Response to Reviewers' Comments on Manuscript: acp-2016-1038

Dear Gregory Frost,

Thank you so much for your consideration! Also, the anonymous reviewer's comments are highly appreciated! So far, we have revised the manuscript accordingly. Our point-by-point responses (in blue) to each reviewer's comments are listed below. And the modifications in the revised manuscript with marks are marked in red. Please see the manuscript for details.

Thanks a ton!

Sincerely,

Dr. Yingjun Chen

Referee #1

General comments

The authors have addressed most of my concerns in this revised manuscript. Quality of the presentation and text is much improved, although as mentioned below some proofreading is still needed. I still have other concerns about the dataset and presentation of the results that are highlighted below; therefore, I cannot support publishing the manuscript as is.

My most important comment is related to the sample size and conclusions drawn from the results (#1 below).

Comments #1: In response to comment #9 from the 2nd referee, the authors mentioned that "Considering the limit of sample size of our study, it was difficult to calculate the influence of the fuel quality and the emission standards on PM constituents separately."; Yet, in abstract (and p. 12, line 12-13) it is suggested that the lower EF_{PM} in stage 2 compared to pre-stage 1 is due to the regulations. A few

sentenced lower, it's also mentioned that "Although the EF_{PM} for excavators and trucks was reduced by the constraint of stringent emission standards,...". P11, line 23-24: "The wide range in EF_{PM} values here could be due to the difference in the selection of excavators emission standards"; p13, line 5-8: "As shown in Figure 4, reductions in the measured EF_{PM} between the China II and China IV trucks and between the China III and China IV trucks were 63.5% and 65.6%, indicating that improvement in the emission standards for diesel trucks could significantly reduce PM emissions." Conclusions: "The average EF_{PM} for excavators with different emission standards decreased by 58% from pre-stage 1 to stage 2" and "Moreover, the reductions in EF_{PM} from the China II to the China IV truck and from the China III to the China IV truck were 63.5 and 65.6%, respectively, Indicating that improvements to the emission standards for diesel trucks and excavators have significantly decreased PM emissions." Consistent with what both referees showed concerns for and the fact that the authors also admitted this shortcoming in their study, I believe the conclusions made in various parts of the paper (as highlighted above) are not valid and need to be rephrased.

Response: Thanks for the comments, from which we get to know some confusion has been caused in last run of response, and make several corrections in the revised manuscript.

(1) The sentence “Considering the limit of sample size of our study, it was difficult to calculate the influence of the fuel quality and the emission standards on PM constituents separately.” has been revised to “considering the limitation of the experimental design of our study, it was difficult to determine, fuel quality or emission standard, which has the more significant influence on constituents of PM from excavator emissions.”

(2) We have extended the discussions about the influences of emission standard and fuel quality on EF_{PM} and rephrased some improper discussions and conclusions in the revised manuscript. The revisions are listed as below.

“Given that there is no government supervision of diesel used for non-road vehicles, the reduction of average EF_{PM} from pre-stage 1 to stage 2 could mainly attribute to

both the different emission standards and diesel quality. As shown in Table S5, the average EF_{PM} from E5 to E6 with the same fuel quality but different emission standards reduced 87.1%. Similarly, EF_{PM} reduced 38.2% from E2 to E1. From which it indicated that emission standards have significant impacts on EF_{PM}. Likewise, the average EF_{PM} for E3, E1 and E6 that were under the same emission standard decreased with improvement of fuel quality, suggesting the influence of diesel quality." (Page 13: 21-27).

"The diesel used for trucks was assumed to have identical quality because of strict diesel quality regulations of on-road trucks. Therefore, the reductions of EF_{PM} for different trucks could be mainly attributed to the improvement in the emission standards." (Page 14: 28-30).

"Although the EF_{PM} for excavators and trucks was reduced with the constraint of regulations, the elemental fractions for excavator emissions ranged from 0.49 to 3.03% from pre-stage 1 to stage 2, and the fraction of WSIs for the China IV truck was 6-fold higher than the average value of WSI for all other-levels trucks." (Page 2: 21-25).

"The average EFPM for excavators with different emission standards excavators was decreased by 58% from pre-stage 1 to stage 2. Moreover, the reductions in EFPM from the China II to the China IV truck and from the China III to the China IV truck were 63.5 and 65.6%, indicating that the improvements to of the emission standards and fuel quality for diesel trucks and excavators have significantly effects on the reduction of PM emissions." (Page 23: 9-15).

Table S5 PM Fueled-based emission factors for excavators (mg kg^{-1} fuel)

ID	Emission standards	Produced year	Sulfur in fuel (ppm)	Idling	Moving	Working	Average
E6	Stage 2	2013	200	141	75	97.8	96.5
E5	Pre-stage 1	2007	200	1,336	/	603	749
E1	Stage 2	2013	400	75.3	88.7	340	289
E2	Pre-stage 1	2007	400	845	582	422	468
E3	Stage 2	2012	700	513	331	1,214	1,047
E4	Pre-stage 1	2004	1100	559	636	2,750	2,323

Comments #2: In response to one of my previous comments (#17) authors mentioned that ambient PM throughout the paper refers to particles smaller than 100 μm. Line 4, page 4, I can't imagine that in a country where dust can also contribute significantly to ambient PM, >90% of PM is from diesel vehicles. What size range (and under what conditions) are these statistics applicable to?

Response: Thanks. This statement reviewer mentioned was inaccurate and the correct one was that "based on the China vehicle environmental management annual report for 2015, 0.56 million tons $PM_{2.5}$ were emitted from on-road mobile sources, of which 90% resulted from on-road diesel vehicle emissions". Note that part of "PM" are not specially defined in the test were mainly referred to ambient fine particle (Dp ≤ 2.5 μm), because almost all of the particles emitted from diesel combustion are fine particles (An et al. 2011). Although we used TSP sampler to collect PM (Dp ≤ 100 μm) in this study, the PM collected in this study was primarily as fine particles with aerodynamic diameter less than 2.5 μm. As shown in Figure R1, ambient fine PM (Dp ≤ 2.5 μm) accounted for around 90% of the PM mass that emitted from excavators in this study. The inaccurate statements have been modified in the revised manuscript (Page 3: 19, 16; Page 4: 14-15; Page 6: 18; Page 8: 20-22).

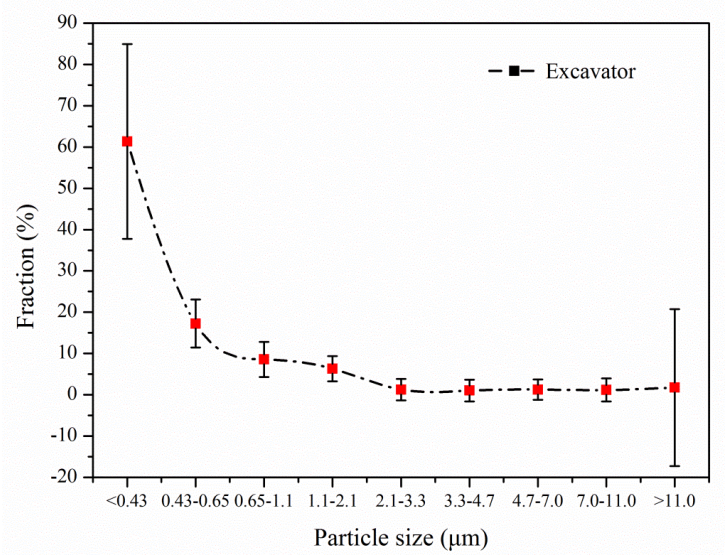

Figure R1 Average mass fraction of PM under different particle size for excavators

Comments #3: comment #4: >100% recovery for some species are reported. Were the

final numbers adjusted for this recovery rate? (also species that had <100% recovery)?

Response: The final concentrations of organic matters were not corrected with the recovery rate (Page 10: 19).

Comments #4: Comment #10: It's unclear why having used a truck for carrying ironstone would lead to higher Fe, Cu, Zn in the exhaust? Your response suggests these species were not coming from the exhaust, but yet the text suggests otherwise. This makes me wonder then if other measurements are also affected by ambient concentrations. The sections on elemental composition and differences are not well supported in my opinion.

Response: Given that the sampling tube was placed directly on the tailpipe, the previous assumption that samples were affected by ambient particles was improper. Wang et al. (2003) reported that the concentrations of the crustal elements (Fe, Ca, and Mg) account for 50% of the total elements in diesel fuel, which is significantly higher than anthropogenic elements emitted from diesel vehicle engines. Besides, Lin et al. (2015) found that Zn and Cu were originated from lubricating oil, except for brake linings. Therefore, we supposed that diesel and lubricating oil combustion were the main sources of elements exhausted from E4. The detail information could be found in the revised manuscript (Page 16: 21-30; Page 17: 1-3).

Comments #5: Comment #11: why not report trace metal EFs for individual excavators? Having the sum for E1+E6 and the rest doesn't make sense.

Response: Thanks. In last run of response, it was not our purpose that reflect individual excavator, therefore, we just reported the average values of E1+E6 and the rest. Now, Trace mental EFs for individual excavators were given separately in the revised manuscript if the review thought it was necessary. The emission factors of elemental were 4.09, 4.10, 1.71, 8.73, 1.56 and 7.24 mg kg^{-1} fuel for E1, E2, E3, E4, E5 and E6, respectively (Page 17: 5-6).

Comments #6: Comment #16: also define BaP(eq) in line 10, page 11

Response: Thank you for the reminding. The BaP(eq) has been defined in the revised manuscript (Page 12:5-9).

Comments #7: Section 3.3 still needs proof-reading

Response: Thanks. The section 3.3 has been proofed-reading.

Comments #8: Section 3.4: fully write out all the PAHs

Response: We take the reviewer's suggestion, and all the PAHs have been fully written in the revised manuscript (Page 20: 18-19; Page 21: 4, 14, 28).

Referee #2

Comments #1: I found a few instances where the language could be improved and I would recommend the authors to go back to their native English speaker to copyedit the manuscript once more.

Response: Thanks for the reviewer's kind suggestion. The manuscript has been reviewed again by our native English speaker.

Comments #2: The response reads very poorly and seems to have been written in a rush (similar to how the manuscript was in the first round). Again, I would recommend the authors to go back to their native English speaker to copyedit the response because the response is published too.

Response: Thanks. The response has been copyedited by our native English speaker.

Comments #3: Add lower bound error bars to Figure 3.

Response: The lower bound error bars have been added in Figure 3 in the revised manuscript (Page 40).

Comments #4: 'Sulfur' misspelled in Figure S5.

Response: The misspelled word has been corrected in the revised Supporting Information (Page 5).

Comments #5: Increase font size for axis labels on Figure 1.

Response: The font size for axis labels on Figure 1 has been increased in the revised manuscript (Page 38).

Comments #6: Emphasize the role of the on-board measurement in this study and state during the comparison to earlier work if the discrepancy in comparison is due to the on-board versus chassis measurement.

Response: Thanks. We have emphasized the role of on-board measurement in the revised manuscript (Page 3: 4-5).

Comments #7: I do not agree with the authors that the quartz fiber filters are equivalent to Teflon filters for gravimetric measurements and that they are insensitive to fiber loss (see comment #7 in response). I would recommend that they provide evidence for that claim.

Response: Thanks. Table R1 listed the results of gravimetric measurements for quartz and Teflon filters in this study. We found that the PM weight from quartz fiber filters were almost equivalent to that from Teflon filters after gravimetric measurements (**$Y=0.89X+0.006$; $R^2=0.74$**) (as shown in Table R1). Furthermore, there were several errors in some weight of samples using Teflon filters (negative values marked with red in Table R1). Therefore, we chose quartz fibers to conduct gravimetric measurements.

Table R1 Results of gravimetric measurements for quartz and Teflon filters

ID	Weight (mg)	Volume (m^3)	Concentration (mg/m^3)[a]
Q1[b]	1.94	0.36	16.23
T1[c]	2.28	0.40	17.10
Q2	2.19	0.29	30.60
T2	3.17	0.35	37.26
Q3	1.50	0.23	16.08
T3	1.05	0.28	9.28
Q4	2.40	0.39	13.57
T4	1.28	0.31	9.14
Q5	1.61	0.46	6.69
T5	1.76	0.32	10.39
Q6	6.67	0.752	14.20
T6	2.48	0.361	10.98
Q7	0.62	0.12	5.00
T7	1.38	0.24	5.75
Q8	3.46	0.13	26.21
T8	2.94	0.21	14.07
Q9	0.81	0.18	4.63
T9	0.99	0.38	2.63
Q10	0.63	0.16	3.87
T10	1.25	0.36	3.49
Q11	0.06	0.18	0.50
T11	0.12	0.12	0.66
Q12	0.86	0.71	1.99
T12	1.00	0.22	2.73
Q13	1.90	0.61	5.29
T13	2.22	0.50	3.56
Q14	1.05	0.49	9.56
T14	2.11	0.40	11.23
Q15	0.50	0.24	12.61
T15	-1.43	0.20	-1.15
Q16	1.19	0.40	7.33
T16	-1.17	0.35	-1.34
Q17	2.19	0.21	10.43
T17	-0.36	0.18	-1.99
Q18	2.17	0.16	13.23
T18	-0.24	0.13	-1.75

a refers to that the concentrations were rectified by dilution ratios;
b refers to quartz filters;
c refers to Teflon filters;

References:

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Wang, Y.F., Huang, K.L., Li, C.T., Mi, H.H., Luo, J.H. and Tsai, P.J. (2003). Emissions of fuel metals content from a diesel vehicle engine. Atmospheric Environment 37(33): 4637-4643.

Measurement of PM and its chemical composition in real-world emissions from non-road and on-road diesel vehicles

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Abstract. With the rapid growth in the number of both non-road and on-road diesel vehicles, the adverse effects of particulate matter (PM) and its constituents ~~such as elemental carbon (EC), and polycyclic aromatic hydrocarbons (PAHs),~~ on air quality and human health have ~~been receiving~~attracted increasing attentions. However, studies on the characteristics of PM and its composition ~~which~~ emitted from diesel

vehicles are still scarce, ~~particularly~~ especially those performed in real-world conditions. In this study, six excavators and five trucks involving a range of emissions standards and operational modes were tested, and ~~to characterize~~ PM emissions as well as its constituents, including organic carbon (OC), elemental carbon (EC), water soluble ions (WSIs), elements, and organic species such as PAHs, n-alkanes, hopane, and sterane were characterized. The average emission factors for PM (EF_{PM}) from excavator~~s~~ and truck emission~~s~~ were 829 ± 806 and 498 ± 234 mg ~~k~~g^{-1} fuel, respectively~~, which are similar to values found in other studies~~. EF_{PM} and PM constituents ~~was~~ were significantly affected by fuel quality, operational mode, and emission standards. ~~A s~~Significant correlation (R^2=0.79, p<0.01) was found between ~~the~~ EF_{PM} for excavators and the sulfur contents in fuel. The highest average EF_{PM} for working excavators was 904 ± 979 mg ~~k~~g^{-1} fuel, because of the high engine load required in this mode. From pre-stage 1 to stage 2~~ emission standards~~, the average EF_{PM} for excavators decreased by 58%. For trucks, the average non-highway EF_{PM} (548 ± 311 mg ~~k~~g^{-1} fuel) was higher than the highway EF_{PM} (497 ± 231 mg ~~k~~g^{-1} fuel). Meanwhile, the reductions ~~when switching from China II and III to China IV standards~~ were 63.5% and 65.6% when switching from China II and III to China IV standards, respectively. Generally, the PM composition emitted from excavators was dominated by OC (39.2 ± 21.0%) and EC (33.3 ± 25.9%), while PM from trucks was dominated by EC (26.9 ± 20.8%), OC (9.89 ± 12%), and WSIs (4.67 ± 5.74%). ~~Several differences in composition were observed among the various operational modes, emission standards, and fuel qualities.~~ The average OC/EC ratios for idling and working excavators were 3 to 4 times higher than those for moving excavators. Although the EF_{PM} for excavators and trucks ~~was~~were reduced ~~by~~with the constraint of ~~stringent emission standards~~regulations, the element~~al~~ fractions for excavators ~~ranged~~ increased from 0.49 (pre-stage 1) to 3.03% ~~from pre-stage 1 to~~ (stage 2), and the fraction of WSIs for the China IV truck was 6-fold higher than the average value of all other-level trucks.~~they were for the other trucks~~. Furthermore, as compared with other diesel vehicles, wide ranges in the ratios of benzo[a]anthracene/(benzo[a]anthracene+chrysene) (0.26-0.86),

indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene +benzo[ghi]perylene) (0.20-1.0) and fluoranthene/(fluoranthene+pyrene) (0.24-0.87) were found for excavators, which might be a result of the complex characteristics of excavator operational modes. Through comparison of our results with literatures, on-board measurements data could reflect real condition better. Although ~~Similar~~ fraction~~s~~ of the 16 priority PAHs ~~(as identified by the U.S. Environmental Protection Agency) were found in the exhaust~~in PM from the excavator~~s~~ and truck emissions were similar~~,s.~~ ~~The~~ the equivalent concentrations of total benzo[a]pyrene, ~~which were used to evaluate carcinogenic risk,~~ were 31 times higher for excavators than ~~they were~~that for trucks, implying that more attention should be paid to non-road vehicle emissions.

Keywords

Diesel vehicles; excavators; trucks; PM; chemical composition; influential factors

1. Introduction

Particulate matter (PM) emitted from diesel vehicles has significant adverse effects on air quality, human health, and global climate change, and therefore merit close examination (Aggarwal et al., 2015, 2016). Previous studies have ~~reported~~ found that diesel vehicle exhaust is a major source of ambient fine PM emissions ($D_p \leq$ ~~100~~ 2.5 μm) (Oanh et al., 2010, Zhang et al., 2015a). For instance, vehicle exhaust was reported to contribute ~~to~~ almost 30% ~~of~~ of ambient ~~ambient~~ $PM_{2.5}$ ~~emissions~~ in 9 cities of China in 2015 (MEP 2016). The International Agency for Research on Cancer (IARC) found that exposure to diesel exhaust could cause~~s~~ lung cancer (IARC 2012). Adar et al. (2015) reported that a disproportionate occurrence of respiratory disease had been caused when breathing polluted air from diesel school buses by a survey for more than 25 million children ~~breathe polluted air on diesel school buses, which then causes a disproportionate occurrence of respiratory disease~~. Nearly 34% of element carbon (EC) emissions, a major contributor to current global warming and

poor human health, comes from off-road diesel vehicle emissions~~s~~ in the USA (USEPA 2015).

The numbers of on-road and non-road diesel vehicles have increased considerably in China, and have ~~contributed to~~caused severe ~~emissions~~environmental problems. On-road diesel vehicles can be classified ~~as~~ into light-duty, medium-duty, and heavy-duty trucks. Non-road diesel vehicles mainly include construction machinery and agricultural equipment (MEP 2014). Airplanes, trains, and vessels are not included as non-road diesel vehicles in this study, because the primary fuels used for these vehicles ~~does~~were not ~~include~~ diesel.

The number of on-road diesel vehicles increased from 11.0 million in 2009 to 32.8 million in 2015, while the number of non-road diesel vehicles increased from 20.6 million in 2006 to 33.6 million in 2012 (CCCMIY et al., 2013, MEP 2016). Based on the China vehicle environmental management annual report for 2015 (MEP 2016), 0.56 million tons of $PM_{2.5}$ were emitted from on-road mobile sources, ~~and more than~~of which 90% ~~of PM~~ resulted from on-road diesel vehicle emissions (Figure S1). However, pollutants emitted from non-road diesel vehicles should not be neglected. In 1991, The U.S. Environmental Protection Agency (USEPA) published a report indicating that PM emitted from non-road diesel vehicles was significantly higher than that emitted from on-road diesel vehicles (USEPA 1991). Wang et al. (2016) ~~estimated~~ compiled an emission inventory for non-road equipment (including agricultural equipment, river/ocean-going vessels, locomotives, and commercial airplanes) and found that there were 349 Gg of PM ~~emissions~~ emitted from non-road vehicles in China during 2012. Construction equipment~~s~~ ~~was~~ contributed as the largest ~~source of PM emissions from~~ non-road diesel vehicles emission source. Zhang et al. (2010) reported that PM_{10} ~~emissions~~ emitted from construction equipment in the Pearl River Delta (PRD) region accounted for 26.5% of the total emission from non-road vehicles in 2006. ~~An important type of non-road diesel vehicle, t~~The number of construction equipment ~~in China~~ increased from 1.97 million to 5.85 million between 2006 and 2012 (CCCMIY 2013). Furthermore, as one of the most abundant types of construction equipment (Figure S1), excavators contributed almost 65% of

the PM emissions from construction equipment (Li et al., 2012).

In order to control PM emissions pollution from diesel vehicles, China began to implement emission standards in early 2001 for light-duty diesel vehicles and heavy-duty diesel vehicles (SEPA et al., 2001). These standards were tightened in the subsequent 12 years, from the China I to China V standards. Although China V emission standards for on-road diesel vehicles has been formulated, insufficient diesel fuel quality slows their implementation (Yue et al., 2015). In addition, the China IV emission standards for on-road diesel vehicles are not fully implemented. Implementation timeline of emission standards for non-road diesel vehicles has lagged behind that of the on-road diesel vehicles. China implemented two emission standards for new non-road diesel engines, stage 1 and stage 2 in 2007 and 2009, respectively. However, the first implementation in China was 7 years later than USA (USEPA 2003, SEPA et al., 2007). The pollution emissions limits for on-road and non-road diesel vehicles are given in Tables S1 and S2.

EF_{PM} is an important parameter in the compilation of emission inventories for on-road and non-road diesel vehicles in China. However, the foundational work towards quantifying EF_{PM} is relatively weak and contains large uncertainties (Huang et al., 2011). Most of the EF_{PM} from trucks have been measured using tunnel and dynamometer tests, which could not evaluate influential factors for PM emissions from a single truck in real-world conditions (Alves et al., 2015b, Mancilla et al., 2012, Pio et al., 2013). Although several studies have measured PM emissions from trucks using on-board tests in real-world conditions (Wu et al., 2016, Wu et al., 2015, Zhang et al., 2015a). Because, the data should be updated frequently (Huo et al., 2012) because EF_{PM} emitted from trucks could change along with improved emission standards. In addition, the data of EF_{PM} emitted from non-road diesel vehicles in real-world conditions is scarce in China. In 2014, the Ministry of Environmental Protection of the People's Republic of China had issued "Technical guide for the preparation of a single source emission inventory of atmospheric fine particulate

matter." However, no measured ~~baseline~~ data ~~for~~ of ~~emission factors of~~ EF_{PM} ~~from~~ for non-road vehicles could be referred in this technical guide, especially for construction machinery (6 g ~~k~~km^{-1} were predicted for uncontrolled standards) ~~could be found in this technical guide~~(MEPPRC 2014). Until now, there was only one study in China by Fu et al. (2012) had ~~, who~~provided EF_{PM} ~~for~~ of 12 excavators using portable emission measurement system (PEMS) ~~for~~ under different operational modes. On-board measurements need to be expanded to improve localization of EF_{PM} for non-road diesel vehicles in China as soon as possible, because of the complexity of real-world conditions, including lagging diesel quality and changing emission standards.

Analysis of the chemical composition of PM is essential for source apportionment, human health, and climate change studies. Primary PM emitted from diesel vehicles contains a variety of chemical components, including organic carbon (OC), elemental carbon (EC), water soluble ions (WSIs), elements, and organic species such as n-alkanes, polycyclic aromatic hydrocarbons (PAHs), hopane and sterane). Several previous field studies have focused on chemical composition of PM emitted from diesel vehicles~~.~~, but specific characteristics of PM emitted from diesel vehicles and its composition still are great unknown, especially for organic compounds. Zhang et al. (2015a) characterized $PM_{2.5}$ compositions (OC, EC, WSIs and elements) emitted from heavy-duty diesel trucks (HDDTs). Wu et al. (2016) reported the detailed chemical composition of $PM_{2.5}$ emitted from China III and China IV diesel trucks, including the OC, EC, WSIs, and element contents. In 2012, Fu et al. (2012) firstly tested 12 excavators using ~~in the first~~ on-board test ~~for excavators~~ in China, but only optically-based EF_{PM} ~~were~~ was given. ~~Therefore, the specific characteristics of PM emitted from diesel vehicles and its composition are still largely unknown, especially for organic compounds.~~

In this study, PM~~—~~ emitted from on-road and non-road diesel vehicles was measured to (I) test emission factors of PM for excavators and trucks in real-world conditions; (II) identify influential factors on the emitted PM and its composition, and (III) characterize chemical components present in the emitted PM. Although ~~The~~ the study results required substantial effort ~~and~~, it provided valuable information for

developing ~~use in the development~~ of effective control policies ~~for~~ to ~~reducing~~ reduce PM emissions from excavators and trucks.

Experimental

2.1 Diesel vehicle and operational mode selection

In this study, six excavators and five trucks were selected to cover a wide range of emission standards, manufacturers and engine loads. Detailed information for the selected excavators and trucks is shown in Table 1. As shown in Figure S2, the annual production of excavators did not change substantially between 2007 and 2009 (an increase from 70,000 to 85,000 ~~excavators~~), during ~~which~~ stage 1 non-road vehicle emission standard was implemented. Therefore, excavators produced with pre-stage 1 and stage 2 emission standards were chosen for this study. Based on China national standard (SEPA 2007), excavators are divided into five types according to their power rating. The excavators in this study were categorized ~~for this study by emission standards and were rated~~ as low (0-75 kw), medium (75-130 kw) or high (130-560 kw) power under different emission standards. Three operational modes were selected for the excavators ~~As a way to~~ reflect actual use ~~environments~~condition, ~~three operational modes were selected for the excavators~~ including idling, moving and working. Further descriptions of these three modes can be found in Fu et al. (2012). In addition, consistent sampling times for the different modes were not strictly required in this study, as long as sufficient amounts of PM were collected to conduct the subsequent chemical analysis. The average sampling times during idling, moving, and working were 41.7, 24.0, and 28.5 min, respectively.

Three types of diesel trucks were selected in this study, including one China II standards truck, three China III standards trucks, and one China IV standards truck. The China III trucks included one of each ~~of~~ light-duty, medium-duty, and heavy-duty diesel truck~~s~~. Based on the traffic rules and driving conditions for on-road diesel trucks, routes were predesigned ~~routes were chosen~~ for the test~~ing~~ ~~the~~ trucks in Yantai, Shandong province of China (Figure 1). Because different trucks drove on different routes, the selected routes in this study were divided into non-highway and highway categories. The selected routes for China III and China IV light-duty trucks included

non-highway 1, non-highway 2 and highway 1. The lengths of these three roads were 19, 35 and 17 km, respectively. The route chosen for the China II heavy-duty truck (yellow label) was non-highway 3 which was 25 km long. The routes chosen for China III medium-duty and heavy-duty trucks included non-highway 4 and highway 2. The lengths of these two roads were 47 and 23 km, respectively. The detailed velocity and road grade information for all of the tested routes are shown in Figures S3 and S4. Although repeated tests were conducted for some vehicles, it should be noted that only one set of integral data was selected for further discussion, which was due to the incompleteness of some monitoring data (e.g. the data of CO_2 and CO concentrations missing). As shown in Tables S3 and S4, the variability ~~in test times~~ for the same operational mode was considered acceptable in test times. Some actions were required to reduce the uncertainty. For example, we combined sampling filters for the repeated experiments for ~~vehicles~~ T1 and T3 to carry out organic compound analysis.

2.2 On-board emission measurement system

The on-board emission measurement system was designed and constructed ~~in~~ by our ~~laboratory~~ research group (Figure 2). A description of the on-board emissions test system was given in our previous report (Zhang et al., 2015b). Briefly, this system consists of two main components: a Photon II analyzer, which was used to analyze the flue gas (HC, CO, CO_2, SO_2, and NOx), and a PM sampling system (TSP sampler). Although we used TSP sampler to collect PM ($D_p \leq 100$ μm) in this study, mainly PM collected in this experiment was considered as fine particles. Because almost all of the particles emitted from engine combustion are fine particles (An et al. 2011). The PM sampling system consisted of a dilution system followed by five exhaust channels. Two channels were connected to PM samplers, and the other three were blocked. Before sampling, the emission measurement system was put on a truck and connected to the excavator exhaust tube by a stainless steel pipe. The system ~~showed~~ had clear improvements over other on-board instruments, such as PEMSs and FPS4000 (Zheng et al., 2015), with better portability and ~~the~~ better ability to collect filter samples for further chemical analysis in the laboratory. The results ~~presented herein~~ this study ~~include~~ presented the first dataset from on-board measurement of non-road diesel

vehicle exhaust in China.

2.3 Chemical analysis

2.3.1 Fuel quality analysis

Fuel quality has ~~a large~~significant effect on PM emissions from vehicles (Cui et al., 2016, Liang et al., 2005, Zhang et al., 2014). Since the fuels used in excavators ~~is often of~~were various and always with poor ~~quality~~qualities, ~~diesel was collected from each of the tested excavators and analyzed.~~ all of the corresponding fuels from each of the tested excavators were collected to have quality analysis. The results of fuel quality analysis are given in Table 2. Comparing the diesel quality used in this study with the ~~diesel quality~~ standards for non-road vehicles (GB 252-2015) (SEPA et al., 2015), it was found that the sulfur contents in most of the diesels used in this study (200-1100 ppm) were higher than which allowed by GB 252-2015 (<350 ppm). Additionally, the sulfur content in the diesel used by E4 was 1100 ppm, which was much higher than that used in the other excavators. Furthermore, the ash content of diesel used by E4 was 4.16%, about 420 times higher than the limit given by GB 252-2015.

2.3.2 PM and chemical composition analysis

Quartz-fiber filters were used ~~for~~ to collect~~ing~~ ~~the~~ PM samples ~~because~~ for ~~the~~ PM weight measurement and chemical analysis. And the weight losses of these filters could be neglected through strict sampling processes~~, and quartz-fiber filters could be used for both the PM weight measurement and chemical analysis~~. ~~The~~ All filters were weighed before and after sampling to determine ~~the collected~~ PM mass concentrations. Before each weighing, the filters were balanced at 25 ℃ and 40% relative humidity for 24 h. Each filter was weighed three times. WSIs were analyzed using ion chromatography (Dionex ICS3000, Dionex Ltd., America) following the method of Cui et al. (2016). Elements analysis was performed using inductively coupled plasma mass spectrometerry (ICP-MS; ELAN DRC II type, Perkin Elmer Ltd., Hong Kong) (Cui et al. 2016).

Because the organic compounds on ~~each~~ filters ~~was~~ were insufficient for quantification, we merged filters ~~from~~ of different operational modes or driving routes

based on the proportion of sampling time during each mode or route for analyzing the characteristic of PM for each diesel vehicle. ~~based on the proportion of sampling time during each mode or route.~~ Quartz filter samples were spiked with internal standards (including acenaphthene-d_{10}, benzo[a]anthracene-d_{12}, pyrene-d_{10}, coronene-d_{12}, cholestane-d_4, *n*-C15-d_{32}, *n*-C20-d_{42}, *n*-C24-d_{50}, *n*-C30-d_{58}, *n*-C32-d_{66}, *n*-C36-d_{74}) and ultrasonically extracted two times in 30 mL of a 1:1 mixture of hexane and dichloromethane for 10 min. All extracts from each sample were combined, filtered and concentrated to approximately 0.5 mL.

Organic species including n-alkanes, PAHs, hopane and sterane were analyzed using GC-MS (Agilent 7890A GC-5975C MS) 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 ℃ for 4 min, increase 5 ℃ min^{-1} to 150 ℃ with 2 min static time , then increase 3 ℃ min^{-1} to 306 ℃ with a 20 min static time. The GC had an injector temperature of 290 ℃, injector volume of 2 μL, helium carrier gas, and gas flow rate of 1.2 mL min^{-1}. The electron impact (EI) mode at 70 eV and selected-ion-monitoring (SIM) mode were selected to determine concentrations of PAHs, hopane, and sterane. For organic matter, blank samples and recovery rates (66.7-128% for five surrogates) were measured. The blank concentrations were subtracted from the sample concentrations. The final concentrations of organic matters were not corrected for the recoveries.

The PM chemical constituents analyzed in this study were OC; EC; WSIs: SO_4^{2-}, NO_3^-, Cl^-, NH_4^+; elements: Na, Mg, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb); n-alkanes: C12 to C40; the sixteen USEPA priority PAHs of naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo [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); Hopane and sterane: ABB-20R-C27-Cholestane (ABB), AAA-20S-C27-Cholestane (AAA), 17A(H)-22,29,30-Trisnorhopane (Tm), 17A(H)-21B(H)-30-Norhopane (30AB), and 17A(H)-21B(H)-Hopane (29AB).

2.4 Data processing

2.4.1 Fuel-based emission factors

Fuel-based emission factors were calculated using the carbon mass balance formula:

$$EF_i = \frac{\Delta X_i}{\Delta CO_2} \cdot \frac{M_i}{M_{CO_2}} \cdot EF_{CO_2} \quad (1)$$

where EF_i and EF_{CO_2} (g kg^{-1} fuel) are the emission factors for species *i* and CO_2, respectively, ΔX_i and ΔCO_2 (mol m^{-3}) are the background-corrected concentrations of species *i* and CO_2, respectively, and M_i and M_{CO_2} (g mol^{-1}) represent the molecular weights of species *i* and CO_2, respectively.

The CO_2 emission factors (EF_{CO_2}) were calculated as:

$$EF_{CO_2} = R_{FG} \cdot c(CO_2) \cdot M_{CO_2} \quad (2)$$

where $c(CO_2)$ (mol m^{-3}) is the molar concentration of CO_2, and R_{FG} (m^3 kg^{-1} fuel) represents the flue gas emission rate.

The flue gas emission rates ~~were~~ was calculated as:

$$R_{FG} = \frac{C_F}{c(C_{CO}) + c(C_{CO_2}) + c(C_{PM})} \quad (3)$$

where C_F (g C kg^{-1} fuel) represents the mass of carbon in 1 kg ~~of~~ diesel fuel, and c(C_{CO}), c(C_{CO_2}), and c(C_{PM}) (g C m^{-3}) represent the flue gas mass concentrations of carbon as CO, CO_2, and PM, respectively.

2.4.2 Average fuel-based emission factors for excavators and trucks

The average fuel-based emission factor for each excavator in each relevant operational mode was calculated as:

$$\mathrm{EF}_{i,j} = \sum EF_{\mathrm{i,j,g}} \times P_{j,\mathrm{g}} \quad (4)$$

where $EF_{i,j}$ (g kg^{-1} fuel) is the average emission factor of species *i* from excavator *j*, $EF_{i,j,g}$ (g kg^{-1} fuel) is the emission factor of species *i* from excavator *j* in mode *g*, and $P_{j,g}$ (%) is the proportion of activity time (Fu et al., 2012) for excavator *j* in mode g.

The average fuel-based emission factor for each truck in different driving conditions was calculated as:

$$EF_{i,j} = \sum EF_{i,j,s} \times P_{j,s} \quad (5)$$

where $EF_{i,j}$ (g ~~k~~kg^{-1} fuel) is the average emission factor for species *i* from truck *j*, $EF_{i,j,s}$ (g ~~k~~kg^{-1} fuel) is the emission factor of species *i* for truck *j* in driving condition s, and $P_{j,s}$ (%) is the proportion of activity time for truck *j* in driving condition s.

2.4.3 Benzo[a]pyrene equivalent concentration (BaP_{eq})

The various PAHs have a wide range of carcinogenic risks. Therefore, it is not accurate to evaluate the harmful effects of PAHs on human health using the total combined mass concentration. BaP_{eq} is typically used to evaluate the carcinogenic risks associated with individual PAH (Mirante et al., 2013~~).), The BaP$_{eq}$~~which was calculated as:

$$BaP_{eq} = \sum PAH_i \times PEF \quad (6)$$

where PAH_i is the measured concentration of an individual PAH for excavator *i*, and *PEF* is the potency equivalence factor for that PAH obtained from Wang et al. (2008).

3. Results and discussion

3.1 Fuel-based PM emission factors ~~of PM in~~for excavator exhaust

The EF_{PM} values for excavator exhaust are illustrated in Figure 3, with detailed information given in Table S5. The maximum fuel-based PM emission factor was 37 times higher than the minimum. In general, the average EF_{PM} for different excavators ranged from 96.5 to 2323 mg ~~k~~kg^{-1} ~~f~~fuel, with an average of 829 ± 806 mg ~~k~~kg^{-1} fuel. The EF_{PM} values of excavators reported by Fu et al. (2012) were within the range of EF_{PM} values in this study. The wide range ~~in~~ of EF_{PM} values here ~~might~~ could be due to the difference in ~~the selection of excavators~~ emission standards for excavator. The excavators ~~selected~~ tested by Fu et al. (2012) included stage 1 and stage 2 emission standards, while ~~our study tested~~ the excavators in this studies were with the emissions standards of pre-stage 1 and stage 2 ~~emission standards~~.~~

~~EF_{PM} is affected by many factors. In this study, the EF_{PM} range for excavators with different power ratings was 96.5 (35 kw) to 2323 (110 kw) mg kg^{-1} fuel, but the correlations between EF_{PM} and engine power (See Figure S5) were weak. Conversely, fuel quality, emission standard and operational mode significantly affected the EF_{PM}.~~

~~Fuel quality had a large impact on EF_{PM} for the excavators. As shown in Figure 3, a significant correlation (R^2 = 0.79, P < 0.01) was found between the average emission factors for excavators and the fuel sulfur contents, which is consistent with results reported by Yu et al. (2007).~~

~~The EF_{PM} also decreased with stricter emission standards for the excavators.~~ The EF_{PM} measured for pre-stage 1 excavators during idling, moving and working were 914 ± 393, 609 ± 38 and 1258 ± 1295 mg kg^{-1} fuel, respectively, whereas for stage 2 excavators, ~~they were~~it was 243 ± 236, 165 ± 144 and 551 ± 587 mg kg^{-1} fuel, respectively. ~~The~~ That is, the EF_{PM} ~~of~~ for the stage 2 excavators under idling, moving and working modes, were reduced by 73%, 73% and 56% ~~from~~ compared to the pre-stage 1 ~~values under idling, moving and working modes,~~ excavator, respectively, while ~~. The~~ the average EF_{PM} for excavator~~s of different emission standards~~ decreased by 58% from pre-stage 1 to stage 2.~~, suggesting the effectiveness of the emissions control policy.~~ EF_{PM} ~~is~~could be ~~affected~~influenced by many factors. In this study, the EF_{PM} range for excavators with different power ratings ~~was~~ranged from 96.5 (35 kw) to 2323 (110 kw) mg kg^{-1} fuel, ~~but~~however, the correlations between EF_{PM} and engine power (See Figure S5) were weak. Additionally, ~~Conversely,~~ fuel quality, emission standard and operational mode significantly ~~affected~~influenced the EF_{PM}. ~~The EF_{PM}~~ Given that there is no government supervision of diesel used for non-road vehicles, the reduction of average EF_{PM} from pre-stage 1 to stage 2 could mainly attribute to both the different emission standards and diesel quality. As shown in Table S5, the average EF_{PM} from E5 to E6 with the same fuel quality but different emission standards reduced 87.1%. Similarly, EF_{PM} reduced 38.2% from E2 to E1. From which it indicated that emission standards have significant impacts on EF_{PM}. Likewise, the average EF_{PM} for E3, E1 and E6 that were under the same emission standard decreased with improvement of fuel quality, suggesting the influence of diesel quality.~~also decreased with stricter emission standards for the excavators.Fuel quality had a large impact on EF_{PM} for the excavators.~~ As shown in Figure 3, ~~a significant~~good correlation (R^2 = 0.79, P < 0.01) was found between the average ~~emission factors~~EF_{PM} for excavators and ~~the fuel~~ sulfur contents in fuels, which ~~is~~was

consistent with the results reported by Yu et al. (2007). Furthermore, ~~The~~ the EF_{PM} for the various excavators varied ~~sharply~~ significantly ~~between~~ under different operational modes ~~for the various excavators~~. Specifically, working excavators ~~had~~ exhibited the highest EF_{PM}, which was more than double the values for idling and moving excavators. The average EF_{PM} for excavators were 578 ± 467 while idling, 343 ± 264 while moving, and 904 ± 979 mg kg^{-1} fuel while working. Excavators under ~~Working~~ working mode produced the highest average EF_{PM}, which might be ~~because~~ascribed to that ~~–~~ the higher engine load ~~,~~ caused a lower air-fuel ratio and thus prompted PM production.

3.2 Fuel-based PM emission factor~~s of PM~~ for trucks

The EF_{PM} for all measured trucks varied from 176 to 951 mg kg^{-1} fuel. The maximum EF_{PM} for trucks was three times ~~more than~~higher than the minimum. The average EF_{PM} for the tested diesel trucks was 498 ± 234 mg kg^{-1} fuel~~.~~. Consistent with that reported by ~~In comparison,~~ Wu et al. (2016) (range: 95.6-1147 mg kg^{-1} fuel; average: 427 mg kg^{-1} fuel). ~~reported an average EF_{PM} for diesel trucks of 427 mg kg^{-1} fuel (95.6-1147 mg kg^{-1} fuel) , which was similar to the range for our results.~~

The average EF_{PM} of diesel trucks under real-world conditions with different emission standards ~~and~~, vehicle sizes, ~~while using different~~and driving patterns were ~~provided~~ given in ~~under real-world conditions (~~Figure 4~~)~~. The measured EF_{PM} for China II, China III, and China IV diesel trucks varied from 200 to 548 mg kg^{-1} fuel. The EF_{PM} for the China II truck measured in this study was lower than that reported by Liu et al. (2009) (910-2100 mg kg^{-1} fuel). The average EF_{PM} for light-duty, medium-duty and heavy-duty diesel trucks were 524 ± 457, 459, and 492 mg kg^{-1} fuel, respectively. The average EF_{PM} for trucks under non-highway and highway driving patterns were 548 ± 311 and 497 ± 231 mg kg^{-1} fuel, respectively. As shown in Figure 4~~.~~, reductions ~~in the measured~~of EF_{PM} ~~between~~ from the China II ~~and~~ to China IV trucks, and ~~between~~ from the China III ~~and~~ to China IV trucks were 63.5% and 65.6%, respectively. The diesel used for trucks was assumed to have identical quality because of strict diesel quality regulations of on-road trucks. Therefore, the reductions of EF_{PM} for different trucks could be mainly attributed to the improvement in the emission

standards.~~, indicating that improvement in the emission standards for diesel trucks could significantly reduce PM emissions.~~ Of particular note was that the EF_{PM} for China III and light-duty diesel trucks were higher than the values for the other corresponding trucks. The reason might be ~~a~~ the result~~s~~ of poor driving conditions, i.e., low average speed and highly varied speed (Figures S3 and S4). The same tendency is apparent in Figure 4, with diesel trucks ~~emitting more PM while~~ driving on the non-highway (average speed of 28.5 km h^{-1}) emitted more PM than ~~while~~ that driving on the highway (average speed of 60.7 km h^{-1}). The road grade further affected the EF_{PM} of the on-road diesel trucks. For example, the EF_{PM} for T5 driving on the highway was lower than those for T1 driving on the highway, because of lower road grade for T5 (Figure S4).

3.3 Particulate matter composition for individual diesel vehicles

Four types of constituents were considered for reconstituting PM mass in this study: (1) organic matter, which was ~~estimated~~ calculated by multiplying the corrected OC by a factor of 1.6 (Almeida et al., 2006); (2) EC; (3) WSIs; and (4) elements. The reconstituted masses for the excavator samplers were 74.7-123% of the measured mass, while the reconstituted masses for the diesel truck samples were only 43.2-54.4% of the measured mass (Figure 5). In addition to uncalculated components, this discrepancy might be due to a distribution error ~~from~~ between OC and EC by using TOR, ~~moisture~~ droplet effects, or ~~metal oxidation~~oxides when metal elements were only considered.

3.3.1 Particulate matter composition for individual excavator

The chemical composition of PM for each excavator is shown in Figure 5 and Table S6. For each excavator, the carbonaceous component (OM+EC) was the dominant species, which is consistent with results ~~from~~ of a previous study by Liu et al. (2005) who reported that the proportions of OC and EC in PM ranged from 70 to 91% (Liu et al., 2005). Because the OC/EC ratio is also used to identify the source of atmospheric particulate pollution, further assessment was performed on the OC/EC ratios in different operational modes for each excavator (Figure 6). The average OC/EC ratios during idling, moving, and working were 1.57, 0.57, and 2.38, respectively. The

OC/EC ratio during idling was ~~greater~~ higher than 1 because soot hardly generated at low temperatures and fuel-rich zone. These results were consistent with those ~~in~~ from Liu et al. (2005). Furthermore, Liu et al. (2005) reported that the OC/EC ratios decreased with ~~an increase in the~~ load increasing for non-road engines. Although the trend of OC/EC ratios from idling (low load) to moving (medium load) was consistent with those reported by Liu et al. (2005), ~~However, this trend was not observed in this study. The~~ the OC/EC ratio under working (high load) was ~~2.38~~higher than those under idling and moving ~~while working, and increased with increasing load,~~ which was accorded ~~consistent~~ with the results reported by Zhang et al. (2014). As shown in Figure 6, the differences between OC/EC ratios for different excavator operational modes were ~~profound~~significant, and could be affected by a number of factors, including transient working conditions, diesel sulfur content, and extensive OC sources (Cocker et al., 2004, Liu et al., 2005, Ruiz et al., 2015).

As shown in Figure 5, WSIs and elements fractions ranged from 0.335 to 1.21% and from 0.163 to 7.50%, respectively, for all excavators. The total proportion of WSIs and elements to PM was the highest in excavator E6, followed by excavator E1. Generally, the total proportion of WSIs and elements to PM in exhaust from excavator E6 was 4 to 14 times higher than the corresponding proportions in exhaust from the other excavators. Sulfate and nitrate were the main WSIs (79.1-90.0% of WSIs) for almost all of the excavators, except for E1, in which the proportion of Cl^- (67.2%) was the highest (Table S6). Fe, Ca, Na, Mg, and K were the relatively dominant element~~s~~s, except for E4 that~~,~~ Fe, Zn, and Cu were the most abundant elements. Wang et al. (2003) reported that the concentrations of~~–~~ the crustal elements of Fe, Ca, and Mg ~~that~~ accounted for 50% of the total elements in diesel fuel, which were significantly higher than anthropogenic elements emitted from diesel vehicle engines~~,~~. ~~which~~ That is consistent with the results from our study. Similarly, we supposed that diesel was the dominant source for these elements because the sampling tube was placed directly on the tailpipe. In addition, it was different from other excavators that ~~The abundance of Fe,~~ Zn ~~,~~ and Cu were also abundant elements ~~in the exhaust of~~for E4. ~~could have been affected by E4 being used to transport ironstone~~. Lin et al. (2015) found that Zn

and Cu were originated from lubricating oil, except for brake linings~~(Lin et al. 2015)~~. Therefore, we supposed that diesel and lubricating oil combustion were probably the main sources of element emitted from E4 (produced in 2004). ~~In addition~~Furthermore, the elements fractions for the two excavators manufactured in 2013 (1.42% for E1, 7.50% for E6 and 4.09 mg ~~k~~g^{-1} fuel for E1 and 7.24 mg ~~k~~g^{-1} fuel for E6~~5.66 mg kg^{-1} for E1 + E6~~) were higher than those for the other excavators (4.10, 1.71, 8.73, 1.56 ~~a total of 4.02~~ mg ~~k~~g^{-1} fuel for E2, E3, E4, and E5). This indicates that elements emissions were deteriorating and more stringent control technology should be developed to avoid adverse health effects from the total elements composition of PM in the exhaust.

The n-alkanes, PAHs, hopane and steranes fractions in the exhaust from the excavators were 3.6 to 9.6%, 0.03 to 0.24%, and 0.001 to 0.09% respectively. Liang et al. (2005) characterized diesel particulate matter emitted from non-road engines using a dynamometer test and found that n-alkanes accounted for 0.83% of PM, which was lower than the proportion found in this study.~~,~~ It was possibly ~~because~~ caused by ~~they used~~the low sulfur diesel fuel they used and the different sampling methods. In contrast to the fractions of WSIs and elements, the fractions of n-alkanes, hopane and steranes were the highest in excavator E4, while the fraction~~s~~ of PAHs was the highest for the exhaust from E3. ~~In a comparison of the fuel quality between E3 and E4,~~ E4 had poorer diesel quality compared with E3, which might be the reason for high n-alkane, hopane and steranes concentrations. Similarly, Rogge et al. (1993) found that n-alkanes, hopane and steranes were mostly derived from the incomplete combustion of fuel and lubricant oil. However, we speculated that PAHs were affected by combustion conditions (i.e., combustion temperature) in this study, because E3, with the stage 2 standard, had better performance and superior fuel quality. PAH isomer ratios have been widely used to conduct source apportionment for environmental receptors (such as sediments) (Liu et al., 2012). Yunker et al. (2002) found that the ratios of the principal masses of PAH 178, 202, 228 and 276 had the best potential to distinguish between natural and anthropogenic sources. For the excavators, the ranges of the ratios ~~ranges~~ for BaA/(BaA+Chry), IcdP/(IcdP+BghiP),

and Flua/(Flua+Pry) were 0.26-0.86, 0.20-1.0, and 0.24-0.87, respectively, with averages of 0.47 ± 0.27, 0.44 ± 0.38, and 0.48 ± 0.27, respectively (Figure 7). The average ratios of PAHs in excavator exhaust obtained in this study were similar to those from Liu et al. (2015). The E4 excavator had ~~a clear~~ obvious differences in the ratios of BaA/(BaA+Chry), IcdP/(IcdP+BghiP), and Flua/(Flua+Pry) to those from the other excavators. The isomer ratios of BaA/(BaA+Chry), IcdP/(IcdP+BghiP) and Flua/(Flua+Pry) for E4 were 0.86, 1.0 and 0.87, respectively. These were different from the ranges for fuel combustion defined by Yunker et al. (2002). The ratios of PAHs emitted from diesel vehicles reported by Yunker et al. (2002) mainly referred to those from on-road diesel vehicles. However, the operational mode and fuel quality for non-road diesel vehicles are more complicated than those for on-road diesel vehicles. Therefore, the results obtained in this study ~~provides~~ could provide references values for the isomer ratios of PAHs in non-road diesel vehicle exhaust.

3.3.2 Particulate matter composition for individual diesel trucks

For diesel trucks, the total carbonaceous composition (OM+EC) accounted for 44.0% (T1), 27.9% (T2), 43.9% (T3), 51.6% (T4) and 46.3% (T5) of PM, ~~which~~ that are all lower than the values reported in previous studies (Chow et al., 2011, Wu et al., 2015). One of the main reasons was inferred as ~~because of was~~ the different OC and EC detection methods used in our study. Through a comparison of two common thermal-optical methods (NIOSH and IMPROVE) of OC and EC analysis for~~Cheng et al. (2011) collected~~ 333 $PM_{2.5}$ samples collected ~~and analyzed OC and EC~~ by Cheng et al. (2011),~~two common thermal-optical methods (NIOSH and IMPROVE). They~~ it was found that NIOSH-defined EC was lower (up to 80%) than that of defined by IMPROVE. The IMPROVE thermal-optical method was used in this study, which ~~would~~ could cause under-~~-~~valuation of OC. Except for ~~the~~ T2 and T4 trucks, almost all of the OC/EC ratios for diesel trucks calculated in this study were lower than 1, which is consistent with conclusions from previous studies (Figure 6). The OC/EC ratios for T2 during highway and non-highway driving were 5.64 and 15.5, respectively, which ~~may~~ might be a result of the effect by China IV emission standard. Other study also found ~~Alves et al. (2015b) reported~~ that modern diesel passenger cars

(Euro 4 and Euro 5) ~~have~~ had high OC/EC ratios (Alves et al. 2015b). ~~As shown in Figure S3,~~The OC/EC ratio for T4 while driving on the non-highway was 4.10, which might be caused by the low driving aped. Because ~~the driving speed for T4 was zero for the first 500 seconds.~~ Cheng et al. (2015) have reported that the OC/EC ratios were substantially above 1 ~~while~~ under idling or with low load. ~~Therefore~~And, the ~~OC/EC ratio~~driving speed was zero for the first 500 seconds for T4 as shown in Figure S3.~~while driving on the non-highway was 4.10, which might have been caused by the low driving speed.~~

The sum of WSIs and elements fractions ~~were~~ was lower than 5% of PM for ~~the exhaust from~~ all of the diesel trucks, except for ~~that from~~ T2, which is consistent with the results ~~in~~ of Zhang et al. (2015a). SO_4^{2-} was the most abundant ion for trucks T2 and T5, while NO_3^- was the most abundant ion for trucks T1, T3 and T4. For T2, WSIs (13.8%) were the most significant component of PM, followed by OC, which was 4 to 10 times higher than ~~it was for the~~ other trucks (Table S6). The main reason was inferred as that T2 was a China IV diesel vehicle with well-controlled combustion conditions leading to more water emissions, which accelerates the transformation from the gas phase to WSIs (e.g., the transformation of SO_2 to SO_4^{2-}). As can be seen in Table S6, Fe was the most abundant element for trucks T1 and T5, while Ca was the most abundant element for trucks T2, T3, and T4. The total element fraction of T2 (China IV) was 16 times higher than that of T1 ~~exhaust~~ (China III). Although the EF_{PM} for diesel trucks decreased with stricter emission standards, the WSIs and element contents increased instead. It is well know that sulfate and nitrate are major precursors of ~~Because~~ acid rain, elements emitted by diesel engine also have significant ~~is caused by sulfate and nitrate and~~ adverse health effects on human and attention ~~are caused by elements, attention~~ needs to be paid to this phenomenon.

The n-alkanes, PAHs, hopane and steranes fractions were 0.85- 4.78%, 0.01-0.54% and 0.002- 0.024%, for the trucks. As shown in Table S6, C20 was the most abundant n-alkane in ~~exhaust~~ PM from T1, T2 and T4, while C19 was the most abundant n-alkane ~~in exhaust from~~of T3 and T5. ~~Of the PAHs,~~ And the most abundant species of PAHs was pyrene. N-alkanes, PAHs, hopane and steranes accounted for the highest

proportions of PM for the exhaust from T3, ~~and~~ which might be affected by many factors, including differences in the engine power rating, complex reactions in the engine (combustion process and pyrolysis reactions related to temperature, humidity, etc.), and driving conditions. As shown in Figure 7, the isomer ratios for diesel trucks were 0.28-0.35 for BaA/(BaA+Chry), 0.08-0.22 for IcdP/(IcdP+BghiP) and 0.08-0.39 for Flua/(Flua+Pry), with averages of 0.31 ± 0.03, 0.15 ± 0.06 and 0.23 ± 0.12, respectively. These are similar to results reported by Schauer et al. (1999).

3.4 Average chemical composition of PM emitted from diesel vehicles

3.4.1 Average chemical composition of PM in excavator exhaust

The average PM chemical compositions for excavator exhaust are listed in Table 3. Carbonaceous matter was the dominant component and accounted for 72.5% of the PM for excavators, whereas OC was the most abundant species (39.2%) for PM. The total element fraction was the second largest group and contributed 1.76% of PM. Of the elements, emissions were dominated by Fe at 46.3%. In addition, the proportion of n-alkanes in PM from excavator exhaust (5.14%) was higher than the proportions of the other organic matter types (PAHs were 0.098% while hopane and sterane were 0.026%) and C20/C19 was the most abundant n-alkane. For parent PAH, emissions were dominated by ~~P~~pyrene~~ry~~ and ~~Fluo~~fluoranthene, followed by ~~Nap~~ naphthalene and ~~Chry~~chrysene.

Table 3 summarizes the average source profiles of PM in excavator exhaust as derived in this study, as well as ones previously reported by others for comparison. As shown in Table 3, the average fraction of total carbonaceous components for the excavators tested in this study was consistent with that for a marine engine, while the element fraction was lower than that for a marine engine (Sippula et al., 2014). Iron oxide is recognized as a catalyst and can promote soot burnout during combustion processes (Kasper et al., 1999). The EC fraction of PM in the excavator exhaust was higher than that reported by Sippula et al. (2014), which might be the result of a lower metal fraction in the excavators used for their study. The proportions of n-alkanes measured in this study were significantly higher than those emitted from a marine engine (4-fold) and non-road generator (6-fold) in another study (Liang et al.,

2005), which could be the result of different aliphatic compounds in the diesel fuels (Sippula et al., 2014). For the marine engine and non-road generators, C22 and C17 were the most abundant n-alkane species. PAHs were domina~~n~~ted by ~~Phe~~ phenanthalene for a marine engine and ~~Fluo~~ fluoranthene for non-generators, which was different from the result obtained for the excavators. This could indicate that the PM emitted from different types of non-road diesel vehicles has varying source profiles based on the operational conditions.

3.4.2 Average source profile of PM for trucks

As shown in Table 3, PM from trucks was dominated by carbonaceous matter (36.8%), followed by WSIs (4.67%) and elements (0.941%). For individual species, sulfate and nitrate were the most abundant WSIs, and Fe was the most abundant element. Moreover, for organic matter, the average proportions of n-alkanes, PAHs, hopanes and steranes were 1.73%, 0.130%, and 0.011%, respectively. C20 was the most abundant n-alkane, and the PAHs were dominated by pyrene~~Pry~~.

In comparison, total carbon emissions in this study were lower than those in previous studies, whereas the WSIs and elements fractions were higher (Alves et al., 2015a, Cui et al., 2016, Schauer et al., 1999, Wu et al., 2016). Several factors could have influenced these differing results, including fuel quality, driving condition, engine parameters (fuel injection timing, compression ratio, and fuel injector design) and experimental methods (Sarvi et al., 2008a, Sarvi et al., 2008b, Sarvi et al., 2009, Sarvi et al., 2010). As shown in Table 3, Fe was the dominant element in studies using on-road tests and tunnels, which is similar to our results, while Zn and Na were dominant in elements from results obtained by a dynamometer. Therefore, the results obtained from real world (on-road tests and tunnels) were different from those obtained in a laboratory. For organic matter, the proportion of PAHs, hopane and sterane to PM were consistent with the results from Schauer et al. (1999) and Cui et al. (2016). As in this study, the most abundant in n-alkane was C20 as measured by Schauer et al. (1999), and ~~Pyr~~ pyrene was the most abundant PAH reported by Cui et al. (2016). Thus, the average profile of PM for on-road diesel trucks is relatively stable and consistent across studies.

3.5 ~~Source profile comparison for excavators and trucks~~Comparison of source profile between excavators and trucks

Average EF_{PM} for excavators (836 ± 801 mg kg^{-1} fuel) was higher than that for diesel trucks (498 ± 234 mg kg^{-1} fuel). This result is ~~understandable~~ reasonable because the operations for excavators are more transient than those for trucks. Sarvi et al. (2010) reported that particulate matter emitted from diesel engines was typically low during steady state operation. Although the average EF_{PM} of excavators was higher than that of trucks, the average EF_{PM} of the stage 2 excavators was 477 mg kg^{-1} fuel, which was lower than those for the China II and China III trucks. Thus, appropriate regulations formulated for non-road diesel vehicles could improve their PM emissions.

When we compared the average percentages of chemical components in PM for excavators with those for trucks, several differences were found. In general, the carbonaceous (95.9%) and elements (1.76%) fractions for excavators were higher than those for diesel trucks (42.8% and 0.94%, respectively). As shown in Figure 8, the structures of different ring PAHs in the exhaust from excavators and trucks varied sharply, especially for 5 and 6-ring PAHs, although the average percentage of total PAHs in the PM were consistent between the excavators and trucks. Due to their lipophicity, high molecular weight (5+6 ring) PAHs are considered to be more harmful to human health than the other PAHs. For further distinction, BaPeq was used in this study. The range of total BaPeq for trucks was 5.32 (T5) to 155 (T3) ng m^{-3}, while for excavators, the range of total BaPeq was 38.3 (E1) to 3637 (E4) ng m^{-3}. Moreover, the total average BaPeq for the excavators was 31 times larger than that for the diesel trucks. Almost all of the parent PAH BaP_{eq} values calculated in this study for trucks and excavators were higher than the concentrations that cause 1/10000 of the carcinogenic risk, according to the World Health Organization (WHO). Due to the adverse environmental effects and health hazards caused by carbonaceous composition, elements, and PAHs, the PM emissions from excavators require urgent control.

Conclusions

This study reported the characteristics of PM source profiles for excavators and the EF_{PM} values for exhaust from excavators and trucks with different emission standards and used in different operational modes, or road conditions were obtained. The EF_{PM} for different excavators ranged from 96.5 to 2323 mg ₭g^{-1} fuel, with an average of 810 mg ₭g^{-1} fuel and showed a high correlation (R^2=0.79, P<0.01) with the fuel sulfur contents. The highest average EF_{PM} for excavators that are working (904 ± 979 mg ₭g^{-1} fuel) might be the result of higher engine load causing lower air-fuel ratios. The average EF_{PM} for the tested diesel trucks with different emission standards and vehicle sizes under different driving conditions was 498 ± 234 mg ₭g^{-1} fuel. The average EF_{PM} for ~~excavators with different emission standards~~ excavators was decreased by 58% from pre-stage 1 to stage 2. Moreover, the reductions in EF_{PM} from the China II to the China IV truck and from the China III to the China IV truck were 63.5 and 65.6%, i~~I~~ndicating that the improvements ~~to~~ of the emission standards and fuel quality for diesel trucks and excavators have significantly ~~decreased~~effects on the reduction of PM emissions. It should be noticed that the EF_{PM} for China III and light-duty diesel trucks were higher than those for the other trucks, which could be a result of poor driving conditions that included a low average and highly variable speed. For each excavator, the carbon component (OM+EC) was dominant fraction and accounted for approximately 74.1-123% of the PM. The average ranges of WSIs, elements, n-alkanes, PAHs, hopane and sterane fractions for each excavator were 0.335-1.21%, 0.163-7.50%, 3.6-9.6%, 0.03-0.24% and 0.001-0.09%, respectively. In contrast to the other excavators, Zn and Cu were the second and third most abundant elements in exhaust from E4, which might to the result of poor fuel quality and the vehicle age. Additionally, the element fractions for the two excavators produced in 2013 (E1 (1.42%) and E6 (7.50%)) were higher than other excavators, which might indicate that elements emissions control deteriorated and more stringent control technology should be developed. For excavators, the ranges of the ratios BaA/(BaA+Chry), IcdP/(IcdP+BghiP) and Flua/(Flua+Pry) were 0.26-0.86, 0.20-1.0 and 0.24-0.87, respectively, with average of 0.47 ± 0.27, 0.44 ± 0.38 and 0.48 ± 0.27, respectively. For diesel trucks, the total carbonaceous composition (OM+EC)

accounted for 44.0% (T1), 27.9% (T2), 43.9% (T3), 51.6% (T4) and 46.3% (T5) of PM. For T2, WSIs (13.8%) were the most significant fraction of PM after OC, and it was higher than those for the other trucks by a factor of 4 to 10. The n-alkanes, PAHs, hopane and steranes fractions ranged from 0.85 to 4.78%, 0.01 to 0.54% and 0.002 to 0.024% for trucks, respectively. In comparison with the results from other studies, the characteristics of the average source profiles for different types of non-road diesel vehicles varied sharply, while those for on-road diesel vehicles, showed more stability. Although the PAHs fractions for the excavators and trucks were similar, the total BaP_{eq} that was used to evaluate the carcinogenic risk was 31 times greater for excavators than for trucks.

Acknowledgements. This study was supported by the CAS Strategic Research Program (No.XDB05030303), the Natural Scientific Foundation of China (Nos.41273135 and 41473091), the Fundamental Research Funds for the Central Universities.

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Table captions

Table 1 Specifications for the tested excavators and trucks

Table 2 Diesel contents from excavators

Table 3 Comparison of average chemical constituents of PM for different diesel vehicles

Table 1 Specifications of tested excavators and trucks

ID	Manufacturers	Model years	Emission standards	Powers (kw)	Total weights (kg)	Displacements (L)	Working hours (h)	Mileages (km)
E1	Volvo	2013	stage 2	169	30,500	7.1	2,751	/
E2	Hitachi	2007	pre-stage 1	162	30,200	9.8	16,166	/
E3	Sany	2012	stage 2	128	22,900	/	5,598	/
E4	Doosan	2004	pre-stage 1	110	22,000	8.1	12,000	/
E5	Doosan	2007	pre-stage 1	40	5,250	2.8	/	/
E6	Komatsu	2013	stage 2	35	5,300	2.4	780	/
T1	Futian	2010	China III	68	4,495	2.6	/	100,238
T2	JAC	2014	China IV	88	4,495	2.8	/	/
T3	Futian	2011	China III	70	11,190	3.9	/	99,000
T4	Chunlan	2002	China II	125	15,480	/	/	/
T5	JAC	2011	China III	105	15,590	4.3	/	130,000

Table 2 Diesel contents from excavators

ID	E1	E2	E3	E4	E5	E6	GB 252-2015
Gross thermal value (MJ/kg)	45.1	45.1	45.3	45.3	45.3	45.3	/
Net thermal value (MJ/kg)	42.4	42.4	42.7	42.8	42.6	42.5	/
Kinematic viscosity (20 ℃)(mm^2/s)	4.23	4.23	3.89	4.16	4.60	4.39	3.00-8.00
Moisture (%)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	/
Ash content (%)	0.04	0.04	0.05	4.16	0.03	0.05	0-0.01
C (%)	86.3	86.3	86.4	86.8	85.9	85.9	/
H (%)	11.6	11.6	11.5	11.2	12.0	12.1	/
O (%)	1.99	1.99	2.01	1.85	2.07	1.86	/
N (%)	0.05	0.05	0.05	0.04	0.06	0.05	/
S (ppm)	400	400	700	1100	200	200	<350

n.d. = not detected

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Table 3 Comparison of average chemical constituents of PM for different diesel vehicles (%)

Vehicle types	Excavators	Trucks	Trucks	Medium-duty trucks	Diesel vehicles	Light-duty diesel engines	Marine engine	Non-road generator
Methods	On-road		On-road	Dynamometer	Tunnel	Dynamometer	Dynamometer	Dynamometer
Reference	This study		(Wu et al., 2016)	(Schauer et al., 1999)	(Cui et al., 2016)	(Alves et al., 2015b)	(Sippula et al., 2014)	(Liang et al., 2005)
EC	33.3	26.9	55.3	30.8	39.5	69.9	14.1	
OC	39.2	9.89	31.8	19.7	27.2	12.7	60.0	
Ions	0.614	4.67	1.49	1.96	11.7	0.638		
NH_4^+	0.044	0.215	0.188	0.730	2.06	0.005		
Cl^-	0.098	0.110	0.247		1.06	0.115		
NO_3^-	0.278	1.08	0.529	0.230	3.81	0.459		
SO_4^{2-}	0.193	3.27	0.529	1.00	4.80	0.059		
Elements	1.76	0.941	0.493	0.200	12.8	0.069	3.17	
Na	0.245	0.047			0.287	0.041	0.564	
Mg	0.106	0.079			1.71	0.008	0.422	
K	0.197	0.028			0.872	0.002	0.671	
Ca	0.241	0.211		0.030	5.69	0.017	1.01	
Ti	0.008	0.011	0.145		0.206	0.0001	0.005	
V	0.001	0.000	0.001		0.008		0.044	
Cr	0.035	0.039	0.011	0.010	0.013		0.010	
Mn	0.013	0.009	0.002	0.010	0.064		0.006	

Continued Table 3

Fe	0.815	0.276	0.247	0.050	3.71	0.0003	0.138	
Co	0.001	0.005	0.0002	0.010	0.002		0.006	
Ni	0.015	0.006	0.002	nd			0.016	
Cu	0.042	0.107	0.004	0.010	0.013		0.130	
Zn	0.027	0.111	0.076	0.070	0.213	0.0001	0.130	
Pb	0.011	0.010	0.005	0.010	0.008		0.013	
Alkanes	5.14	1.73		0.222			1.37	0.831
C12	0.003	0.020						0.003
C13	0.003	nd						0.006
C14	0.019	0.0003						0.020
C15	0.057	0.013		0.001				0.056
C16	0.201	0.062		0.005				0.116
C17	0.107	0.144		0.003				0.265
C18	0.587	0.215		0.002			0.049	0.148
C19	0.777	0.308		0.002			0.120	0.126
C20	0.977	0.311		0.052			0.260	0.074
C21	0.516	0.290		0.022				0.014
C22	0.769	0.143		0.028			0.264	0.001
C23	0.349	0.099		0.025			0.177	0.001
C24	0.245	0.061		0.022			0.128	0.001
C25	0.197	0.032		0.014			0.083	0.0004

Continued Table 3

C26	0.119	0.016	0.019	0.075	
C27	0.031	0.009	0.014	0.056	
C28	0.023	0.004	0.011	0.058	
C29	0.013	0.002	0.003	0.046	
C30	0.007	0.001		0.025	
C31	0.010	0.002		0.017	
C32	0.010	0.001		0.007	
C33	0.010	0.00001		0.002	
C34	0.010	0.0004			
C35	0.013	0.00004			
C36	0.016	nd			
C37	0.018	nd			
C38	0.025	nd			
C39	0.031	nd			
C40	0.003	nd			
PAHs	0.098	0.130	0.251	0.021	0.021
Nap	0.008	0.001	0.014		0.0004
Acy	0.005	0.0003	0.006		0.0002
Ace	0.001	0.00004	0.001		0.0003
Flu	0.002	0.0001			0.001
Phe	0.005	0.021	0.007		0.008
Ant	0.001	0.001	0.002		0.0004

Fluo	0.026	0.010		0.027	0.009	0.002
Pyr	0.028	0.088		0.052	0.008	0.007
BaA	0.007	0.001		0.014	0.001	0.0005
Chry	0.008	0.002		0.025	0.003	0.0005
BbF	0.002	0.001		0.016		0.0003
BkF	0.001	0.0001		0.003		0.0002
BaP	0.0004	0.00001		0.009		0.0004
IcdP	0.001	0.00002		0.013	0.0004	0.001
DahA	0.000	0.001		0.001		0.0002
BghiP	0.003	0.004		0.062	0.0003	0.0003
Hopane, sterane	0.026	0.011	0.014	0.167	0.143	
ABB	0.001	0.0005	0.0004	0.007		
AAA	0.002	0.001	0.001	0.006		
Tm	0.001	0.001	0.001	0.014	0.012	
30AB	0.011	0.005	0.006	0.065	0.069	
29AB	0.011	0.004	0.006	0.075	0.061	

8 n.d. = not detected

Figure captions

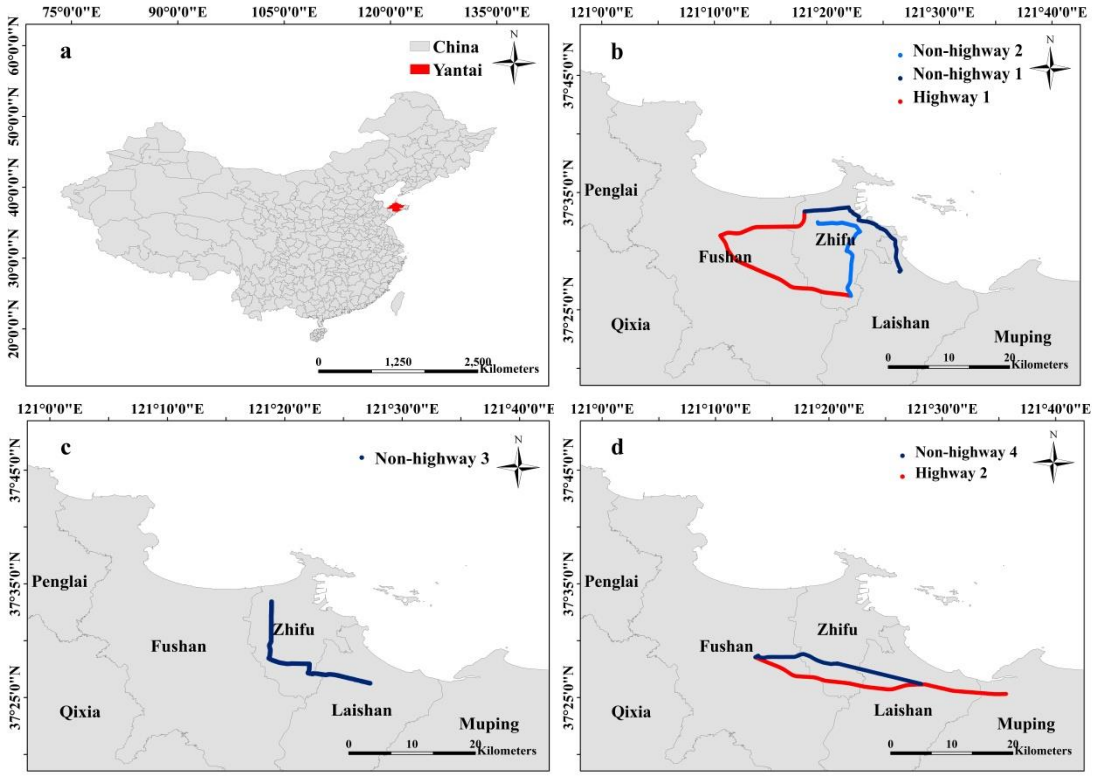

Figure 1The routes for diesel trucks; a was the site of Yantai; b was the route for China III and China IV light-duty diesel trucks; c was the rout for China II heavy-duty diesel truck-; d was route for China III medium-duty and heavy-duty trucks

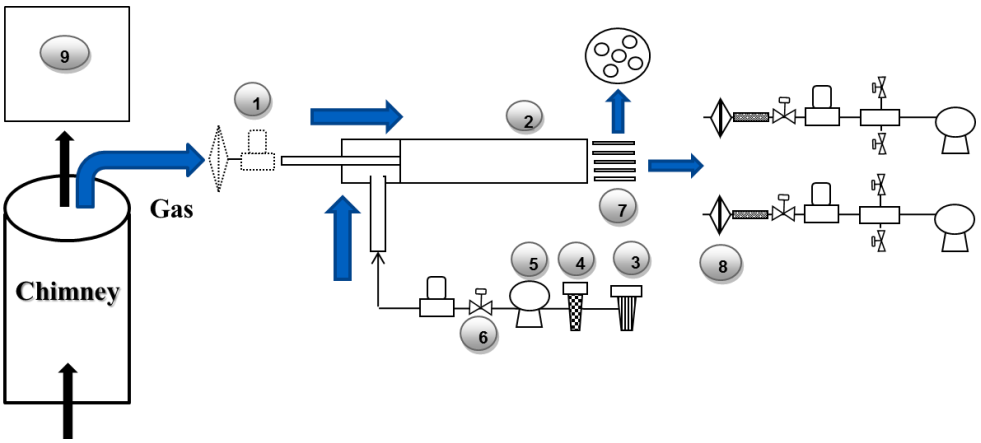

Figure 2 Particulate matter sampling system; 1 is the flowmeter; 2 is the dilute tunnel; 3 is the filtrator; 4 is the activated carbon; 5 is the fan; 6 is the valve; 7 is the flow divider; 8 is the filter membrane sampler; and 9 is the exhaust analyzer

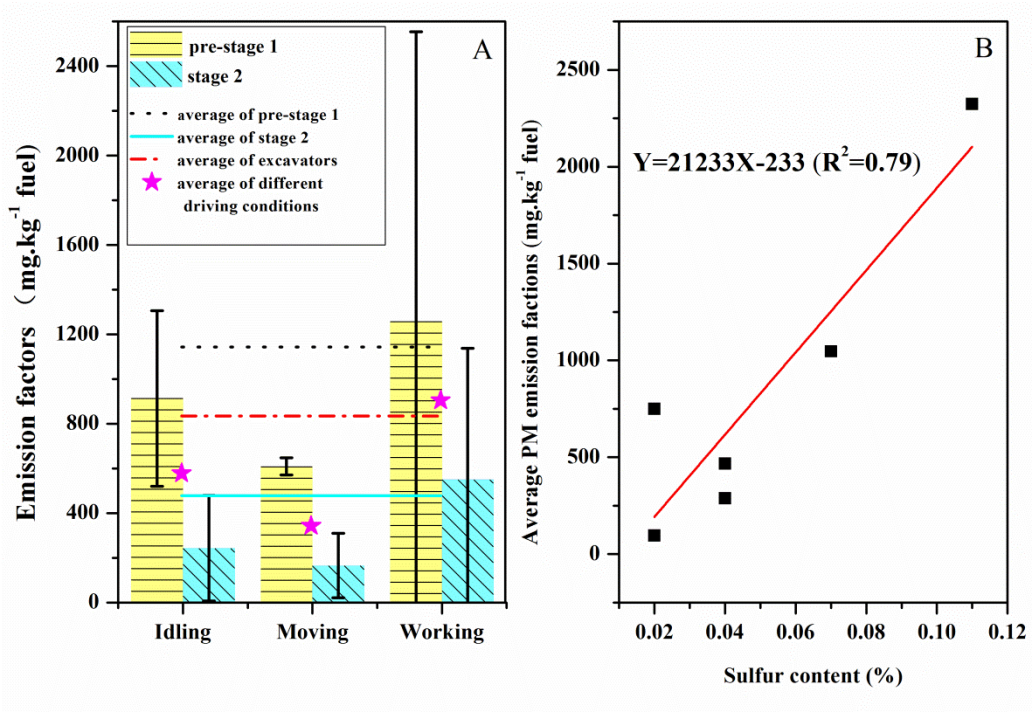

Figure 3 EF_{PM} for excavators with different operational modes and emission standards (A) and the correlation with sulfur contents (B)

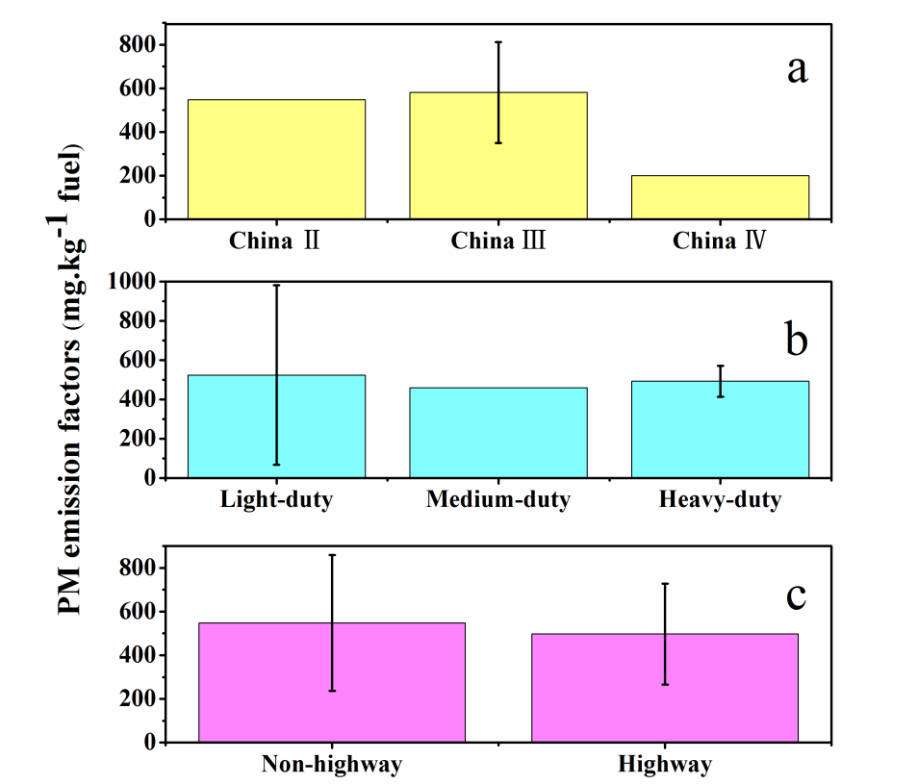

Figure 4 Diesel trucks EF_{PM} for different emission standards (a), vehicle sizes (b) and driving conditions (c)

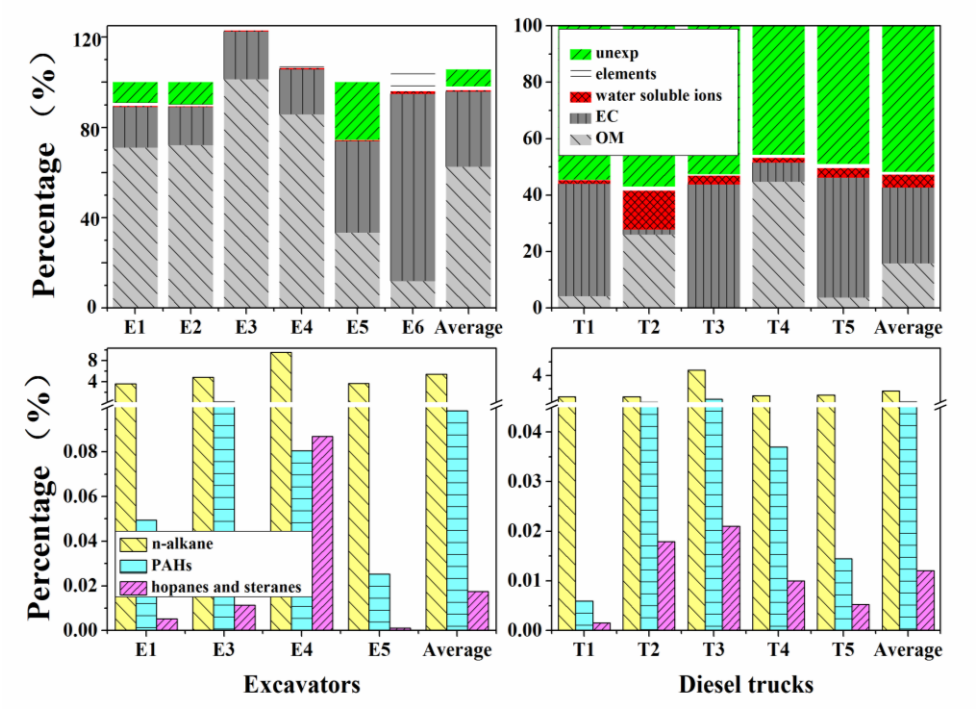

Figure 5 Compositional constituents of PM for individual vehicles (%)

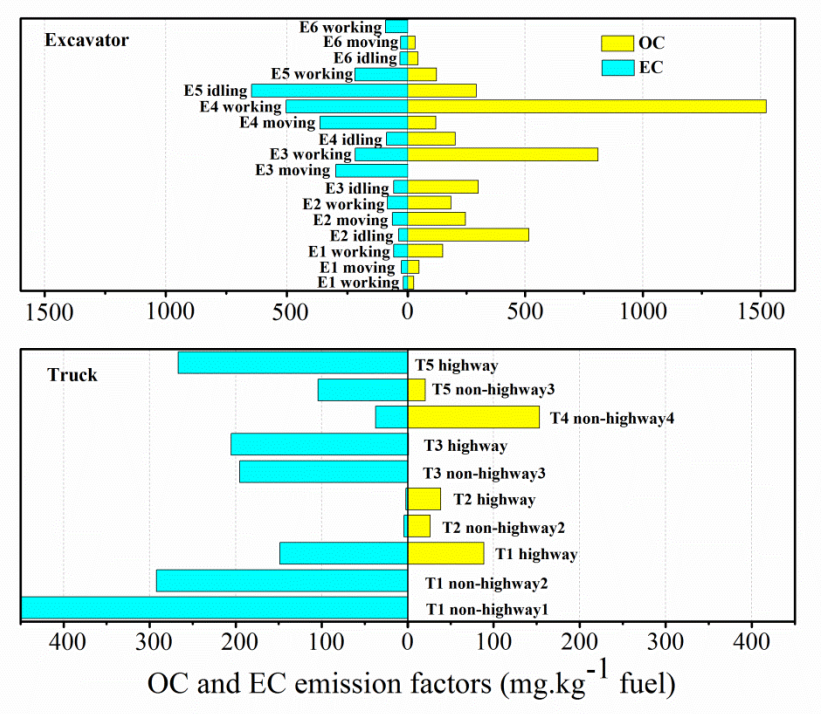

Figure 6 OC/EC ratios in different operational modes and driving conditions for excavators and trucks

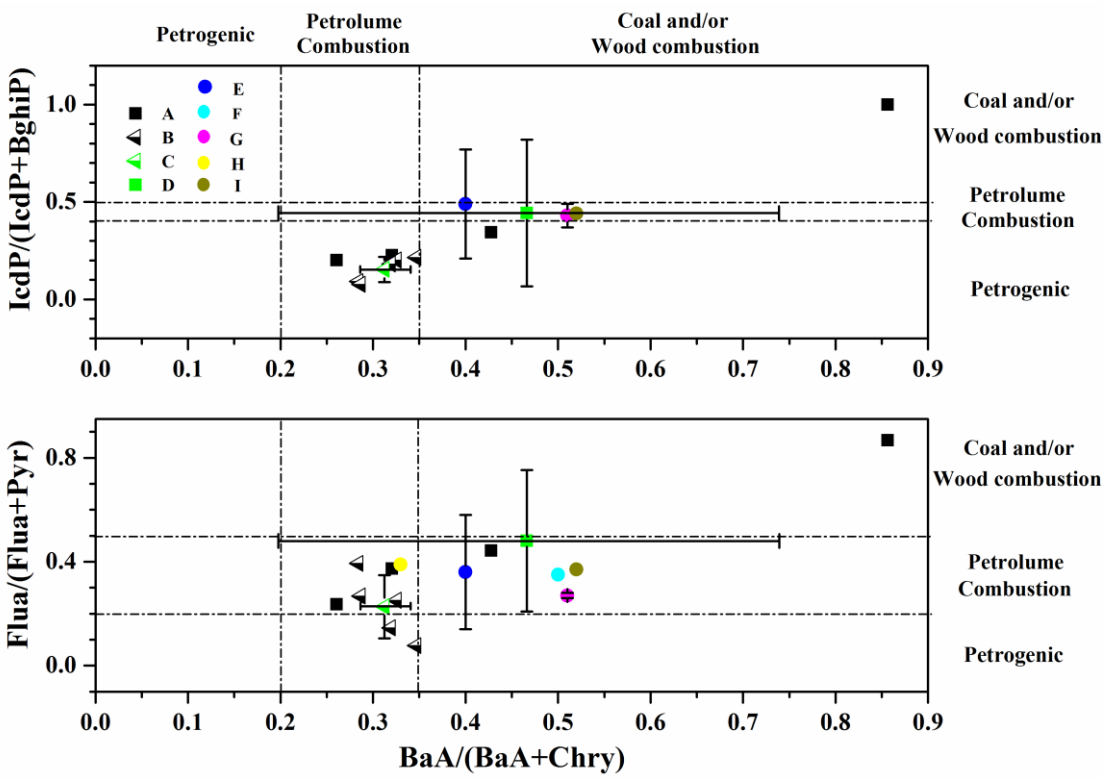

Figure 7 Cross plots for the ratios of BaA/(BaA+Chry) vs IcdP/(IcdP+BghiP) and BaA/(BaA+Chry) vs Flua/(Flua+Pry) and comparison with those from other diesel vehicle sources. A and B are the isomer ratios of the PAHs from the excavators and trucks, respectively, tested in this study; C and D are the average isomer ratios of PAHs for trucks and excavators tested in this study; E, F, G, H, I are results obtained from Liu et al. (2015), Wang et al. (2015), Shah et al. (2005), Schauer et al. (1999), Chen et al. (2013)

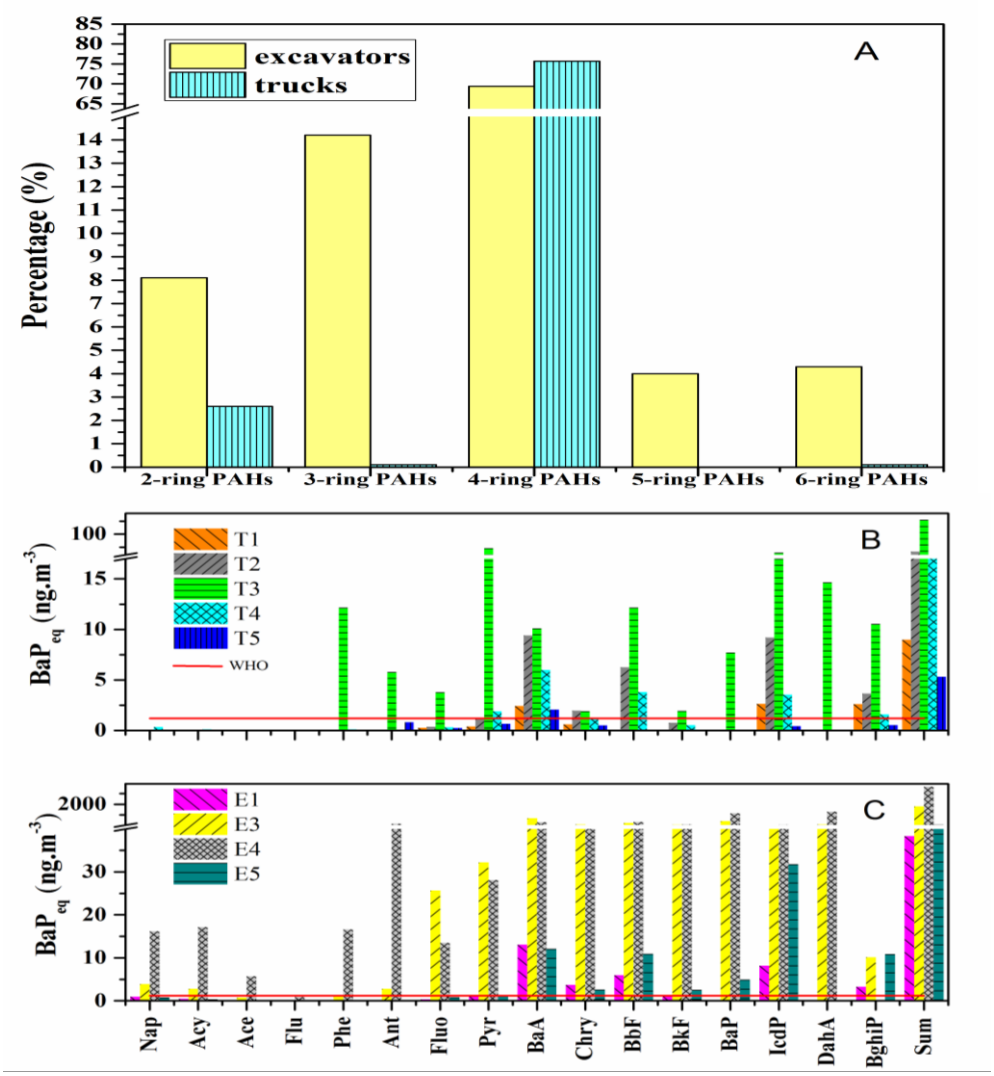

Figure 8 Percentages of each ring PAHs to total PAHs (A); BaPeq for parent PAHs in each tested trucks (b) and excavators (c)