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Interactive comment on “Characteristics and sources of carbonaceous aerosols from Shanghai, China” by J.-J. Cao et al.

J.-J. Cao et al.

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Anonymous Referee #3 Received and published: 6 September 2012 This manuscript provides various measurement results for carbonaceous aerosol at heavy pollution area in China during 20 days to characterize temporal variation of carbonaceous aerosol and to evaluate their origin. I believe the data presented in this manuscript are valuable, especially the measurement data of stable C isotopes OC and EC, because of the limitation of these measurement data in this field and give significant information to the atmospheric community. However, estimation of source for carbonaceous aerosol using diagnostic ratios and EC tracer method used in this study have high uncertainty and QA/QC data for analysis of carbonaceous aerosols are insufficient in the manuscript, thus, it is difficult to follow the results and the conclusion of the manuscript

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in this stage. So, before the manuscript can be accepted for publication, more concrete supporting evidences are required.

Reply: We added more descriptions about the QA/QC data for carbon analyses in the following text. In this study, one purpose is to demonstrate a new way for source apportionment estimation based on the different carbon data. We think the manuscript can arise more interests for the deep understanding of routine carbon data.

The specific comments are as follows: 1. The authors applied injection port-TD method to extract PAHs and n-alkanes from the aerosol. This method is not traditional and new approach, so own QA/QC data should be provided before accepting this method in this manuscript. Although previous studies, for example, Ho and Yu, 2004 and Ho et al., 2011 provided sufficient QA/QC data for TD-GC-MS analysis, these data is not available to this study due to difference of laboratory and users. Thus, just use of reference is not acceptable. Also, more details for analytical process of PAHs and n-alkanes are needed. Did internal standards apply to GC-MS analysis in this study? What kind of internal standards are applied?

Reply: 1.0cm²-3.2cm² (sample size was based on the aerosol loading in each sample) quartz-fiber filter samples were taken using a stainless steel punch from 410cm² high volume sampling filters over a pre-baked clean surface sheet glass. Each filter piece was divided into four roughly equal portions with a razor blade to facilitate the subsequent loading of the filter pieces into the TD glass tube. The Pyrex glass tube baked at 450 °C for at least 5 h that was custom fabricated to be the same dimensions (78 mm long, 4 mm I.D., and 6.35 mm O.D.) as the Agilent 5890A GC/5975C MSD (Santa Clara, CA, USA) injector liner. A small amount of pre-baked silane-treated glass wool (Sigma-Aldrich, Bellefonte, PA, USA) was inserted at both ends of the liner to prevent the filter from sliding out and large particles from entering the column. The loaded glass tubes were stored inside capped test tubes and were kept in the desiccator before analysis. Calibration standards were prepared by spiking known amounts of two kinds (n-alkanes and PAHs) of liquid standard mixtures (Sigma-Aldrich, Bellefonte, PA,

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USA) onto pre-baked (780 °C for at least 4 h) quartz-fiber filters (1.0 cm²). After air drying for a few minutes to guarantee complete evaporation of the organic solvent from the application of the mixed standards, the standard-loaded filters were then cut and placed into the TD tubes in the same way as for the sample filters. Calibration curves were constructed by plotting the peak area versus the amount of each species in the analytes. In this study, the injector temperature was first lowered to 50 °C to allow hand-handling of the liner for loading the tube into the injection port. Once the tube was in place inside the injector port, the injector was immediately closed and its temperature was set to 275 °C (It took about 8.0 min to reach the new setting.) for desorption in a splitless mode manually and then kept that temperature during the whole GC run. During this period, the GC oven temperature was kept at 30 °C. After the injector temperature reached 275 °C, the GC analysis began. The GC oven program was initially held at 30 °C for 2min, ramped at 12 °C min⁻¹ to 120 °C, ramped at 8 °C min⁻¹ to 280 °C, then ramped at 12 °C min⁻¹ to 325 °C, and held at 325 °C for 20 min until the end of the analysis. The quadrupole mass spectrometer was operated in the electric impact mode at 70eV. The MSD was scanned from 50 to 550 amu. The GC was equipped with an HP-5MS (5% diphenyl/95% dimethylsiloxane, 30 m×0.25 mm×0.25 µm) capillary column with ultra high purity helium (99.9999%) as the carrier gas at a constant pressure of 8.4 psi and flow of 1.0 ml min⁻¹. Alkanes were quantified by the ions at m/z 57 except the C19 (using the molecular ion: m/z 268). PAHs were quantified by their respective molecular ions. Identification was achieved by comparing the mass spectra and retention times of the chromatographic peaks with those of authentic standards. National Institute of Standards and Technology (NIST) Standard Reference Material® (SRM) 1649b was employed to validate the accuracy of PAHs concentrations in this study. The relative error between the certified values in SRM 1649b and the calibration standard concentrations was < 9.6%, demonstrating the reliable accuracy of PAHs concentrations measured by our TD-GC/MS method. The limit of detection (LOD) of the method is defined as the minimum amount of an n-alkane or a PAH that generates the minimum

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distinguishable signal plus three times the standard deviation of the blank signals. No peaks were detected for either n-alkanes or PAHs in the blank calibration samples. As a result, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the y (peak area) estimate. By this approach, the LODs in nanograms per sample were calculated to be in the range of 0.016 - 0.075 ng for n-alkanes and 0.025 - 0.560 ng for PAHs (Table 1). Replicate analyses were conducted on every 10th sample. The relative standard deviations (RSDs) for the samples were 1.5 - 9.3% for targeted compounds. The good reproducibility demonstrates the quantitative desorption of the non-polar compounds from the filter as well as the stability of the MS system.

Table 1. Limit of detections (LODs) for the measured species in this study

n-alkanes (abbreviation)	LOD (ng)	PAHs (abbreviation)	Rings	LOD (ng)	heptadecane (C17)	0.063	phenanthrene (PHE)	3	0.165	octadecane (C18)	0.055	anthracene (ANT)	3	0.115	nonadecane (C19)	0.075	fluoranthene (FLU)	4	0.061	icosane (C20)	0.074	pyrene (PYR)	4	0.073	heneicosane (C21)	0.073	benzo[a]anthracene (BaA)	4	0.025	docosane (C22)	0.081	chrysene (CHRY)	4	0.041	tricosane (C23)	0.052	benzo[b]fluoranthene (BbF)	5	0.063	tetracosane (C24)	0.038	benzo[k]fluoranthene (BkF)	5	0.055	pentacosane (C25)	0.033	benzo[a]fluoranthene (BaF)	5	0.059	hexacosane (C26)	0.037	benzo[e]pyrene (BeP)	5	0.026	heptacosane (C27)	0.032	benzo[a]pyrene (BaP)	5	0.026	octacosane (C28)	0.023	perylene (PER)	5	0.026	nonacosane (C29)	0.021	indeno[1,2,3-cd]pyrene (IcdP)	6	0.036	triacontane (C30)	0.018	dibenzo[a,h]anthracene (DahA)	5	0.034	hentriacotane (C31)	0.016	benzo[ghi]perylene (BghiP)	6	0.066	dotriacontane (C32)	0.023	coronene (COR)	7	0.165	tritriactotane (C33)	0.025	dibenzo[a,e]pyrene (DaeP)	6	0.560	tetratriactoane (C34)	0.034	pentatriaccontane (C35)	0.032	hexatriaccontane (C36)	0.035	heptatriaccontane (C37)	0.039	octatriaccontane (C38)	0.026	nonatriaccontane (C39)	0.033	tetracontane (C40)	0.046
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2. For the sampling artifacts: If there are no equipment system of removal of gas phase organic compounds for the sampling of SVOCs (semi-volatile organic compounds) in

PM, high sampling artifacts could be occurred due to adsorption of gas phase SVOCs to the filter. The possibility of sampling artifacts for the measurements of SVOCs should be clarified.

Reply: For the present study, the samples for organic compounds analysis were collected by using a Tisch Hi-vol PM2.5 sampler (TE-6001, Tisch Environmental, Village of Cleves, Ohio, USA) over a period of 24 h at a flow of 1000 l min⁻¹. Given its high flow rate, it is not useful and actual to provide a gas organic compounds removal equipment. So the blank filter subtracting methods were used here to reduce the possibility of sampling artifacts for SVOCs, which is also a popular and acceptable way in carbonaceous aerosol research.

3. Several diagnostic ratios applied in this manuscript have high uncertainty to estimate emission sources (please note the reference Galarneau, E. (2008) "Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment" published in *Atmospheric Environment*) because of a variety of the values even in the same source. Also, the references applied in this manuscript for the diagnostic ratios are most published before 2000. Thus, these ratios may not be similar to the diagnostic ratios of recent emission sources. The high uncertainty of these ratios should be verified and comparison of the recent studies with the previous results is required.

Reply: We agree with the reviewer that the diagnostic ratios of PAHs have high uncertainty, but they have been widely used as a reference to roughly estimate the PAH emission sources in previous international studies. And some ratios have been proved to be useful. PHE/(PHE+ANT) ratios show substantial intrasource variability and intersource similarity (Galarneau E., 2008), but it has been widely used for source apportionment in previous studies. However, our finding, "The PHE/(PHE+ANT) ratios in our study ranged from 0.69 to 0.81 (average=0.76): this suggests that coal combustion was the dominant source for PAHs and that the incomplete combustion of other fossil fuels, especially diesel oil, also may also contribute to the ambient PAHs.", observed in this study are similar to those (Figure 1) in the reference Galarneau, E. (2008) and

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Pies et al. (2008). Moreover, Oliveira et al. (2011) found that the diagnostic ratio of BeP/(BaP+BeP) of fresh aerosol is around 0.5, if the ratio is larger than 0.5, it means the photo decomposition of aerosol happened (aged aerosol). After comparison with the recent studies, we found that the diagnostic ratios used are close to the finding in the previous results and are reliable.

Oliveira, C., Martins, N., Tavares, J., Pio, C., Cerqueira, M., Matos, M., Silva, H., Oliveira, C., and Camoes, F., Size distribution of polycyclic aromatic hydrocarbons in a roadway tunnel in Lisbon, Portugal, *Chemosphere*. doi:10.1016/j.chemosphere. 2011. 01. 011. Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., and Hofmann, T., Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Chemosphere* 72, 1594-1601, 2008.

4. line 20 in 16818: The authors suggest that a slightly higher D/N for soot (1.3) compared with char (1.1) implies that the emissions of primary soot particles, possibly from motor vehicles, were somewhat greater during the daytime. For supporting this suggestion, the data arranged in Table 2 should be included standard deviation of the data because if the deviation of the data is large, it is difficult to suggest the value of 1.3 is higher than 1.1. Reply: We have provided the standard deviation of D/N for soot and char in new Table 2. Because the ratios is an average index and keeping almost constant during a special period, the deviation of the data is not so large, so it is reasonable to give the conclusion of slightly higher D/N for soot (1.3) compared with char (1.1).

Table 2 Day/night (D/N) ratios and their standard deviation for the concentrations of PM mass, OC, EC, char, soot in PM2.5 and TSP D/N ratio PM mass OC EC char soot PM2.5 1.38 ± 0.45 1.41 ± 0.63 1.13 ± 0.44 1.14 ± 0.68 1.33 ± 0.81 TSP 1.34 ± 0.46 1.57 ± 1.15 1.15 ± 0.55 1.33 ± 1.05 1.40 ± 0.98

5. lines 12-17 in 16820: The authors explained that if a CPI value is close to unity, the aerosols are influenced from anthropogenic source materials, while, if a CPI value

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is around 10, higher plant waxes is major source. And they suggested that the relatively low CPI values (1.0 to 1.7) indicated that anthropogenic and biogenic sources for nalkanes were both important but that the anthropogenic ones were stronger. In this suggestion, the reviewer can't understand why anthropogenic and biogenic sources for n-alkanes were both important although the CPI values measured in this study are close to unity. Please clarify this sentence and re-write English.

Reply: The CPI values were close to or slightly higher than 1.0, suggesting important contributions of petroleum, diesel residues and gasoline emissions in Shanghai during the sampling time. The Cmax in our study was nonacosane (C29), this indicated that the primary biogenic source had made contribution to the atmosphere of Shanghai, in spite of the biogenic source was not the most important source to n-alkanes.

6. Low concentration of BaP compared to BeP: Generally, BaP concentration is similar to or higher than BeP concentration in the urban atmosphere. However, BaP concentrations reported in this study are very low compared to BeP concentration. BaP is more unstable than BeP at high temperature, thus, it is possible to decompose BaP when thermal desorption is applied for PAHs analysis. Thus, the possibility of decomposition of BaP during thermal desorption should be explained.

Reply: In this study, the sampling was conducted at Pudong, Shanghai which is closed to a park and far away from the major roads. Therefore, the impacts of fossil-fuel emissions from vehicles were not significant and low concentrations of BaP were observed. In previous study in Hong Kong (Zhang and Fang, 2000), the average concentration of BaP in six sampling sites was 0.5 ng m⁻³ which was close to the BaP concentration determined in our study. Feng et al (2006) found that the ratios of BeP/(BaP+BeP) in Shanghai were 0.73 in summer and 0.75 in winter which were similar to the result in our study (0.76). Moreover, Gu et al (2010) also found that the annual average of BeP/(BaP+BeP) ratio (2007 to 2008) in Shanghai was 0.63 which is close to our result. During the sampling period, the average wind speed in Pudong was around 1 m s⁻¹, which was not favourable for the dispersion of air pollutants and

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increased the decomposition rate of BaP. Moreover, the analytical theory and method used in this study are the same as in Ho and Yu (2004) and Ho et al., (2008, 2011). In Ho and Yu (2004), the correlation coefficient of BaP standards analyzed by TD-GC/MS method was 0.991, the recovery was close to 100% and the LOD was 1.01 ng per sample, therefore the TD-GC/MS method used for BaP analysis is even better than solvent extraction method. In addition, Ho et al. (2008) used the TD-GC/MS method to analyze National Institute of Standards and Technology (NIST) Standard Reference Material[®] (SRM) 1649b, and the concentrations of BaP determined by TD method and solvent extraction (SE) method were compared: the regression equation was $TD=1.01 \times SE^{0.97}$ was 0.97. In conclusion, the low concentration of BaP observed in Shanghai is not due to analytical errors of TD-GC/MS method.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/12/C8347/2012/acpd-12-C8347-2012-supplement.pdf>

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