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Primary particulate matter emissions and estimates of secondary organic aerosol formation potential from the exhaust of a China V diesel engine

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Abstract

Vehicle emissions contribute to ambient particulate matter (PM) pollution directly via emissions of PM and indirectly by secondary aerosol formation, as a result of trace gas emissions. In this paper, we determined the emission factors of primary pollutants and estimated the secondary organic aerosol (SOA) formation potential of a China V heavy-duty diesel engine tested under ETC (European Transient Cycle) and ESC (European Stationary Cycle) and different types of fuels with an engine dynamometer. Volatile organic compounds (VOCs) emission factors were 55.7~121 mg/kwh, while primary PM emission factors were 15.0~26.8 mg/kwh. These are substantially lower than older diesel vehicles that meet pre-China V standards. Based on the SOA yields of the measured VOCs, the SOA formation potential of diesel engines were estimated to be 2.8~15.9 mg/kg fuel. The ratios of potential SOA / primary PM ranged from 0.07 to

0.16. We further showed that VOCs emission factors, SOA formation potential and the ratios of SOA/ primary PM were highly dependent on test cycles, whereas the primary PM emission factors on both test cycles and fuel quality.

Keywords: Vehicle emission; Secondary organic aerosol; Diesel particulate matter; Volatile organic compounds; Driving test cycles; Fuel quality

1 Introduction

With more than 1.6 billion vehicles globally, Vehicle exhaust contributes substantially to particulate matter with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) in urban agglomerations (Chen et al., 2012, Cui et al., 2015, Gentner et al., 2017). $PM_{2.5}$ has important impacts on climate and human health by causing radiative force, respiratory and cardiopulmonary diseases (Liu et al., 2015; Lelieveld et al., 2015). Diesel vehicles contribute significantly to the particulate air pollution burden. In China, diesel vehicles contribute more than 90% of primary PM emitted from vehicles, although they only account for 9.4% of China's on-road vehicle population (MEE, 2018a).

$PM_{2.5}$ comprises a complex mixture of burned and unburned organic matter (OM) from fuel and lubrication oil, elemental carbon (EC), sulfate, nitrate, ash and others (Kittelson, 1998). Organic matter is mostly present in the form of organic aerosols. Organic aerosols consist of primary organic aerosol (POA) and secondary organic aerosol (SOA). POA is the OA emitted directly into the atmosphere; SOA is formed from gas-phase oxidation, heterogeneous reactions on aerosol surfaces, and multiphase chemistry of gas-phase organic compounds (Donahue et al., 2009; Hallquist et al.,2009).

SOA could be measured in smog chamber (Suarez-Bertoa et al., 2015) or estimated by models (Zhang et al., 2017). Many studies have been carried out to estimate the SOA formation of the Volatile organic compounds (VOCs) emitted from anthropogenic and biogenic sources (Donahue et al., 2009; Feng et al., 2019). Vehicle emission was one of the important anthropogenic sources (Gentner et al., 2012; Gordon et al., 2014a, b;

Huang et al., 2015). There are some existing models to estimate SOA formation potential, such as fractional aerosol coefficients (FAC), secondary organic aerosol potential (SOAP), and SOA yield methods (e.g. Goldstein et al., 2007; Robinson et al., 2007; de Gouw et al., 2011). The FAC method estimates SOA formation potential using reported FAC values (the ratio of the aerosol yield from a specific compound to its initial concentration) (Grosjean, 1992) and the measured VOCs concentrations (Huang et al., 2011). Wipawee et al. (2004) suggested that the main sources of anthropogenic SOA precursor emissions in the Houston area should be point sources, mobile and area sources which could be expected to be significant sources of SOA using FAC method. The SOAP represents the SOA formation propensity of an organic compound when an additional mass emission of that compound is added to the ambient atmosphere relative to the SOA formed when the same mass of toluene is added (Derwent et al., 2010). SOAPs are expressed as an index relative to toluene which is set to 100. SOA yield methods use the yield for each SOA precursor (Gentner et al., 2012) to estimate SOA formation potential. Zhang et al. (2017) concluded that, 27 VOCs were considered to calculate the SOA concentration with SOA yield method (more than FAC and SOAP methods), the assumption conditions of SOA yield method are closer to the real conditions. Recently SOA yields of IVOCs (intermediate volatile organic compounds) and SVOCs (semi volatile organic compounds) were considered important, and IVOCs could dominate the SOA production from exhaust form diesel engines (Zhao et al., 2015, Gentner et al., 2017).

Many previous studies indicated that vehicle emissions were important sources of SOA precursors, but the relative importance of each vehicle type remained controversial due to conflicting evidence. Historically, gasoline engines have been identified as the major vehicle VOCs emissions (McDonald et al., 2015; Warneke et al., 2012), but recently it has been found that the diesel contributes increasingly to overall VOCs emissions (Bishop et al., 2008; Parrish et al., 2009; Gentner et al., 2017).

China V diesel vehicle emission standards were implemented in Beijing-Tianjin-Hebei (Jing-Jin-Ji) since April 2016 and in the rest of China since Jan 2017. The stricter standard required stricter after-treatment devices, such as DPF (Diesel Particulate

Filter), DOC (Diesel Oxidative Catalyst) and SCR (Selective catalytic reduction), which could reduce primary vehicle emissions, but their influence on secondary products still remained unknown. In addition, little data is available on the impact of emission standard, fuel quality and driving cycle on primary emission and SOA formation potential from China V diesel vehicles.

In this study, a heavy-duty diesel engine meeting China V was tested under different test cycles and different types of fuels with an engine dynamometer. We first estimated primary DPM (Diesel Particulate Matter) and VOCs emission factors. Then the SOA yields of VOCs emissions under different conditions were presented to give some preliminary discussions about the effects of fuel quality and driving cycle on SOA formation potential. Finally, we calculated the ratios of SOA to primary DPM emission factors. Results of our study quantified the primary and secondary PM pollution from China V diesel emission, which could be helpful for vehicle emission and air quality control policy.

2 Materials and methods

2.1 Drive cycles

Table 1 lists four dynamometer tests with YC6L280-50 diesel engine in this study. There was only one replicate each of four different test conditions. The driving cycles used in this study were ETC (European Transient Cycle) and ESC (European Stationary Cycle). ETC include three modes, namely, urban driving, rural driving, and motorway driving. The duration of each mode was 600s. ESC is a 13-mode, steady-state procedure. The duration of each mode, Engine Speed, load and weight were determined. More details of ETC and ESC are available online (Diesel Net, 2000a, b). Due to the use of a single filter in each test, only the integrated result of all modes (ETC was 3-mode, ESC was 13-mode) was reported. Fuels used in this study were China Ⅵ and China Ⅵ added with detergent meeting the standard of GB T32859-2016(SAMR,2016). The contents of the detergent were mainly Amine-containing high molecular compounds, which were used to remove sediments and improve the efficiency of fuel atomization.

2.2 Bench Test

The test engine was mounted on a bench testing system (AVL, Graz, Austria) which could perform both stationary and transient testing for engine emission measurement. Detailed description of the testing system can be found in Jin et al. (2014). The engine was tested on an engine dynamometer. The engine model was installed on many urban buses in Tianjin, China in 2017. Table 2 lists the properties of the engine.

2.3 DPM sampling and emission factor calculation

In the engine dynamometer test, DPM was sampled with organic membrane filter at 47 ± 5°C. The diameter and porosity of membranes were 47 mm and 0.3 μm respectively. The filters were weighed before and after sampling. The measurement uncertainty of weighing was 10^{-3} mg. Before weighing, the filters were stored in a room with temperature of 25 ± 5°C and humidity of 45 ± 5% for 72 hours. The filters were dark stored in a freezer with a set temperature of -19°C before extraction. Details about sample analytical procedure were given in Jin et al. (2014).

Emission factors (EF) of DPM expressed in mg/kwh were estimated directly from the sampling line after the dilution stage. The calculation of emission factor was carried out as below (MEE, 2018b):

$$EF_{PM} = \frac{PM_{mass}}{W_{act}} \quad (1)$$

$$PM_{\mathrm{mass}} = \frac{M_f}{M_{SAM}} \times \frac{M_{TOTW}}{1000} \quad (2)$$

Where EF_{PM} is the emission factor of PM in mg/kwh, PM_{mass} is the total PM mass of each test in mg, W_{act} is the real power of engine in kwh, M_f is the total PM mass on the filter in each test in mg, M_{TOTW} is the total mass of diluting gas in each test in kg, M_{SAM} is the mass of diluting gas passing the filter in kg.

The emission factor of PM in mg/kg or mg/km was obtained on basis of fuel consumption or travel distance instead of real power of engine.

2.4 VOC Sampling and Analysis

VOCs samples emitted from each test were collected after being diluted by 3.2 L stainless steel SUMMA canisters (Entech Instruments Inc., USA) with a Teflon connector. The samples collected in the Summa canisters were analyzed in a GC/MS (7890A Gas Chromatograph System, 5975C VL Mass Spectrometer Detector, 7683B

Series Injector, Agilent Technologies), the detection limit, quantitative limit and measured ranges of which were 6 ppb, 10 ppb and from 10 to 20000ppb, respectively. Alkane, alkene and aromatic samples were pre-concentrated, and CO_2, H_2O, O_2, N_2 and other interferents in the samples were removed by a triple module in a pre-concentration system (Entech Model 7100) before the samples were injected into the GC/MS. The carrier gas was helium. These canisters were cleaned in the laboratory following USEPA method TO-14 through repeated evacuation and pressurization with high purity nitrogen before sampling (USEPA, 1997).

In this study, quantitative detected VOCs were show in Table 3. Emission factor of total VOCs was also calculated using the followed equation:

$$EF_{VOC} = \frac{V\rho}{10^3 D_f W} \quad (3)$$

where EF_{VOC} is the emission factor of VOCs, in mg/kwh; V is the volume of stainless-steel SUMMA canisters which equals 3.2 L in this study; ρ is the concentration of VOCs samples in the SUMMA canisters, in μg/m^3; Df is the dilution factor and varied for each sampling; W is the total power, in kwh.

2.5. Quality assurance (QA)/quality control (QC)

The QA/QC protocol of the monitoring sequence was followed at all stages from sample preparation to chemical analysis. Blank field filters were placed unopened next to the samplers for the duration of sampling, after which they were returned to the laboratory and treated as regular samples to ensure there was no significant back-ground interference. A blank sample was run for each chemical analysis. Results showed that all analyte concentrations in the blank organic membrane filters were less than the method detection limits (MDL). All the fittings and tubing used by VOC sampling were made of either stainless steel or polytetrafluoroethylene (PTFE) to provide an inert sampling environment. Zero-air supply was used to dilute the exhaust gas and was collected separately as field blank. No VOC was detected in the field blank.

2.6 SOA Formation Potential Estimation

The SOA formation potential emitted from the diesel engines is calculated based on the SOA yields of the measured VOCs. We did not measure IVOCs and SVOCs and

thus the SOA estimation which represented the contribution was only from VOCs. Measured VOCs are apportioned into five categories: aromatics, cycloalkanes, branched alkanes, straight-chain alkanes, and alkenes. The SOA formation potential of each category (P_{SOA}, g/kg fuel) is calculated by the following equations (Zhang et al., 2017):

$$\mathrm{SOAj} = \sum\left(Y_{i,j} \times VOC_{i,j}\right) \quad (4)$$

$$P_{SOA} = \frac{\sum SOAj}{M_{fuel}} \quad (5)$$

where j represents different categories of VOCs, *i* represents the number of carbons in category *j*, SOA_j is the mass of SOA formed by VOCs of category *j* (g). $Y_{i,j}$ is the yield of species *i* in category j (unitless), $VOC_{i,j}$ is the mass of SOA precursors of species *i* in category j (g). Identified non-SOA precursors were excluded from total VOC emissions. M_{fuel} is the mass of fuel consumed in one test in kg, P_{SOA} is the SOA formation potential in one test in g/kg fuel.

The yields for each SOA precursor were referenced from Gentner et al. (2012), which listed the high-NOx SOA yields of known compounds using a combination of measured SOA yields derived from laboratory-chamber experiments and approximate SOA yields based on box modeling. For all compounds, high-NOx SOA yields were modeled assuming an average organic particle concentration of 10 μg/m^3, which was used in chamber studies, urban areas and downwind urban areas (Gentner et al., 2012; Chan et al., 2009; Zhang et al., 2007). In addition, the SOA yields of straight alkanes increased by an average 16% in the range of 6-12 carbon atoms, C6–12 aromatics increased by 19 % (Huang et al., 2015). Table 3 lists SOA yields in this study.

3 RESULTS AND DISCUSSION

3.1 Total and speciated VOCs emission factors

Figure 1 shows VOCs emission factors (mg/kg fuel) from diesel engines in this study. Emission factor under ESC ranged from 108 to 115 mg/kg (or from 55.7 to 59.7 mg/kwh), which were significantly (p=0.044) lower than those under ETC (399 and 559 mg/kg or 87.7 and 121 mg/kwh). The results indicated that test cycles had a major

impact on the VOCs emission factors.

Figure 2 compares VOCs emission factors determined in this study with published data. Our results (37.2~87.9 mg/km) were higher than those from a Euro V engine (16.4~26.3 mg/km) reported by Lopes et al. (2014) but lower than those from China Ⅱ (120~456 mg/km) and China Ⅲ (60~116 mg/km) by Yao et al. (2015a, b) and Pre-Euro to Euro Ⅳ (191 to 1912mg/km) by Huang et al. (2015). This suggests that stricter emission regulation significantly reduced VOCs emissions.

Propene and benzene were the two most abundant species of VOCs emitted from the test engine, accounting for 39% and 13% of the total measured VOCs, respectively. Wang et al. (2013) reported that ethylene (12%) was the most abundant VOCs followed by toluene (11%) and benzene (8.8%) from light duty gasoline vehicles meeting China Ⅲ during ECE/EUDC test.

Figure 3 compares the composition of major categories of VOCs (including alkanes, alkenes, alkynes and aromatics) in this study and those from other studies. High proportions of alkenes were measured in the exhausts from test 1 and 3 (51% and 52%), which were higher than those in other studies. The VOC compositions of T2 and T4 were similar to those by Huang et al. (2015).

3.2 Primary PM emission factors

Figure 1 also shows primary PM emission factors (mg/kg fuel) from the diesel engine in this study. Emission factor under ESC ranged from 36.7 to 51.6 mg/kg (or from 19 to 26.8 mg/kwh), while those under ETC condition were 69.2and 110 mg/kg (or 15 and 24.2 mg/kwh). There were some low-speed modes including idle in ESC, and so the fuel consumption per kwh under ESC is higher than that under ETC. The results also indicated that PM emission factors were dependent on both driving test cycles and fuel quality.

Table 4 reports dynamometer results of China Ⅴ diesel engine in this study and other studies (in some studies, the primary PM emission factors were estimated as the sum of BC and POA emission factors). Our results were close to those of Guo et al. (2013), in which China Ⅴ engine was used, but were slightly higher than those of

Georgios et al. (2012), where Euro Ⅴ engine was used. On the other hand, our results were lower than those of Gordon et al.(2014b), Chirico et al. (2010), Deng et al. (2017), Huang et al. (2016) and He et al. (2015). These results suggest that the PM emission factors of China V diesel engines in China become much lower.

3.3 SOA formation potential

Figure 1 also shows the SOA formation potential in 4 tests in this study. SOA formation potential under ESC ranged from 2.8 to 3.6 mg/kg fuel (or from 1.4 to 1.9 mg/kwh), which were significantly ($p=0.062$) lower than those under ETC condition (10.7 and 15.9 mg/kg or 2.3 and 3.5 mg/kwh). Due to the uncertainties of SOA yields, there may be a large difference (even as much as twice) in the SOA formation potential.

In addition, the ratio of SOA formation potential of VOCs to primary PM emissions were estimated. The ratios under ESC ranged from 0.07 to 0.08, which were significantly lower than those under the ETC condition (0.15 and 0.16). The results indicated that test cycles had a major impact on the SOA formation potential whereas fuel quality had little impact.

Benzene, p-Ethyltoluene and methylbenzene were major precursor species, accounting for 76%, 9.9% and 6.4% of the potential SOA, respectively. This is mainly due to the very high yield of Benzene (Table 3), while the yield of propene was zero. IVOCs were not measured in our study. Thus, the total SOA potential may be significantly higher, potentially by an order of magnitude (Zhao et al., 2015; Huang et al., 2018).

Figure 4 shows the comparison of our results and those from other studies. The results of all other studies were measured in smog chambers, which were about a magnitude higher than our results. Considering the absence of IVOCs and SVOCs measurement in our study, our results are consistent with literature.

4 CONCLUSIONS

In this paper, a heavy-duty diesel engine was tested under different test cycles and different types of fuels to estimate VOCs, PM emission factors and SOA formation potential with an engine dynamometer.

VOCs emission factors were 55.7~121 mg/kwh, while primary PM emission factors were 15~26.8 mg/kwh. As the engine emission standards were tightened in China, the VOC and primary PM emission factors of diesel engines were reduced. Based on the SOA yields of the measured VOCs, the SOA formation potential of diesel engines were estimated and the results were 2.8~15.9 mg/kg fuel. Benzene, p-Ethyltoluene and methylbenzene were major precursor species, accounting for 76%, 9.9% and 6.4% of the potential SOA, respectively. The ratios of SOA/ Primary PM ranged from 0.07 to 0.16. Due to the absence of IVOCs measurement, the real SOA formation potential and ratios of SOA/ Primary PM could be enlarged by about an order of magnitude based on what others have observed for other diesel sources. The differences of VOCs emission factors, SOA formation potential and ratios of SOA/ Primary PM were more affected by test cycle, while the differences of primary PM emission factors were affected by both test cycle and fuel quality.

Results of our study shed light on the VOCs, primary PM and SOA formation potential of diesel engines meeting China V emission standard, which were rarely reported by other researchers. However, there are some uncertainties in these estimations. More investigations are needed to validate the results observed in this study. Future studies can pay more attention to some neglected components, such as IVOCs and SVOCs.

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REFERENCES

Bishop, G. A., Stedman, D. H. 2008. A Decade of On-road Emissions Measurements. Environ. Sci. Technol. 42 (5), 1651−1656.

Chan A.W.H., Kautzman K.E., P. S. Chhabra P. S., Surratt J. D., Chan M. N., Crounse J. D., Kürten A. Wennberg P. O., Flagan R. C., Seinfeld J. H. 2009. Secondary organic aerosol formation from photooxidation of naphthalene

and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs). Atmos. Chem. Phys. 9:3049-3060.

Chen Y J, Zheng M, Edgerton E S, Ke L, Sheng G Y, Fu J M. 2012. PM2.5 source apportionment in the southeastern U.S.: spatial and seasonal variations during 2001-2005. J. Geophys. Res. Atmos. 117, D08304.

Chirico, R., DeCarlo, P. F., Heringa, M. F., Tritscher, T., Richter, R., Prévôt, A. S. H., Dommen, J., Weingartner, E., Wehrle, G., Gysel, M., Laborde, M., and Baltensperger, U. 2010. Impact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments. Atmos. Chem. Phys. 10, 11545-11563.

Cui H, Chen W, Dai W, Liu H, Wang X, He K. 2015. Source apportionment of PM2.5 in Guangzhou combining observation data analysis and chemical transport model simulation. Atmos Environ. 116, 262–271.

Goldstein, A.H.; Galbally, I.E. 2007. Known and unexplored organic constituents in the Earth's atmosphere. Environ. Sci. Technol. 41, 1514-1521.

de Gouw, J.A., Middlebrook, A.M., Warneke, C., Ahmadov, R., Atlas, E.L., Bahreini, R., Blake, D.R., Brock, C.A., Brioude, J., Fahey, D.W., Fehsenfeld, F.C., Holloway, J.S., Le Henaff, M., Lueb, R.A., McKeen, S.A., Meagher, J.F. 2011. Organic aerosol formation downwind from the Deepwater Horizon oil spill. Science. 331, 1295-1299.

Deng W, Hu Q H, Liu T Y, Wang X M, Zhang Y L, Song W, Sun W L, Bi X H, Yu J Z, Yang W G, Huang X Y, Zhang Z, Huang Z H, He Q F, Mellouki A, George C. 2017. Primary particulate emissions and secondary organic aerosol (SOA) formation from idling diesel vehicle exhaust in China. Sci. Total Environ. 593-594, 462-469.

Derwent, R. G., Jenkin, M. E., Utembe, S. R., Shallcross, D. E., Murrells, T. P., Passant, N. R. 2010. Secondary organic aerosol formation from a large number of reactive man-made organic compounds. Sci. Total Environ. 408, 3374-3381.

Diesel Net. 2000a. Emission test cycle: European stationary cycle. (ESC). https://www.dieselnet.com/standards/cycles/esc.php.

Diesel Net. 2000b. Emission test cycle: European transient cycle. (ETC). https://www.dieselnet.com/standards/cycles/etc.php.

Donahue, N.M., Robinson, A.L., Pandis, S.N., 2009. Atmospheric organic particulate matter: From smoke to secondary organic aerosol. Atmos Environ. 43, 94–106.

Feng T., Zhao S. Y., Bei N. F., Wu J. R., Liu S. X., Li X., Liu L., Qian Y., Yang Q. C., Wang Y. C., Zhou W. J., Cao J. J., Li G. H. 2019. Secondary organic aerosol enhanced by increasing atmospheric oxidizing capacity in Beijing–Tianjin–Hebei (BTH), China. Atmos. Chem. Phys. 19, 7429-7443.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu S, Day D A, Russell L M, Wilson K R, Weber R, Guha A, Harley R A, Goldstein A H. 2012. Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions. Proc. Natl. Acad. Sci. 109, 18318-18323.

Gentner, D. R., Jathar S H, Gordon T D, Bahreini, R, Day D A, El Haddad I, Hayes P L, Pieber S M, Platt S M, de Gouw J, Goldstein A H, Harley R A, Jimenez J L, Prevot A S H, Robinson A L. 2017. Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions. Environ. Sci. Technol. 51: 1074−1093.

Georgios F, Giorgio M, Urbano M, Alessandro M, Alois K, Francesco M, Roberto T, Mauro C. 2012. Assessment of on-road emissions of four Euro V diesel and CNG waste collection trucks for supporting air-quality improvement initiatives in the city of Milan. Sci. Total Environ. 426, 65-72.

Gordon, T. D., Presto, A. A., May, A. A., Nguyen, N. T., Lipsky, E. M., Donahue, N. M., Gutierrez, A., Zhang, M.; Maddox, C., Rieger, P., Chattopadhyay, S., Maldonado, H.; Maricq, M. M., Robinson, A. L. 2014a. Secondary organic aerosol formation exceeds primary particulate matter emissions for light-duty gasoline vehicles. Atmos.

Chem. Phys. 14 (9), 4661-4678.
Gordon, T. D.; Presto, A. A.; Nguyen, N. T.; Robertson, W. H.; Na, K.; Sahay, K. N.; Zhang, M.; Maddox, C.; Rieger, P.; Chattopadhyay, S.; Maldonado, H.; Maricq, M. M.; Robinson, A. L. 2014b. Secondary organic aerosol production from diesel vehicle exhaust: impact of aftertreatment, fuel chemistry and driving cycle. Atmos. Chem. Phys. 14 (9), 4643-4659.
Grosjean, D. 1992. In situ organic aerosol formation during a smog episode: Estimated production and chemical functionality. Atmos. Environ. Part A 26, 953-963.
Guo H S，Shi Y W，Lu H Y, Fu T Q, Cao L, Li J Y. 2013. Study of the Effects of Diesel Fuel Quality on SOF and PAHs of Particle Matter for Chinese V Heavy-Duty Diesel Engine. Small Internal Combustion Engine and Motorcycle. 42(1), 70-74 (in Chinese).
Hallquist M, Wenger J C, Baltensperger U, Rudich Y, Simpson D, Claeys M, Dommen J, Donahue N M, George C, Goldstein A H, Hamilton J F, Herrmann H, Hoffmann T, Iinuma Y, Jang M, Jenkin M E, Jimenez J L, Kiendler-Scharr A, Maenhdut W, McFiggans G, Mentel T F, Monod A, Prevot A S H, Seinfeld J H, Surratt J D, Szmigielski R, Wildt J. 2009. The formation, properties and impact of secondary organic aerosol: Current and emerging issues. Atmos. Chem Phys. 9 (14), 5155-5236.
He L Q，Hu J N，Zu L, Song J H, Chen D. 2015.Emission characteristics of exhaust PM2.5 and its carbonaceous components from China Ⅰ to China Ⅲ heavy-duty diesel vehicles. Acta Scientiae Circumstantiae. 35(3), 656-662 (in Chinese).
Huang, C., Wang, H. L., Li, L., Wang, Q., Lu, Q., Gouw, J. A. de, Zhou, M., Jing, S. A., Lu, J., Chen, C. H. 2015. VOC species and emission inventory from vehicles and their SOA formation potentials estimation in Shanghai, China, Atmos. Chem. Phys. 15, 11081-11096.
Huang, C., Hu, Q.Y., Li, Y.J., Tian, J.J., Ma, Y.G., Zhao, Y.L., Feng, J.L., An, J.Y., Qiao, L.P., Wang, H. L., Jing, S. A., Huang, D.D., Lu, S.R., Zhou, M., Zhu, S.H., Tao, S.K., Li, L., 2018. Intermediate volatility organic compound emissions from a large cargo vessel operated under real-world conditions. Environ. Sci. Technol. 52: 12934−12942.
Huang, X.H.H., Ip, H.S.S., Yu, J.Z. 2011. Secondary organic aerosol formation fromethylene in the urban atmosphere of Hong Kong: a multiphase chemical modeling study. J. Geophys. Res. Atmos. 116, D03206, doi:10.1029/2010JD014121
Huang Z，Li X L，Lv T, Xu Z, Guan C, Luo Y. 2016. Effect of Fuel Properties on Physicochemical Characteristics of Diesel Engine Exhaust PM. Transactions of CSICE. 34(2), 97-104 (in Chinese).
Jin, T., Qu, L., Liu, S., Gao, J., Wang, J., Wang, F., Zhang, P., Bai, Z., Xu, X. 2014. Chemical characteristics of particulate matter emitted from a heavy duty diesel engine and correlation among inorganic and PAH components. Fuel. 116, 655-661.
Kittelson D B. 1998. Engines and nanoparticles: a review. Aerosol Sci. 29, 575-588.
Lelieveld J, Evans J S, Fnais M, Giannadaki D, Pozzer A. 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature. 525, 367-371.
Liu Z, Guan D, Wei W, Davis S J, Ciais P, Bai J, Peng S, Zhang Q, Hubacek K, Marland G, Andres R J, Crawford-Brown D, Lin J, Zhao H, Hong C, Boden T A, Feng K, Peters G P, Xi F, Liu J, Li Y, Zhao Y, Zeng N, He K. 2015. Reduced carbon emission estimates from fossil fuel combustion and cement production in China. Nature. 524, 335-338.
Lopes M, Serrano L, Ribeiro I, Cascao P, Pires N, Rafael S, Tarelho L, Monteiro A, Nunes T, Evtyugina M, Nielsen O J, da Silva M G, Miranda A I, Borrego C. 2014. Emissions characterization from EURO 5 diesel/biodiesel passenger car operating under the new European driving cycle. Atmos. Environ. 84, 339-348.
May, A.A., Nguyen, N.T., Presto, A.A., Gordon, T.D., Lipsky, E.M., Karve, M., Gutierrez, A., Robertson, W.H., Zhang, M., Brandow, C., Chang, O., Chen, S., Cicero-Fernandez, P., Dinkins, L., Fuentes, M., Huang, S.-M., Ling,

R., Long, J., Maddox, C., Massetti, J., McCauley, E., Miguel, A., Na, K., Ong, R., Pang, Y., Rieger, P., Sax, T., Truong, T., Vo, T., Chattopadhyay, S., Maldonado, H., Maricq, M.M., Robinson, A.L., 2014. Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. Atmos. Environ. 88, 247-260.

McDonald, B. C.; Goldstein, A. H.; Harley, R. A. 2015. Long-term trends in California mobile source emissions and ambient concen- trations of black carbon and organic aerosol. Environ. Sci. Technol. 49 (8), 5178−5188.

Ministry of Ecology and Environment of the People's Republic of China (MEE), 2018a. China vehicle environmental management annual report. Beijing, China. http://dqhj.mee.gov.cn/jdchjgl/zhgldt/201806/P020180604354753261746.pdf. (in Chinese)

Ministry of Ecology and Environment of the People's Republic of China (MEE), 2018b. Limits and measurement methods for emissions from diesel fueled heavy-duty vehicles (CHINA Ⅵ) (GB 17691-2018). Beijing, China http://kjs.mee.gov.cn/hjbhbz/bzwb/dqhjbh/dqydywrwpfbz/201807/W020180703397013304274.pdf (in Chinese).

Parrish, D. D.; Kuster, W. C.; Shao, M.; Yokouchi, Y.; Kondo, Y.; Goldan, P. D.; de Gouw, J. A.; Koike, M.; Shirai, T. 2009. Comparison of air pollutant emissions among mega-cities. Atmos. Environ. 43 (40), 6435−6441.

Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R., Pandis, S.N. 2007. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. Science. 315, 1259-1262.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks. Environ. Sci. Technol. 33, 1578-1587.

State Administration for Market Regulation of the People's Republic of China (SAMR), 2016. Detergent additive for diesel fuel (GB/T 32859-2016). Beijing, China (in Chinese).

Suartz-Bertoa, R., Zardini, A.A., Platt, S.M., Hellebust, S., Pieber, S.M., Haddad, I.E., Temime-Roussel, B., Baltensperger, U., Marchand, N., Prevot, A.S.H., Astorga, C., 2015. Primary emissions and secondary organic aerosol formation from the exhaust of a flex-fuel (ethanol) vehicle. Atmos. Environ. 117: 200-211.

United States Environmental Protection Agency (USEPA), 1997. Compendium Method TO-14A: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography. Report No. EPA/625/R-96/010b.

Wang, J., Jin, L.M., Gao J.H., Shi J.W., Zhao, Y.L., Liu, S.X., Jin, T.S., Bai, Z.P., Wu. C.Y., 2013. Investigation of speciated VOC in gasoline vehicular exhaust under ECE and EUDC test cycles. Sci. Total Environ. 445-446,110-116.

Warneke, C.; de Gouw, J. A.; Holloway, J. S.; Peischl, J.; Ryerson, T. B.; Atlas, E.; Blake, D.; Trainer, M.; Parrish, D. D. 2012. Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions. J. Geophys. Res. Atmos. 117, D00V17, doi:10.1029/2012JD017899.

Wipawee D, Matthew R, David T A. 2004. Estimates of Anthropogenic Secondary Organic Aerosol Formation in Houston, Texas. Special Issue of Aerosol Science and Technology on Findings from the Fine Particulate Matter Supersites Program. Aeros. Sci. Technol.38, S1, 156-166.

Yao Z L, Wu B B, Shen X B, Cao X Y, Jiang X, Ye Y, He K B. 2015a. On-road emission characteristics of VOCs from rural vehicles and their ozone formation potential in Beijing, China. Atmos. Environ. 105: 91-96.

Yao Z L, Shen X B, Ye Y, Cao X Y, Jiang X, Zhang Y Z, He K B. 2015b. On-road emission characteristics of VOCs from diesel trucks in Beijing, China. Atmos. Environ. 103, 87-93.

Zhang Q, Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun,

J. Y., Zhang, Y. M., Worsnop, D. R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. Geophys. Res. Lett. 34: L13801

Zhang, Z. J., Wang, H., Chen, D., Li, Q. Q., Thai, P., Gong, D. C., Li, Y., Zhang, C., Gu, Y. G., Zhou, L., Morawska, L, Wang, B. G. 2017. Emission characteristics of volatile organic compounds and their secondary organic aerosol formation potentials from a petroleum refinery in Pearl River Delta, China. Sci. Total Environ. 584-585.

Zhao, Y.L., Nguyen, N.T., Presto, A.A., Hennigan C.J., May, A.A., Robinson A.L., 2015. Intermediate volatility organic compound emissions from on-road diesel vehicles: chemical composition, emission factors, and estimated secondary organic aerosol production. Environ. Sci. Technol. 49: 11516−11526.

Table 1 Design of four dynamometer tests

Test	Drive cycle	Aftertreatment	Fuel
T1	ESC	SCR	China Ⅵ[a]
T2	ESC	SCR	China Ⅵ
T3	ETC	SCR	China Ⅵ[a]
T4	ETC	SCR	China Ⅵ

a. Added with detergent.

Table 2 Properties of the diesel engines

Item	YC6L280-50
Structure	Turbocharged 6 cylinder in line
Displacement(L)	8.424
Maximum power(kW)	206
Maximum torque (Nm)	1100
Minimum fuel consumption at full load(g/kWh)	≤198
Emission regulation	China Ⅴ

Table 4 Emission factors of primary PM from diesel engine in our and other studies.

Reference	Emission regulation	Primary PM emission factors	
		mg /kg fuel	mg/kwh
This study	China Ⅴ	36.7~110	15.0~26.8
Georgios et al. (2012)	Euro V		3.5~12.7
Guo et al. (2013)	China Ⅴ		15.5~28.5
Gordon et al.(2014b)	Tier 2	578~1134	
Chirico et al. (2010)	Euro Ⅲ	573~906	
Deng et al. (2017)	Euro Ⅲ	354~1286	
Huang et al. (2016)	China III		32.3~92.7
He et al. (2015)	China Ⅰ	1588~3980	
	China Ⅱ	521~853	
	China Ⅲ	188~633	

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464 **Table 3**. **Measured VOCs and their SOA yields in this study**

VOCs	Category	Carbon Number	SOA yields
Acetone	ketone	3	
Dichloromethane	Haloalkane	1	
propene	Alkene	3	
Butane	Straight-chain Alkanes	4	
Hexane		6	
N-heptane		7	
n-Octane		8	0.000696
n-Nonane		9	0.001392
Decane		10	0.003016
Undecane		11	0.006148
Dodecane		12	0.0116
Isobutane	Branched Alkanes	4	
2-methylbutane		5	
2,3-dimethylpentane		7	
3-methylhexane		7	
Cyclopentane	Cycloalkanes	5	
Cyclohexane		6	0.0004±0.0003
Methylcyclopentane		6	
Methylcyclohexane		7	0.0007±0.0006
2-methylheptane		8	0.0015±0.0011
benzene	Aromatics	6	0.167
Toluene		7	0.099
Ethylbenzene		8	
M-xylene		8	0.057
Styrene		8	
P-ethyltoluene		9	0.092±0.068
M-ethyltoluene		9	

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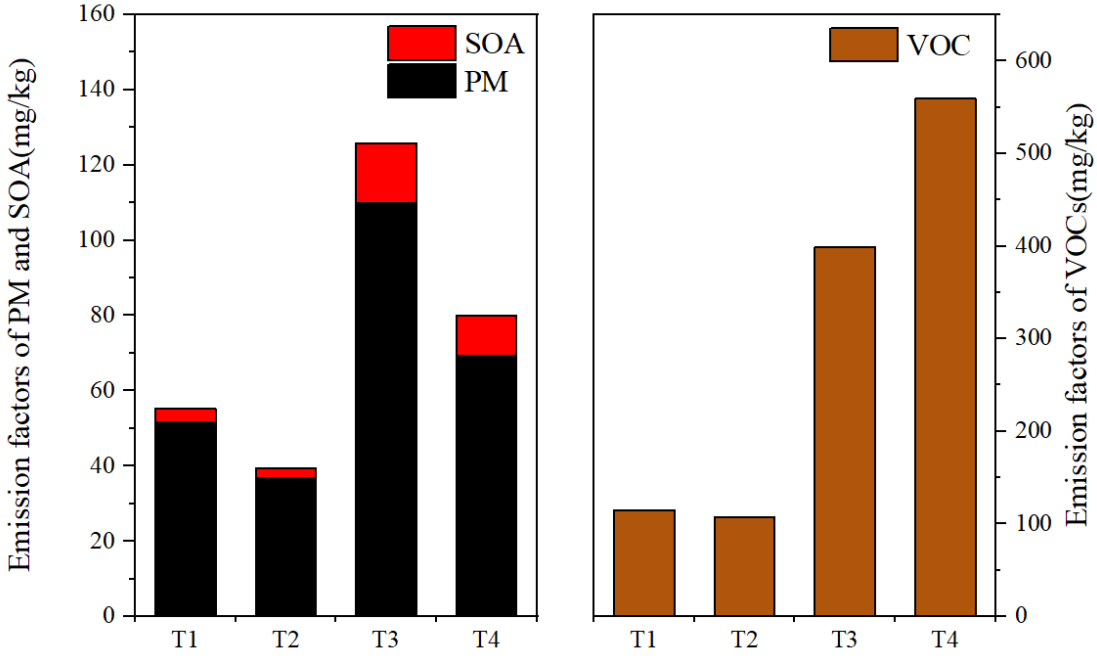


Figure 1. Emission factors of potential SOA, primary PM and VOC

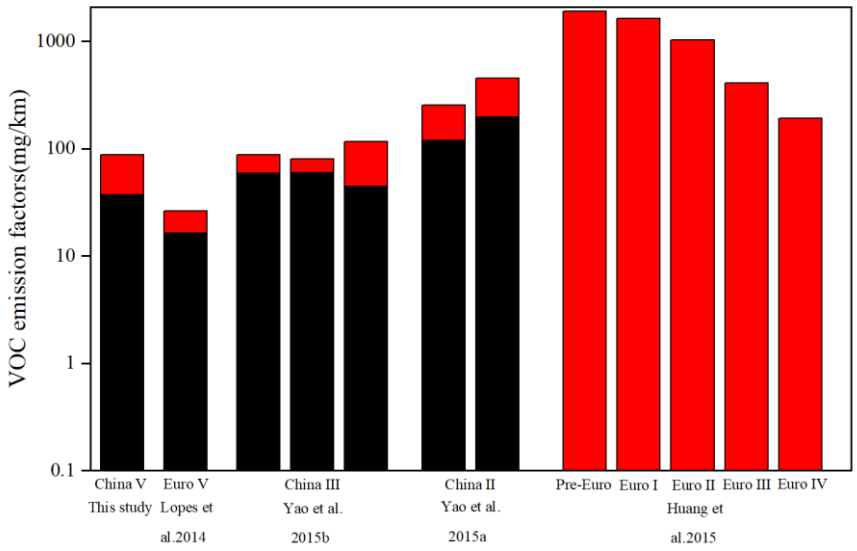
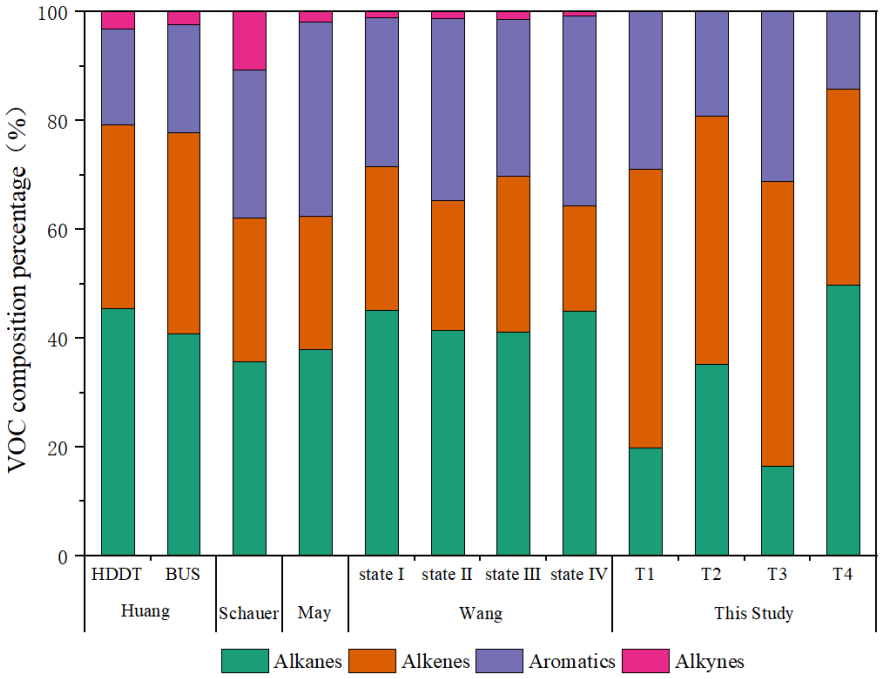


Figure 2. VOC emission factors from diesel engines in our study and other studies



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476 **Figure 3. VOC composition for each test comparing to other studies**

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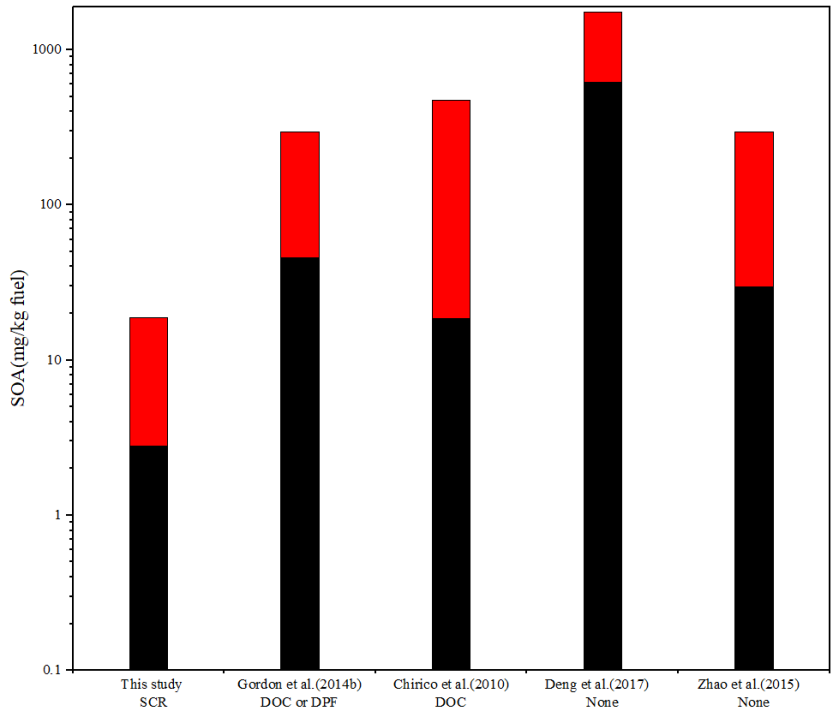

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479 **Figure 4. SOA from diesel engines in our study and other studies**

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