Response to comments

Interactive comment on "Chemical and stable carbon isotopic composition of PM2.5 from on-road vehicle emissions in the PRD region and implication for vehicle emission control policy" by Dai et al.

Anonymous Referee #1

Received and published: 21 December 2014

General comments:

Air pollution and haze episodes in recent years are drawing more and more concerns all around the world, and vehicle emissions are believed to be responsible for the worsen of air quality. Representative emission factor of vehicles considering the fleet composition is thus very important for the reasonable estimation of contributions to ambient fine particles from on-road traffic. Detailed information on the characteristics of fine particles was obtained in this study by means of tunnel sampling. The data set is useful and important for the air quality study in China, especially for the source apportionment of PM2.5. Generally speaking, the manuscript is well organized and clearly presented.

We would like to thank the reviewer for his/her useful comments and recommendations to improve this manuscript.

Specific comments and suggestions:

1. p28889, the authors have described the sampling and the tunnel in quite detail. But more information should be included if possible. One is that if the Zhujiang Tunnel is equipped with or without ventilation devices? Second is the fleet composition in the Zhujiang Tunnel similar to the vehicle composition in Guangzhou as a total?

Response: *The ventilation system of the tunnel was turned off during the sampling period, thus the dispersion of air pollutants in the tunnel was mainly brought from the piston effect arising from the traffic flow. The fleet composition in the Zhujiang Tunnel was not as the same as the vehicle composition in Guangzhou. Taken year*

2013 as an example, the average proportions of DV, GV and LPGV in Zhujiang Tunnel were 13.7, 59.8 and 26.5% respectively, while those in Guangzhou were 7.12, 86.1, and 6.75% respectively (http://data.gzstats.gov.cn/gzStat1/chaxun/njsj.jsp)(Feng, 2014). Therefore, the fleet composition in this study cannot be regarded as representative for Guangzhou. However, the aim of this study is to compare the study conducted in the same tunnel in 2004, and to get a view of the effectiveness of the implementation of vehicle emission control policies from 2004 to 2013 in the PRD region. We have clarified them in the text. Please refer to Lines 102-104, 124-126 in the revised manuscript.

2. p28892, line 10, I think the uncertainties in the weighing process should be an important cause of the uncertainty in mass closure. Elements such as Si and S (not in form of sulfate) should not have contributions large enough to account for the discrepancy observed.

Response: *We agreed with the comments. Combining with the second reviewer's suggestion, we have re-estimated the reconstructed PM mass: "PM2.5 mass was also obtained by summing OM, EC, geological component, sea salt, and major water soluble inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-). OC was multiplied by 1.4 to estimate mass of OM (He et al., 2008). The geological component of 35 mg vehicle^{-1} km^{-1} was estimated based on the Al emission data as present in Table 1. A typical road dust Al composition is 9% on average (Tiittanen et al., 1999). Sea salt of 9 mg vehicle^{-1} km^{-1} was estimated by Na assuming sea salt contains 32% of Na. Thus, the average PM2.5 reconstructed mass was 91.8% of the gravimetric value. This discrepancy can be attributed to the uncertainties in the weighing process, the estimation methods and uncalculated components." Please refer to Lines 205-213 in the revised manuscript.*

3. p28897, the authors discussed the difference in alkane distribution between results of this study and the study in 2004 in the same tunnel. Actually, the difference is quite small (shift of Cmax from C23 to C24), and this difference could be explained by the shift of gas-particle partitioning as alkanes of <C26 are semi-volatile. I would suggest

the authors to provide more information such as ambient temperature to confirm that the observed difference is meaningful, and to avoid the over explanation.

Response: *The average ambient temperature in this study is 33.0 ± 2.3 ℃, while it is 31.8±1.0 ℃ in the study of 2004 in the same tunnel. A significant T-test (p = 0.14) shows that the temperature in this study is not significantly different from that in the study of 2004. Thus the differences due to different* C_{max} *between this study and the study in 2004 can not be regarded as a result of temperature differences. Furthermore,* C_{max} *was found to be C24 in every test of this study, although the temperature ranged from 28.6 to 36.1 ℃. So we don't think that the ambient temperature in this study would make the shift of* C_{max} *from C23 to C24. Please refer to Lines 351-357 in the revised manuscript.*

4. p28898, the part of implication should be shortened and focus more on the application/implication of the current results. Repeat of the figures in Tables should be avoided.

Response: *We have rewritten this section and focus on the application and implication of the results. Please refer to Lines 385-401, 410-414 in the revised manuscript. Additionally, we have moved Tables 1 and 2 to the Supplementary material, and revised the table number accordingly in the revised manuscript.*

Anonymous Referee #2

Received and published: 6 January 2015

General

This paper describes PM2.5 and chemically speciated measurements of emissions in a tunnel in the PRD region in China. PM2.5 emissions and composition are compared with those in the same tunnel in 2004. Differences are discussed with respect to regulations enacted in the interim period.

We would like to thank the reviewer for his/her useful comments and recommendations to improve this manuscript.

Specific comments and suggestions:

1. The paper is generally well constructed, although I suggest that the paper be carefully edited for proper English. For example, p. 28887, line 5, “are of our concern”, p. 28889, line 20, “hygrothermostat”.

Response: *The paper has been edited by a native speaker. We have changed “are of our concern” and “hygrothermost” to “have been our concern” and “hygrothermostat”. Please refer to Lines 55, 141 in the revised manuscript.*

2. Regarding the methodology, PM2.5 was collected on quartz fiber filters. These have a strong potential for absorbing volatile organic compounds. Without a means of correcting for this positive sampling artifact, OC and semi-volatile compound concentrations will be high-biased. This should be acknowledged and discussed.

Response: *We agreed with the comments. Other special devices such as diffusion denuders and foam plugs were not used due to the difficulties in applying these devices. Consequently, volatilization losses or adsorption artifacts may occur on the filter for semi-volatile organic compounds especially for the low molecular weight compounds because these compounds exhibit high volatility (Kavouras et al., 1999). However, the calculation of emission factors were based on the concentration differences between the exit and entrance of the tunnel, the potential losses or adsorption artifacts of semi-volatile organic compounds would be partly deducted. We have clarified them in the revised paper. Please refer to Lines 115-123 in the revised manuscript.*

3. del-13C is calculated using a reference standard. What is the standard?

Response: *del-13C is calculated using a reference standard material (GBW04408, China National Institute of Metrology). The del-13C value is -36.91 ±0.10* $\delta^{13}C_{VPDB}\times10^{-3}$*. We have clarified it in the supplement. Please refer to Lines 71-73 of Supplementary material.*

4. Relatively high emissions of NaCl were measured in the tunnel, indicative of

resuspended sea salt, considering that the authors discounted road salting. Elemental Na,Ca, Mg, and K were higher than their water-soluble forms. This is understandable for K, whose water-soluble fraction in mineral dust is expected to be low. However, the authors' suggestion that non-soluble Na was chelated with organics is implausible.

Response: *The higher elemental Na, Ca, Mg, and K than their water-soluble forms in PM2.5 from vehicle emission were also found in previous tunnel studies (Cheng et al., 2010; Chiang and Huang, 2009; Pio et al., 2013), in which experimental conditions were similar to our study. For K, water-soluble forms only accounted for 42.8% 7.65%, and 7.96% in the Shing Mun tunnel (Hong Kong), the Chung-Liao tunnel (Taiwan), and the Marquês de Pombal tunnel (Portugal). The non-soluble forms are probably due to the occurrence of calcium and magnesium carbonates and Na-K-Mg bearing aluminosilicate species and so on (Pio et al., 2013). We have clarified them in the revised paper. Please refer to Lines 203-204 in the revised manuscript.*

5. The high correlation between EC and Fe suggests that Fe comes from tailpipe emissions. However, Fe is also moderately correlated with crustal elements Al and Ca. EC is also moderately correlated with Al and Ca, suggesting that some EC comes from resuspended dust. For completeness, Table S4 and a discussion of the correlations should also contain PM2.5 and OC. It is clear that while PM2.5, OC and EC emission rates decreased from 2004 to 2013, Fe, Al, Ca, Na and Cl emission rates increased significantly by more than a factor of three. The authors attribute this to increased resuspended road dust in 2013 which was explained by higher wind speed (3.8 m/s in 2013 versus 3.0 m/s in 2004). It is unlikely that this minor difference in wind speed could account for the large increase in resuspended dust/salt from 2004 to 2013. This could be due to heavier traffic in 2013 but examination of the number of vehicles per hour in 2013 and 2004 suggests that there were fewer vehicles per hour in 2013. A more plausible explanation is that there was a lot more dust on the road in 2013. It would have been helpful had the authors sampled the road dust directly and measured its composition.

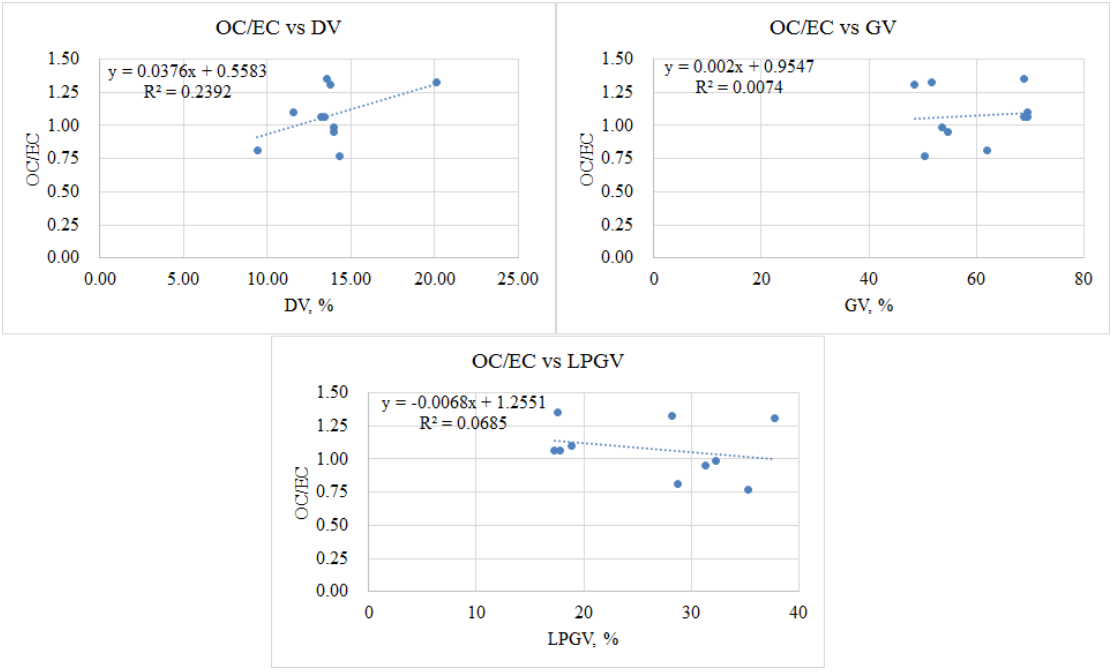
Response: *We agreed with the comments. However, in this part, we want to discuss*

the reason that the emission factors of metal elements increased. The correlation analysis between metal elements and EC can not provide strong evidence for the sources. Strong correlation show their similar sources or atmospheric processes, so we delete the discussion on the correlation and Table S4. Also, we agreed with the comments on the discussion about road dust. Wind speed could not account for the increase in resuspended dust/salt from 2004 to 2013 due to the minor difference in wind speed. The higher emissions of the metal elements could be explained by the higher application of metal-containing oil additive (Mg, Ca, Cu, Zn. (Cadle et al., 1997)) and the wear of engines (Fe) (Cadle et al., 1997; Garg et al., 2000), brakes and tires (Al, Fe,Cu, Mn, Cd, Ni, Pb and Zn. (Garg et al., 2000; Pio et al., 2013)). Another more plausible explanation is that there was a lot more dust on the road in 2013 as the reviewer suggested. This needs further investigation. We have clarified them in the text. Please refer to Lines 331-341 in the revised manuscript.

6. The authors attribute lower PM2.5, OC, and EC emissions to a higher percentage of low-emission LPGV and lower percentage of DV vehicles in 2013. There is indeed a lower percentage of DV vehicles in 2013 but the percentage of LPGV vehicles is not given in the He et al. (2008) paper with respect to 2004. While fleet composition is discussed, it would be helpful to systematically relate variations in chemical composition to fractional abundance of vehicle type over the 10 sample periods. For example, this could be done for OC/EC, non-volatile PAH/OC and hopane/OC.

Response: *We agreed with the comments. He et al. (2008) collected the samples in 2004. LPG was rarely used in the PRD region in 2004, and it was gradually popularized after 2005 especially in buses and taxis. Therefore, the fleet composition in the study by He et al. (2008) is certainly different from that in this study. Actually, we did consider discussing the relationship between fleet composition and chemical composition including OC/EC, non-volatile PAH/OC and hopane/OC over the 10 sampling periods. However, the correlation between fleet composition and chemical composition is very weak as presented in the following plots. The reason might be that the fleet compositions in the 10 sampling periods were not much different (DV*

average 13.7 ± 2.7%; GV average 59.8 ± 8.8%; LPGV average 26.5 ± 7.9%), so we did not discuss these here. We have added the standard deviation of fleet composition in the text. Please refer to Line 135 in the revised manuscript.



7. The characterization of del-13C is interesting but I don't believe it uniquely identifies vehicle emissions. The coal/fuel oil signature is roughly the same.

Response: *We agreed with the comments. For total carbon in PM2.5 sample, $\delta^{13}C$ (‰) of coal and fuel oil combustion are -23.9‰ and -26.0‰ respectively, while that of vehicle emission is -25.9~-25.0‰. Obviously, the $\delta^{13}C$ (‰) of vehicle emission is not significantly different from that of coal and fuel oil combustion. However, they are obviously different from other sources, like dust particle (-21~-18.4‰), C3 plant (-19.3~-13‰), and C4 plant (-34.7~-27‰). Therefore, $\delta^{13}C$ might be used to distinguish the fossil fuel combustion from the other sources. We have revised this section. Please refer Lines 284-290 in the revised manuscript.*

8. Finally, the estimation of reconstructed mass should be revisited. The geological component can be estimated from Al. From the literature, a typical road dust Al composition is 8-10% (9% average). From Table 1, we have: resuspended geological

dust = (100/9)*3.15=35. Sea salt is 3.125*2.88=9 (assuming sea salt is 32% Na). Add these to NH4+SO4 (0.77), EC (16.4), 1.4*OC (23.4) and the sum is 84.6 or 92% of PM2.5.

Response: *We agreed with the comments. In our previous version, we calculated the reconstructed mass by summing all determined components, overtaking the conversion of geological components and sea salt. Now we have re-estimated the reconstructed PM mass accordingly: "PM2.5 mass was also obtained by summing OM, EC, geological component, sea salt, and major water soluble inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-). OC was multiplied by 1.4 to estimate mass of OM (He et al., 2008). The geological component of 35 mg vehicle^{-1} km^{-1} was estimated based on the Al emission data as present in Table 1. A typical road dust Al composition is 9% on average (Tiittanen et al., 1999). Sea salt of 9 mg vehicle^{-1} km^{-1} was estimated by Na assuming sea salt contains 32% of Na. Thus, the average PM2.5 reconstructed mass was 91.8% of the gravimetric value. This discrepancy can be attributed to the uncertainties in the weighing process, the estimation methods and uncalculated components." Please refer to Lines 205-213 in the revised manuscript.*

References:

Cadle, S.H., Mulawa, P.A., Ball, J., Donase, C., Weibel, A., Sagebiel, J.C., Knapp, K.T., Snow, R., 1997. Particulate emission rates from in use high emitting vehicles recruited in Orange County, California. Environmental Science & Technology 31, 3405-3412.

Cheng, Y., Lee, S.C., Ho, K.F., Chow, J.C., Watson, J.G., Louie, P.K.K., Cao, J.J., Hai, X., 2010. Chemically-speciated on-road PM2.5 motor vehicle emission factors in Hong Kong. Science of the Total Environment 408, 1621-1627.

Chiang, H.L., Huang, Y.S., 2009. Particulate matter emissions from on-road vehicles in a freeway tunnel study. Atmospheric Environment 43, 4014-4022.

Feng, Q., 2014. Research on emission mechanism of oxygenated volatile organic compounds in vehicle emissiom. Master Dissertation Research Paper, Jinan University.

Garg, B.D., Cadle, S.H., Mulawa, P.A., Groblicki, P.J., Laroo, C., Parr, G.A., 2000. Brake wear particulate matter emissions. Environmental Science & Technology 34, 4463-4469.

He, L.Y., Hu, M., Zhang, Y.H., Huang, X.F., Yao, T.T., 2008. Fine particle emissions from on-road vehicles in the Zhujiang Tunnel, China. Environmental Science & Technology 42, 4461-4466.

Kavouras, I.G., Lawrence, J., Koutrakis, P., Stephanou, E.G., Oyola, P., 1999. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. Atmospheric Environment 33, 4977-4986.

Pio, C., Mirante, F., Oliveira, C., Matos, M., Caseiro, A., Oliveira, C., Querol, X., Alves, C., Martins, N., Cerqueira, M., Camoes, F., Silva, H., Plana, F., 2013. Size-segregated chemical composition of aerosol emissions in an urban road tunnel in Portugal. Atmospheric Environment 71, 15-25.

Tiittanen, P., Timonen, K.L., Ruuskanen, J., Mirme, A., Pekkanen, J., 1999. Fine particulate air pollution, resuspended road dust and respiratory health among symptomatic children. European Respiratory Journal 13, 266-273.