND	8.53 ± 5.38	0.570 ± 1.21	5.50 ± 1.30	0.300 ± 0.323	0.616 ± 2.77			
Na	0.054 ± 0.156	1.19 ± 1.25	0.360 ± 2.02	0.540 ± 3.10					
Mg	0.173 ± 0.676	7.10 ± 5.40	0.055 ± 0.510	0.630 ± 0.430					1.12 ± 0.249
K	0.070 ± 0.276	3.62 ± 2.21		2.00 ± 0.570					0.383 ± 0.296
Ca	ND	23.6 ± 10.2		1.60 ± 0.560					1.95 ± 0.547
Ti	0.003 ± 0.061	0.854 ± 0.490		0.500 ± 0.150	0.004 ± 0.007	0.018 ± 0.016			0.330 ± 0.074
V	0.00002 ± 0.002	0.035 ± 0.014	0.019 ± 0.000	0.006 ± 0.001	0.001 ± 0.011	0.053 ± 0.120			
Cr	0.001 ± 0.003	0.056 ± 0.022		0.038 ± 0.001	0.061 ± 0.074	0.317 ± 0.458			0.023 ± 0.003
Mn	0.012 ± 0.021	0.267 ± 0.164		0.088 ± 0.023	0.013 ± 0.008	0.053 ± 0.112			0.074 ± 0.015
Fe	0.672 ± 1.23	15.4 ± 9.79		2.60 ± 0.890	0.462 ± 0.396	1.41 ± 1.99			0.011 ± 1.32
Co	0.00001 ± 0.001	0.008 ± 0.005		0.030 ± 0.010	0.011 ± 0.015	0.018 ± 0.056			
Cu	0.024 ± 0.013	0.054 ± 0.104	0.027 ± 0.030	0.071 ± 0.038	0.122 ± 0.106	0.792 ± 1.36			0.828 ± 0.065
Zn	ND	0.883 ± 0.127		0.480 ± 0.097	0.131 ± 0.104	1.46 ± 1.64			0.175 ± 0.079
As	ND	0.011 ± 0.004							
La	0.00003 ± 0.002	0.024 ± 0.014							
Pb	0.005 ± 0.005	0.035 ± 0.037		0.093 ± 0.000	0.040 ± 0.033	0.088 ± 0.321			0.019 ± 0.014
Naphthalene	ND	0.059 ± 0.023							
Acenaphthylene	ND	0.023 ± 0.024					0.48	30.09	
Acenaphthene	0.001 ± 0.002	0.003 ± 0.010							
Fluorene	0.002 ± 0.0005	ND							
Phenanthrene	0.0005 ± 0.002	0.030 ± 0.015							
Anthracene	ND	0.007 ± 0.002							
Fluoranthene	ND	0.113 ± 0.036					2.75	137	
Pyrene	ND	0.215 ± 0.057					4.17	243	0.002 ± 0.0001
Benzo[a]anthracene	ND	0.058 ± 0.007					4.54	73	0.002 ± 0.0006
Chrysene	ND	0.102 ± 0.013					4.92	58.9	0.003 ± 0.0004
Benzo[b]fluoranthene	0.0004 ± 0.001	0.065 ± 0.011					5.21	66.5	
Benzo[k]fluoranthene	0.0004 ± 0.0002	0.011 ± 0.016					4.12	47.9	
Benzo[a]pyrene	0.0001 ± 0.001	0.039 ± 0.007					5.42	50.8	
Indeno[1,2,3-cd]pyrene	ND	0.052 ± 0.013					4.07	10	0.002 ± 0.002
Dibenzo[a,h]anthracene	ND	0.006 ± 0.002					0.34	1.28	
Benzo[ghi]perylene	ND	0.259 ± 0.064					10.3	52.9	0.005 ± 0.001
ABB-20R-C27-Cholestane	0.0002 ± 0.001	0.030 ± 0.006					0.24	1.46	0.0003 ± 0.0004
AAA-20S-C27-Cholestane	0.0002 ± 0.001	0.026 ± 0.005					1.53	14.5	0.0003 ± 0.0004
17A(H)-22,29,30-Trisnorhopane	0.0003 ± 0.001	0.058 ± 0.010					1.8	17.8	0.0001 ± 0.0002
ABB-20R-C28-Methylcholestane	0.0001 ± 0.0005	0.022 ± 0.004							
ABB-20R-C29-Ethylcholestane	0.0001 ± 0.001	0.036 ± 0.005							
17A(H)-21B(H)-30-Norhopane	0.001 ± 0.006	0.270 ± 0.044					4.38	45.15	0.003 ± 0.002
17A(H)-21B(H)-Hopane	0.0001 ± 0.007	0.310 ± 0.054					4.21	38.4	0.005 ± 0.002

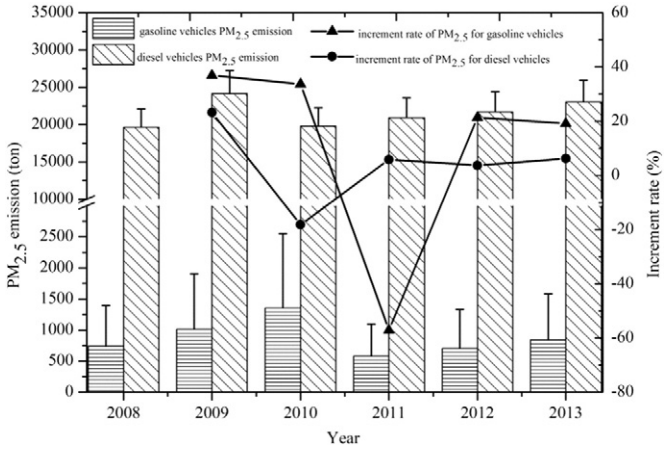

Fig. 4. The $PM_{2.5}$ emission of gasoline and diesel vehicles in Yantai (2008–2013).

18.9% for vehicles in Yantai during 2008–2010, which was higher than the average increment rate of pollutions from vehicles in China during 2005–2010 (6.4%) (Wang, 2013).

4. Conclusions

The sampling campaign for this study was conducted in the WZS and KXL tunnels, to explore the chemical characteristics of the $PM_{2.5}$ emissions from vehicles. Various vehicle types crossed the two tunnels during the sampling periods. Video observation showed that DV accounted for 14.4% of the total vehicles passing through the WZS tunnel, while only 3.4% crossed the KXL tunnel. The vehicle type was the main influencing factor of $PM_{2.5}$ and the associated component of EFs in the tunnels. The EFs of all the species in the WZS tunnel were higher than were those in the KXL tunnel. The proportions of the different constituents of $PM_{2.5}$ in the WZS tunnel were OC (27.7%), EC (32.1%), elements (13.9%), and water soluble ions (9.2%). The chemical profiles of $PM_{2.5}$ in the KXL tunnel were OC (17.7%), EC (10.4%), elements (8.90%), and water soluble ions (8.87%). Comparing of the emission factors of $PM_{2.5}$ and its constituents with that from other tunnels, and found that the emission factor of $PM_{2.5}$ and its constituents were decreased by carrying out vehicle emission standards. The emission factors of $PM_{2.5}$ for gasoline and diesel vehicles were 7.36 $mg \cdot veh^{-1} \cdot km^{-1}$ and 415 $mg \cdot veh^{-1} \cdot km^{-1}$, respectively. It is clear that OC (0.974 $mg \cdot veh^{-1} \cdot km^{-1}$) was the most abundant component in $PM_{2.5}$ for gasoline vehicles, followed by Fe, Cl^- and Mg. The relative proportions of the different constituents in $PM_{2.5}$ for diesel vehicles EC (35.9%), OC (27.2%), elements (12.9%), and water soluble ions (11.7%). The proportions of the higher molecular weight PAHs were higher for both gasoline and diesel vehicles than the lower molecular weight PAHs. It seems that the diagnostic ratios of PAHs were not valid for distinguishing the proportions of gasoline and diesel vehicles in the tunnels, especially when the pyrogenic source was dominant in diesel vehicles. Finally, the estimated $PM_{2.5}$ emissions of gasoline vehicles in Yantai ranged from 581 ± 514 tons to 1353 ± 1197 tons during 2008 to 2013, while the estimated $PM_{2.5}$ emissions of diesel vehicles in Yantai ranged from 19,627 ± 2477 tons to 23,042 ± 2887 tons during 2008 to 2013, i.e., 14.6 to 36.0 times that of the $PM_{2.5}$ emissions of the gasoline vehicles. Consequently, the use of diesel vehicles should be strictly controlled because of the higher emission rate and the increasing trend for $PM_{2.5}$ emissions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.01.077.

References

Adar, S.D., Gold, D.R., Coull, B.A., Schwartz, J., Stone, P.H., Suh, H., 2007. Focused exposures to airborne traffic particles and heart rate variability in the elderly. Epidemiology 18 (1), 95–103.
Ameur-Bouddabbous, I., Kasperek, J., Barbier, A., Harel, F., Hannoyer, B., 2012. Transverse approach between real world concentrations of SO_2, NO_2, BTEX, aldehyde emissions and corrosion in the Grand Mare tunnel. J. Environ. Sci. 24 (7), 1240–1250.
Bureau BMEP (2014). The result of $PM_{2.5}$ source apportionment was released in Beijing. 2014, from http://www.bjepb.gov.cn/bjepb/323474/331443/331937/333896/396191/index.html.
Bureau JEP (2010–2013). The result of fine particulate matter ($PM_{2.5}$) source apportionment in Ji'nan city. 2014, from http://www.jnepb.gov.cn/moudle/mainsubend.aspx?id=6D18B163BB76908C.
Cadle, S.H., Mulawa, P.A., Hunsanger, E.C., Nelson, K., Ragazzi, R.A., Barrett, R., et al., 1999. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. Environ. Sci. Technol. 33 (14), 2328–2339.
Che, W.W., 2010. A Highly Resolved Mobile Source Emission Inventory in the Pearl River Delta and Assessment of Motor Vehicle Pollution Control Strategies Master. South China University of Technology.
Chen, F., Hu, W., Zhong, Q., 2013. Emissions of particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Fu Gui-shan Tunnel of Nanjing, China. Atmos. Res. 124, 53–60.
Cheng, Y., Lee, S.C., Ho, K.F., Louie, P.K.K., 2006. On-road particulate matter ($PM_{2.5}$) and gaseous emissions in the Shing Mun Tunnel, Hong Kong. Atmos. Environ. 40 (23), 4235–4245.
Cheng, Y., Lee, S.C., Ho, K.F., Chow, J.C., Watson, J.G., Louie, P.K.K., et al., 2010. Chemically-speciated on-road $PM_{2.5}$ motor vehicle emission factors in Hong Kong. Sci. Total Environ. 408 (7), 1621–1627.
Chiang, H.L., Huang, Y.S., 2009. Particulate matter emissions from on-road vehicles in a freeway tunnel study. Atmos. Environ. 43 (26), 4014–4022.
Dai, S., Bi, X., Chan, L.Y., He, J., Wang, B., Wang, X., et al., 2015. Chemical and stable carbon isotopic composition of $PM_{2.5}$ from on-road vehicle emissions in the PRD region and implications for vehicle emission control policy. Atmos. Chem. Phys. 15 (6), 3097–3108.
Durbin, T.D., Johnson, K., Miller, J.W., Maldonado, H., Chernich, D., 2008. Emissions from heavy-duty vehicles under actual on-road driving conditions. Atmos. Environ. 42 (20), 4812–4821.
El-Fadel, M., Hashisho, Z., 2001. Vehicular emissions in roadway tunnels: a critical review. Crit. Rev. Environ. Sci. Technol. 31 (2), 125–174.
Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 1998. Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. Environ. Sci. Technol. 32 (14), 2051–2060.
Frey, H.C., Zhang, K.S., Rouphail, N.M., 2008. Fuel use and emissions comparisons for alternative routes, time of day, road grade, and vehicles based on in-use measurements. Environ. Sci. Technol. 42 (7), 2483–2489.
Gao, B., Guo, H., Wang, X.M., Zhao, X.Y., Ling, Z.H., Zhang, Z., et al., 2013. Tracer-based source apportionment of polycyclic aromatic hydrocarbons in $PM_{2.5}$ in Guangzhou, southern China, using positive matrix factorization (PMF). Environ. Sci. Pollut. Res. 20 (4), 2398–2409.
Gao, B., Wang, X.M., Zhao, X.Y., Ding, X., Fu, X.X., Zhang, Y.L., et al., 2015. Source apportionment of atmospheric PAHs and their toxicity using PMF: impact of gas/particle partitioning. Atmos. Environ. 103, 114–120.
Gillies, J.A., Gertler, A.W., Sagebiel, J.C., Dippel, W.A., 2001. On-road particulate matter ($PM_{2.5}$ and PM_{10}) emissions in the Sepulveda Tunnel, Los Angeles, California. Environ. Sci. Technol. 35 (6), 1054–1063.
Handler, M., Puls, C., Zbiral, J., Marr, I., Puxbaum, H., Limbeck, A., 2008. Size and composition of particulate emissions from motor vehicles in the Kaisermuhlen-Tunnel, Vienna. Atmos. Environ. 42 (9), 2173–2186.
He, L.Y., Hu, M., Zhang, Y.H., Huang, X.F., Yao, T.T., 2008. Fine particle emissions from on-road vehicles in the Zhujiang Tunnel, China. Environ. Sci. Technol. 42 (12), 4461–4466.
Ho, K.F., Ho, S.S.H., Lee, S.C., Cheng, Y., Chow, J.C., Watson, J.G., et al., 2009. Emissions of gas- and particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Shing Mun Tunnel, Hong Kong. Atmos. Environ. 43 (40), 6343–6351.
Huo, H., Zhang, Q., He, K.B., Yao, Z.L., Wang, X.T., Zheng, B., et al., 2011. Modeling vehicle emissions in different types of Chinese cities: importance of vehicle fleet and local features. Environ. Pollut. 159 (10), 2954–2960.
Kam, W., Liacos, J.W., Schauer, J.J., Delfino, R.J., Sioutas, C., 2012. On-road emission factors of PM pollutants for light-duty vehicles (LDVs) based on urban street driving conditions. Atmos. Environ. 61 (0), 378–386.
Liacos, J.W., Kam, W., Delfino, R.J., Schauer, J.J., Sioutas, C., 2012. Characterization of organic, metal and trace element $PM_{2.5}$ species and derivation of freeway-based emission rates in Los Angeles, CA. Sci. Total Environ. 435–436 (0), 159–166.

Liu, H., He, K.B., Lents, J.M., Wang, Q.D., Tolvett, S., 2009. Characteristics of diesel truck emission in China based on portable emissions measurement systems. Environ. Sci. Technol. 43 (24), 9507–9511.
Liu, C., Huang, X.F., Lan, Z.J., He, L.Y., 2012. A tunnel test for $PM_{2.5}$ Emission factors of motor vehicles in Shenzhen. Environ. Sci. Technol. 12, 150–153.
Liu, Y., Gao, Y., Yu, N., Zhang, C., Wang, S., Ma, L., et al., 2015a. Particulate matter, gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) in an urban traffic tunnel of China: emission from on-road vehicles and gas–particle partitioning. Chemosphere 134, 52–59.
Liu, W.T., Ma, C.M., Liu, I.J., Han, B.C., Chuang, H.C., Chuang, K.J., 2015b. Effects of commuting mode on air pollution exposure and cardiovascular health among young adults in Taipei, Taiwan. Int. J. Hyg. Environ. Health 218 (3), 319–323.
Lowenthal, D.H., Zielinska, B., Chow, J.C., Watson, J.G., Gautam, M., Ferguson, D.H., et al., 1994. Characterization of heavy-duty diesel vehicle emissions. Atmos. Environ. 28 (4), 731–743.
Mancilla, Y., Mendoza, A., 2012. A tunnel study to characterize $PM_{2.5}$ emissions from gasoline-powered vehicles in Monterrey, Mexico. Atmos. Environ. 59 (0), 449–460.
Na, K., Biswas, S., Robertson, W., Sahay, K., Okamoto, R., Mitchell, A., et al., 2015. Impact of biodiesel and renewable diesel on emissions of regulated pollutants and greenhouse gases on a 2000 heavy duty diesel truck. Atmos. Environ. 107, 307–314.
Oanh, N.T.K., Thiansathit, W., Bond, T.C., Subramanian, R., Winijkul, E., Paw-armart, I., 2010. Compositional characterization of $PM_{2.5}$ emitted from in-use diesel vehicles. Atmos. Environ. 44 (1), 15–22.
Pakbin, P., Ning, Z., Schauer, J.J., Sioutas, C., 2009. Characterization of particle bound organic carbon from diesel vehicles equipped with advanced emission control technologies. Environ. Sci. Technol. 43 (13), 4679–4686.
Phuleria, H.C., Geller, M.D., Fine, P.M., Sioutas, C., 2006. Size-resolved emissions of organic tracers from light- and heavy-duty vehicles measured in a California roadway tunnel. Environ. Sci. Technol. 40 (13), 4109–4118.
Pietikainen, M., Valiheikki, A., Oravisjarvi, K., Kolli, T., Huuhtanen, M., Niemi, S., et al., 2015. Particle and NOx emissions of a non-road diesel engine with an SCR unit: the effect of fuel. Renew. Energy 77, 377–385.
Pio, C., Mirante, F., Oliveira, C., Matos, M., Caseiro, A., Oliveira, C., et al., 2013. Size-segregated chemical composition of aerosol emissions in an urban road tunnel in Portugal. Atmos. Environ. 71 (0), 15–25.
Pope, C.A., Thun, M.J., Namboodiri, M.M., Dockery, D.W., Evans, J.S., Speizer, F.E., et al., 1995. Particulate air-pollution as a predictor of mortality in a prospective-study of us adults. Am. J. Respir. Crit. Care Med. 151 (3), 669–674.
Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42 (13), 2895–2921.
Sandhu, G.S., Frey, H.C., Bartelt-Hunt, S., Jones, E., 2014. In-use measurement of the activity, fuel use, and emissions of front-loader refuse trucks. Atmos. Environ. 92 (0), 557–565.
Shah, S.D., Johnson, K.C., Miller, J.W., Cocker, D.R., 2006. Emission rates of regulated pollutants from on-road heavy-duty diesel vehicles. Atmos. Environ. 40 (1), 147–153.
Shen, X.B., Yao, Z.L., Huo, H., He, K.B., Zhang, Y.Z., Liu, H., et al., 2014. $PM_{2.5}$ emissions from light-duty gasoline vehicles in Beijing, China. Sci. Total Environ. 487, 521–527.
Simoneit, B.R., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliations. Int. J. Environ. Anal. Chem. 22 (3–4), 203–232.
Sternbeck, J., Sjodin, A., Andreasson, K., 2002. Metal emissions from road traffic and the influence of resuspension — results from two tunnel studies. Atmos. Environ. 36 (30), 4735–4744.
Tavares, M., Pinto, J.P., Souza, A.L., Scarminio, I.S., Solci, M.C., 2004. Emission of polycyclic aromatic hydrocarbons from diesel engine in a bus station, Londrina, Brazil. Atmos. Environ. 38 (30), 5039–5044.
Wang, T., 2013. The Research of the Vehicular Emission Inventory in the Urban of Chongqing based on IVE Model Master. Chongqing Jiaotong University.
Wu, Y., Wang, R.J., Zhou, Y., Lin, B.H., Fu, L.X., He, K.B., et al., 2011. On-road vehicle emission control in Beijing: past, present, and future. Environ. Sci. Technol. 45 (1), 147–153.
Yanli, Z., Wang, X., Li, G., Yang, W., Huang, Z., Zhang, Z., et al., 2015. Emission factors of fine particles, carbonaceous aerosols and traces gases from road vehicles: recent tests in an urban tunnel in the Pearl River Delta, China. Atmos. Environ. 122, 876–884.
Yue, X., Wu, Y., Hao, J.M., Pang, Y., Ma, Y., Li, Y., et al., 2015. Fuel quality management versus vehicle emission control in China, status quo and future perspectives. Energ Policy 79, 87–98.
Zhang, F., Chen, Y., Tian, C., Wang, X., Huang, G., Fang, Y., et al., 2014. Identification and quantification of shipping emissions in Bohai Rim, China. Sci. Total Environ. 497–498 (0), 570–577.
Zheng, J.Y., Zhang, L.J., Che, W.W., Zheng, Z.Y., Yin, S.S., 2009. A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment. Atmos. Environ. 43 (32), 5112–5122.
Zhou LY, Ji YD, Dong RY. Ten environmental protection events in Shandong. 2014, from http://www.sdein.gov.cn/dtxx/zhbsdxw/201502/t20150212_274069.html.
Zong, Z., Chen, Y.J., Tian, C.G., Fang, Y., Wang, X.P., Huang, G.P., et al., 2015. Radiocarbon-based impact assessment of open biomass burning on regional carbonaceous aerosols in North China. Sci. Total Environ. 518, 1–7.