

Anonymous Referee #1

Q: There is no mention at all in the paper as to how (or indeed if) the exhaust was diluted with clean air in the chamber, other than the sentence “Depending on the organic aerosol concentration and particle numbers reached inside the reactor as sensed by the affiliated instruments, the exhaust injection time ranged from 5 to 20 min”. From this, I understand that the exhaust was injected into the chamber, until the concentrations reached levels that you thought appropriate. Please clarify how the injection time was decided.

Reply: The exhaust was first diluted by ejector dilutor (DI-1000, Dekati Ltd., Finland), then introduced into the chamber which was pre-filled with purified air. We decided the injection time by the particle mass in the chamber measured by SMPS. When the particle mass reached about $50 \mu\text{g m}^{-3}$, which is comparable to the annual mean value of $\text{PM}_{2.5}$ in Guangzhou (Guangzhou Environmental Protection Bureau, 2014), we stopped injecting the exhaust. (Lines 140-147 in the revised manuscript).

Q: Please also quote the final dilution ratios, as without these, the numbers given in section 2.4 and table 2, and any comparison between experiments, are meaningless.

Reply: We have added the dilution ratios in the revised Table 2.

Q: Do the emission and production factor calculations in sections 2.5 and 3.1 account for dilution? Is the dilution ratio representative of the dilution of diesel exhaust in an urban environment?

Reply: As the CO_2 concentrations used to calculate emission and production factors in equation (1) were background-subtracted, therefore the emission and production factors have taken dilution into account.

As shown in Table 2, the dilution ratios ranged from 66-215, which were lower than the dilution of exhaust in an urban environment ($\sim 1000:1$ as reported by Zhang et al., 2004). But due to detection limits of instruments, reactants in chamber study are usually higher than those in real-world conditions (Odum et al., 1997; Surratt et al., 2007; Hildebrandt et al., 2009). The dilution ratios were comparable with previous diesel exhaust studies (Chirico et al., 2010; Gordon et al., 2014b).

Q: Line 145: “Propene was added to adjust the VOC/NO_x ratios to approximately 3:1 ppbC:ppb”. What concentration of propene was added? Also, I understand that the ratio 3:1 is considered typical of urban environments, but please say so and include references.

Reply: The concentrations of introduced propene were added to Table 1. The VOC/NO_x ratios of approximately 3:1 ppbC:ppb is considered as an typical ratio for urban environments (Guo et al., 2013). We have added the reference in the revised manuscript.

Q: Lines 230-232: This needs to be explained better – what is w?

Reply: ω is a proportionality factor of organic vapor partition to chamber walls and suspended particles. We have explained it in the revised manuscript.

Q: Section 3.1: Here you state “The relatively backward diesel engine technology and lack of

emission aftertreatment devices like diesel oxidation catalyst (DOC) or diesel particulate filter (DPF) would probably be the reasons for higher EFs of POA for China's diesel vehicles in this study", however the EF(POA) reported by the Chirico and Gordon studies were measured without after-treatment (you are aware of this as you state this in the caption of figure 1), so this could not be the reason. Also why do the other studies see higher EF(BC)? In the EF calculation, you assume the same carbon intensity of fuel as Chirico et al. Could this be different?

Reply: Yes, the lack of emission aftertreatment devices could not be the reason for the difference of EFs(POA) between this study and previous studies. As the diesel fuel used in this study is at Euro III standard, in which the sulfur content is approximately 350ppm (Zhang et al., 2010; Yue et al., 2015), which is much more higher than that in previous studies (Euro V). However, the fuel sulfur content can affect the particle emission for diesel vehicle (Rönkkö et al., 2007). Therefore, the difference in engine technology and fuel quality could be the reason of higher emission factors of POA.

When at idling condition for the vehicle without aftertreatment, the EF(BC) of Changan were 0.47-0.51 g kg-fuel⁻¹, which were similar to Chirico et al. (2010) (0.466-0.763 g kg-fuel⁻¹), the EF(BC) of Foton and JAC (0.15-0.19 g kg-fuel⁻¹) were comparable to Gordon et al. (2014b) (~0.260 g kg-fuel⁻¹). Moreover, Zheng et al. (2015) reported EF(BC) for Euro III HDDV as 612 ± 740 mg kg-fuel⁻¹. The EF(BC) could be varied vehicle by vehicle. Generally, we can conclude that EF(BC) in this paper was comparable to the results from previous studies.

The carbon intensity is the mass fraction of carbon in the diesel fuel; it is related to the chemical composition of diesel. As the diesel is mainly comprised of C₁₀-C₂₂ alkane, alkene, aromatics and PAHs, we can calculate the carbon intensity of alkane (0.848 ± 0.003), alkene (0.857), aromatic (0.885 ± 0.011) and PAH (0.943 ± 0.005). Applied the diesel composition in China reported by Yue et al. (2015) (alkene, 20.5%; aromatic, 29.6%; PAH, 8.8%; remained fraction were treated as alkane, 41.1%), the calculated carbon intensity is 0.869, near to the value of fuel as Chirico et al. and this study.

Q: Line 279: Can the authors speculate as to why the difference here? Higher POA?

Reply: As the experiments conditions (VOC/NO_x ratios, OH concentrations) were similar to previous studies, and the photochemistry was also the same according to the manuscript, therefore, the reason of difference could be the higher POA.

In addition, the O:C ratios of POA in this study (0.3-0.5) were higher than previous study (~0.2) (Chirico et al., 2010). As the volatility of organics and O:C are generally inversely correlated (Lanz et al., 2007; Jimenez et al., 2009; Ulbrich et al., 2009), this demonstrated that less organics would partition to gas phase and more organics would partition to particle phase (i.e., POA) during the introduction and dilution of exhaust (Donahue et al., 2006). Moreover, the reaction rate constant in gas phase is higher than that in particle phase (Esteve et al., 2006; Bedjanian et al., 2010). Therefore, the difference in the compositions of primarily emitted organics could be the reason.

Q: Lines 286-290: Have I understood this correctly: there are far more gasoline vehicles than diesel vehicles in China, yet more diesel is consumed for transportation than gasoline?

Reply: Yes. There are far more gasoline vehicles than diesel vehicles in China. While the

gasoline-consuming transportation only contains road transport (Hao et al., 2015), the diesel-consuming transportation includes not only road transport, but also railway transport and waterway transport. Moreover, the emission/production factors of POA/SOA for train and ship were much higher than that for diesel vehicle (Hallquist et al., 2013; Krasowsky et al., 2015).

The information of fuel consumption for motor vehicle was quite limited in China. According to Ou et al. (2010), the fuel consumption of gasoline and diesel in road transport sector were 52.20 and 38.53 million tons in 2007. With these figures the gasoline and diesel derived OA are estimated to be 12.32 and 38.53 thousand tons, respectively.

Q: Line 316: “the discrepancies between predicted and measured SOA were still huge”.

By how much? Please quantify.

Reply: If the SOA yield was assumed to be 30% (Gordon et al., 2014b), the ratio of predicted SOA to measured SOA ranged from 1.6% to 8.9%. The following text has been added to revised manuscript.

“aromatics only accounted for less than 10% of total SOA.”

Q: Table 2, and line 718: Please put the units “ 10^6 molecules cm^{-3} ” in the column header.

Reply: Revised as suggested (Table 2).

Q: Figure 3: Please include ticks on the y-axis below 100 nm, to make the position of the mode clearer.

Reply: Revised as suggested.

References

- Bedjanian, Y., Nguyen, M. L., and Le Bras, G.: Kinetics of the reactions of soot surface-bound polycyclic aromatic hydrocarbons with the OH radicals, *Atmos. Environ.*, 44, 1754-1760, doi:10.1016/j.atmosenv.2010.02.007, 2010.
- Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40, 2635-2643, 2006.
- Esteve, W., Budzinski, H., and Villenave, E.: Relative rate constants for the heterogeneous reactions of NO_2 and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a, *Atmos. Environ.*, 40, 201-211, doi:10.1016/j.atmosenv.2004.05.059, 2006.
- Guangzhou Environmental Protection Bureau, Yearly report of environmental quality in Guangzhou (in Chinese), 2014.
- Guo, H., Ling, Z. H., Cheung, K., Jiang, F., Wang, D. W., Simpson, I. J., Barletta, B., Meinardi, S., Wang, T. J., Wang, X. M., Saunders, S. M., and Blake, D. R.: Characterization of photochemical pollution at different elevations in mountainous areas in Hong Kong, *Atmos. Chem. Phys.*, 13, 3881-3898, 2013.

- Hallquist, Å. M., Fridell, E., Westerlund, J., and Hallquist, M.: Onboard measurements of nanoparticles from a SCR-equipped marine diesel engine, *Environ. Sci. Technol.*, 47, 2013.
- Hao, H., Geng, Y., Li, W., and Guo, B.: Energy consumption and GHG emissions from China's freight transport sector: Scenarios through 2050, *Energy Policy*, 85, 94-101, 2015.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, *Science*, 326, 1525-1529, 2009.
- Krasowsky, T., Daher, N., Sioutas, C., and Ban-Weiss, G.: Measurement of particulate matter emissions from in-use locomotives, *Atmos. Environ.*, 113, 187-196, 2015.
- Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, *Atmos. Chem. Phys.*, 7, 1503-1522, 2007.
- Ou, X., Zhang, X., and Chang, S.: Scenario analysis on alternative fuel/vehicle for China's future road transport: Life-cycle energy demand and GHG emissions, *Energy Policy*, 38, 3943-3956, doi:10.1016/j.enpol.2010.03.018, 2010.
- Rönkkö, T., Virtanen, A., Kannosto, J., Keskinen, J., Lappi, M., and Pirjola, L.: Nucleation mode particles with a nonvolatile core in the exhaust of a heavy duty diesel vehicle, *Environ. Sci. Technol.*, 41, 6384-6389, doi:10.1021/es0705339, 2007.
- Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys.*, 9, 2891-2918, 2009.
- Yue, X., Wu, Y., Hao, J., Pang, Y., Ma, Y., Li, Y., Li, B., and Bao, X.: Fuel quality management versus vehicle emission control in China, status quo and future perspectives, *Energy Policy*, 79, 87-98, 2015.
- Zhang, K. M., and Wexler, A. S.: Evolution of particle number distribution near roadways—Part I: analysis of aerosol dynamics and its implications for engine emission measurement, *Atmos. Environ.*, 38, 6643-6653, 2004.
- Zhang, K., Hu, J., Gao, S., Liu, Y., Huang, X., and Bao, X.: Sulfur content of gasoline and diesel fuels in northern China, *Energy Policy*, 38, 2934-2940, doi:10.1016/j.enpol.2010.01.030, 2010.
- Zheng, X., Wu, Y., Jiang, J., Zhang, S., Liu, H., Song, S., Li, Z., Fan, X., Fu, L., and Hao, J.: Characteristics of on-road diesel vehicles: black carbon emissions in Chinese cities based on portable emissions measurement, *Environ. Sci. Technol.*, 49, 13492-13500, 2015.