

Interactive comment on “Temporal variation of elemental carbon in Guangzhou, China, in summer 2006” by R. L. Verma et al.

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Reply to Anonymous Referee #1

I and all the co-authors appreciated the thorough and constructive comments by the Anonymous Referee#1, which helped us to improve the manuscript. We have fully taken into account those comments while revising the manuscript. Here we reply the comments raised by Referee#1.

Since a good agreement between the methodologies used to measure the EC(thermally) and BC(optically) have been reported we have replaced EC by BC in the revised manuscript, also in reply to referee#1.

General Comments:

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While this study focuses on an area of great interest and concern, the conclusion and analysis contained in this manuscript are largely unremarkable. The stated objective of the study is to use the temporal variations in the relationship between EC and gas-phase combustion markers (CO and CO₂) to validate existing emissions inventories and to characterize emissions from the sources of these species. The authors conclude that traffic patterns and meteorological conditions largely influence variations in EC, CO, and CO₂ concentrations, and while the data presented in the manuscript support these conclusions, such observations are not unique and have been reported extensively in the literature. The data set, however, is extensive and unique, and the authors miss an opportunity to use their observations to estimate the impact of various sources on EC concentrations and thus provide a methodology for estimating health and climate impacts and to more vigorously verify emissions inventory data. Important questions are left unanswered or poorly articulated, e.g., what are the relative impacts (observed) of diesel engines, industrial facilities, and transported pollutants on EC, CO, and CO₂ concentrations? How do the contributions of sources vary with respect to time (hour-of-the-day and day-of-the-week)? From a quantitative perspective, how valid are current emissions estimates?

Reply: The goal of the manuscript is to establish the relationship of BC with its combustion traces (e.g. CO and CO₂) in light of collocated emissions from various sources and changes in both synoptic and local scale meteorological conditions. The major revisions are based on diurnal variations of OC/BC ratio which is an indicator of fresh or primary emissions. The local time dependencies of the roles of wind and mixed layer depth (MLH) on concentrations have been added in the present version of the draft. As discussed, the observation data have been categorized into south and north depending on the directions of air flows. Due to air circulation mostly confined in the PRD during the northerly type of air masses, the detailed comparison with the emission inventory have been focused for the measurements made for northerly flow. On the other hand, the emission from vehicles were closest sources near the site, the diurnal patterns of traffic and OC/BC ratio have been directed compared with measurements made dur-

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ing the southerly flow due to impact of fresh emissions. The patterns of trajectories revealed that northerly air masses were mostly originated within regions of PRD, and represents observed features of regional levels, influenced by the various emissions sources like industries, domestic, transportation etc. To see the relative impacts of these sources on the observations of species, we have compared the observed slopes of BC/CO, BC/CO₂ and CO/CO₂ of northerly air masses with the respective emissions ratios derived from the inventories and emission factors given in literatures. While southerly air masses were continuously diluted by clean marine air, only represents observed features of local or vicinity areas, however, it is hard to define the term local. We discussed diurnal patterns of EC of southerly air flows with traffic of heavy-duty vehicles. We also investigated variations in the concentrations of the species during week-days and week-ends, however, due to limitations of measured data, we can not draw firm conclusion for both types of days.

Specific Comments:

Page 24630, Line 25: Although EC and BC are often used interchangeably, these terms can also be differentiated with respect to the analytical methods used to measure them. In the interests of clarity and the growing body of literature comparing thermal and optical methods, the authors should either clarify this distinction (i.e., BC = optical, EC = thermal) and briefly discuss how comparable these methods are, particularly in light of the comparison data shown in Table 5.

Reply: The comparison between BC and EC have been briefly discussed based on recent studies from our group (Kondo et al., 2010, under revision), also the comparison reported in various literatures. Generally, the agreements have been reported to be good in urban site for EC_{thermal} and BC_{optical}. In the revised draft, we have replaced EC by BC. More information has been added in the text of the draft (experimental section).

Page 24631, Line 5 : While PM has been shown to act as CCN, this reference may not

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be appropriate with respect to EC. It might be more appropriate here to reference works demonstrating the adverse health impacts of exposure to EC and diesel particulate matter (DPM) in light of the high concentrations of EC reported in this paper.

Reply: This suggested correction has been taken into account, now we have removed the phrase and references mentioning effects of BC on clouds formation and cloud albedo. As suggested, new references have been added mentioning the effects of BC on human health.

Page 24633, Line 13: Does the detection limit refer to EC, OC, or TC? Was an external standard used? How often was the EC/OC filter changed during the study?.

Reply: Yes, the detection limit refers to EC, OC, and TC. Internal standard of CH₄ mixture (5% CH₄ in He) was used for online calibration of instrument after every cycle of analysis. Quartz filter was changed every 1–2 weeks by checking the laser correction factor.

Page 24634, Line 16: Where do these emissions data come from? A reference is needed here.

Reply: Reference of Streets et al. (2003) is added in revised manuscript.

Page 24637, Line 10: Throughout the manuscript, the authors report concentrations and mixing ratios +/- standard deviation. What is the purpose of reporting SD? Are the authors assuming that their measurements are normally distributed and the SD is an indicator of whether concentrations are statistically different? Would standard error be a better choice? For example, Figures 5, 7, and 8 give the impression that concentrations and ratios are not significantly different. The authors need to demonstrate that these concentrations and mixing ratios are indeed significantly different in order to support their conclusions.

Reply: The errors in the measurements are assumed to be normally distributed. Hence, throughout the manuscript, we have expressed the variability in concentration

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of the observed species with \pm standard deviation (SD or $\pm 1\sigma$, within 68.2% confidence interval), while correlation slopes are expressed with SD or $\pm 2\sigma$ (within 95.42% confidence interval).

Page 24640, Lines 14 – 15: Can this slope be used to quantitatively estimate the contribution of HDVs to EC concentrations observed at the study site?

Reply: Although, the Figure showing diurnal variation of $\Delta BC/\Delta CO$ slopes have removed from revised manuscript, however, the slopes of $\Delta BC/\Delta CO$ of southerly flows could be used to estimate the contribution of HDVs, as also supported by OC/BC ratio in revised manuscript.

Section 8.2: It is unclear why mass concentrations are compared across these different sites. These data are best left out of the manuscript or included in supplemental material.

Reply: In revised manuscript, we have compared the average BC of northerly flows with the previous measurements conducted in Guangzhou. BC of northerly flows agrees well with the average of all sites of Guangzhou, shows regional features of BC levels at PRD region.

Page 24642, Line 15 - 16: Seems awkward to make conclusions about Tokyo based on data from China when the focus of the paper is China. This sentence should be reworded.

Reply: Comparison with Tokyo is removed in revised manuscript.

Section 8.3: It is difficult to see from this discussion and the figures/tables how a comparison of EC/CO, EC/CO₂, and CO/CO₂ ratios validates emissions inventory data. Can the derived ratios be used to estimate the contribution of each source to the observed EC concentrations via multi-linear regression, for example? How would these contributions compare with the emissions data shown in Table 1?

Reply: We have revised this section. In revised manuscript emissions ratios of EC-C12383

CO, EC-CO₂, and CO-CO₂ are calculated separately for each sectors of emissions. To validate the inventory, these emissions ratios are compared with observed slopes EC/CO, EC/CO₂, and CO/CO₂ of northern air masses, as have said observed features in northern air masses represents the region of Guangzhou or PRD. Relevant discussion is given in revised manuscript.

Page 24643, Lines 10 – 11: What is meant by reasonably well? It is unclear how these data validate the emissions inventory. The authors qualify their conclusion by claiming the emissions inventory is validated “to some extent.” In order to be useful, this conclusion needs to be better quantified.

Reply: The values of observed slopes of EC/CO, EC/CO₂, and CO/CO₂ are within the range of the uncertainty exist in emissions ratios of the inventories, that why we said our measured slopes are agreed reasonably. However, measurement data in this study are limited to one month, and therefore the statement for the validation of inventories may not be conclusive, so we said “to some extent”.

Table 2: Wind data should be relegated to supplemental material.

Reply: We have removed wind data from table.

Table 3: How were the time periods (day/night) decided upon? The caption should indicate what time periods correspond to day and night.

Reply: The hours included for day and night were 8:00 – 18:00 hr, and 20:00 – 6:00 hr, respectively. To avoid the biasness due to transition phase of wind speed and MLH, the data measured during 7:00 hr in morning and 19:00 hr in evening is removed from analysis.

Table 4: As with Table 3, more information on day/night split should be provided in the caption/text.

Reply: Revision is made

Figure 2: It is difficult to accept that traffic patterns/volumes have not changed since 1999. Is there any additional data available that might support this assumption?

Reply: Due to non availability of recent traffic data, we have limitation to use traffic data counted in 1999. However, numbers of the vehicles could have been changed during these years, but we assumed that the diurnal patterns of the traffic would remain same.

Figure 5: See previous comment about using SD in these plots. At first glance, the differences shown here with error bars do not seem to be statistically different.

Reply: We assumed that the errors were normally distributed and ± 1 standard deviation is right choice to the confidence interval of 68.2%.

Figure 6: Again, I am not sure of the appropriateness of comparing data from 1999 and that from 2006. The caption must, at the very least, indicate that the HDV data is not from the same time period, otherwise it is deceptive.

Reply: We agreed with the comment. Since traffic data were not recoded during the present study, and we rely on the previous data reported for Guangzhou city (Xie et al. (2003). Although these data were recorded about 7 years before the present study and can have some limitations in context to present study; however, we assume that the diurnal pattern remains nearly unchanged.

Figure 7: It is difficult to tell from these time-series plots if there is a statistically significant dependence between these variables. The authors should show XY scatter plots complete with R^2 values in order to validate any dependence.

Reply: Revision is made in revised manuscript. We made scattered plots of BC with wind speed and MLH with function of time of measurements.

Figure 8: This graph is confusing and difficult to evaluate. How valid are these diurnal variations if the correlations coefficients are so widely distributed? Do the variations in R^2 coincide with changes in the relative contribution of various sources to EC concentrations? Again, the error bars appear to indicate few statistically significant

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differences in these data.

Reply: The figure is removed in revised manuscript, as it was not consistent with diurnal variations of EC and CO. Instead we used OC/BC ratios an indictor of fresh emissions.

Figure 9: Since the R^2 values are so poor, this figure adds little value and should be placed in supplemental material or left out entirely.

Reply: Moderate correlations between EC-CO, EC-CO₂, and CO-CO₂ are reality of the measurements. These results are expected at the observation site like Guangzhou where the influences of various sources on measurements were exists.

Technical Corrections:

Table 5: Footnote reads " R^2 " but no correlation coefficients are given

Reply: Revision is made

Figure 10: Make sure to include the definitions of HDV and HDDT in the caption

Reply: Revision is made

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24629, 2009.

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