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Comment

# ***Interactive comment on “Chemical and stable carbon isotopic composition of PM<sub>2.5</sub> from on-road vehicle emissions in the PRD region and implication for vehicle emission control policy” by S. Dai et al.***

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General

This paper describes PM<sub>2.5</sub> and chemically speciated measurements of emissions in a tunnel in the PRD region in China. PM<sub>2.5</sub> 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.

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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, PM<sub>2.5</sub> 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  $-36.91 \pm 0.10 \delta^{13}\text{CVPDB} \times 10^{-3}$ . We have clarified it in the supplement. Please refer to Lines 71-

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73 of Supplementary material.

4. Relatively high emissions of NaCl were measured in the tunnel, indicative of re-suspended 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 PM<sub>2.5</sub> 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 PM<sub>2.5</sub> and OC. It is clear that while PM<sub>2.5</sub>, 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

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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 PM<sub>2.5</sub>, 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

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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  $13.7 \pm 2.7\%$ ; GV average  $59.8 \pm 8.8\%$ ; LPGV average  $26.5 \pm 7.9\%$ ), 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 PM<sub>2.5</sub> sample,  $\delta^{13}C$  (‰ of coal and fuel oil combustion are  $-23.9\%$  and  $-26.0\%$  respectively, while that of vehicle emission is  $-25.9\sim-25.0\%$ . 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 ( $-21\sim-18.4\%$ , C3 plant ( $-19.3\sim-13\%$ , and C4 plant ( $-34.7\sim-27\%$ . 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  $NH_4+SO_4$  (0.77), EC (16.4),  $1.4*OC$  (23.4) and the sum is 84.6 or 92% of PM<sub>2.5</sub>.

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: "PM<sub>2.5</sub> mass was also obtained by summing OM, EC, geological component, sea salt, and major water soluble inorganic ions ( $NH_4^+$ ,  $SO_4^{2-}$ ,

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NO<sub>3</sub>-). OC was multiplied by 1.4 to estimate mass of OM (He et al., 2008). The geological component of 35 mg vehicle<sup>-1</sup> km<sup>-1</sup> 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<sup>-1</sup> km<sup>-1</sup> was estimated by Na assuming sea salt contains 32% of Na. Thus, the average PM<sub>2.5</sub> 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.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C12223/2015/acpd-14-C12223-2015-supplement.pdf>

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