

***Interactive comment on* “Size distributions of elemental carbon and its contribution to light extinction in urban and rural locations in the Pearl River Delta region, China” by H. Yu et al.**

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We thank both reviewers for their constructive comments. Our responses to the review comments are listed below. References that are cited in the response document are not listed here, but can be found in the manuscript.

Referee #1

Comment 1 This paper reports different size distributions of EC at several sites (namely, urban and outskirt locations) in the Pearl River Delta, China, where ambient measurements are limited and huge anthropogenic sources of EC are expected. Mixing state of EC has certainly important implications for the earth's radiative balance, as those

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presented here, as well as human health. On the basis of the size-segregated EC data and other chemical composition, the authors calculated the light extinction contribution by the EC-containing particles to show a significant contribution of EC to the observed light extinction in these regions. The present work provides nice information in our understanding on chemical and physical properties of EC in Asia, and the material presented here likely fits with the scientific scope of ACP. However, in many parts, the discussion lacks scientific rigor and careful evaluation of the data (see comments below), which makes discussion rather loose. The authors make a lot of assumption in the calculation of chemical and physical properties of EC, most of which are not supported. I think there are several important issues that need to be worked out before its publication in ACP.

Author Response: In this work, we have made efforts to estimate light extinction due to EC-containing particles using Mie theory with inputs of fundamental particle physical properties (size, mixing state) and chemical composition representative of our study region, the Pearl River delta region. In this bottom-up approach, not all the input parameters required by Mie theory have available observations, due to limited resources available for field measurements. As such, it is necessary to make assumptions of those without corresponding measurement values. Wherever possible, we have provided supporting evidence or justification based on knowledge derived from either our own measurements in the region or in the literature for the assumed values used in our calculations. Please see below for responses to specific comments.

The approach we take in calculating the contribution of EC-containing particles to light extinction shares conceptual similarity to the revised IMPROVE algorithm (Pitchford et al., 2007) in that the particle size-dependence of dry mass extinction efficiencies is recognized and considered. In original IMPROVE algorithm the dry mass extinction efficiencies are simply fixed at 3 m²/g for ammonium sulfate and ammonium nitrate and 4 m²/g for OM (Malm et al., 1994). The revised algorithm accounts for the change of extinction coefficient with particle size by splitting ammonium sulfate, ammonium

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nitrate, and OM into a small size mode representing freshly formed particles and a large size modes representing aged and/or cloud processed particles.

Considering that light extinction coefficient of EC-containing particle also changes with size, we have taken the approach to separate EC into two modes by replacing the smaller mode with the condensation mode and replacing the larger mode with the droplet mode, based on our observations in the PRD region. Because size distributions of aerosol components change from sample to sample, fixed MMADs of 0.2 μm for the small mode and 0.5 μm for the large mode in the revised IMPROVE algorithm are not directly applicable to locations other than those study areas in Pritchford et al. In our calculation approach, $\sigma_{\text{ext,calc}}$ is calculated using measured size distributions of EC in individual samples. Therefore, this approach moves one step further than the revised IMPROVE algorithm and makes more realistic approximation.

Another improvement in our approach is that we have considered the mixing state of aerosol component (EC, OM, sulfate) in Mie calculation, while IMPROVE algorithm assumes that all components are simply externally-mixed, which no doubt brings uncertainties to the calculation. Precise description on mixing state of aerosol components is still a difficult question, which needs both experimental and numerical investigations [Jacobson, 2000; Hasegawa and Ohta, 2002, Cheng et al., 2006]. In our study, the mixing state assumption is based on EC/OC/ions mode observation in the PRD region. We therefore believe our approximation is more realistic than those in previous studies. To address the reviewer's concern on lack of supporting evidence for assumptions made in our calculations, we have included the size distribution data of OC and sulfate in Table 2. Discussion on their relations with EC is provided in section 3.1 and 3.2 to support our assumption on the mixing state (see response to specific comment 2 from referee #1).

Comment 2 Specific comments

In addition to the size distributions of EC, one of the most important factors in the

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authors' discussion is that chemical compositions of non-EC material (i.e., sulfate or OM) that coated EC. Also their relative abundance to EC is certainly important. In many parts of the paper, however, the authors discuss size and chemical compositions of non-EC material without showing any measurement results. I think the authors should show the size distributions and mass concentrations of sulfate, OC, etc. and their relation with EC to support the authors' discussion. Without these information, the assumptions made for the calculations and discussions are weak.

Response We now report the MMAD and concentration values of OC and sulfate modes in Table 2 and the relative abundances of sulfate and OM to EC in Table 3. The following paragraphs are added to section 3.1 and 3.2 to provide detailed information on the size distributions and mass concentrations of sulfate and OC and to elaborate on the relationship of these non-EC materials with EC.

Lines 173-182: "OC and sulfate had the same three modes in the GZ samples. As shown in Table 2, MMADs of OC and sulfate modes were close to those of EC in both sub-groups of the GZ samples. The relative abundances of OC versus EC and sulfate versus EC were dependent on the particle size. The OC/EC ratio in the condensation mode is 0.8 on the non-haze days and 0.9 on the haze days, significantly smaller than those in the droplet mode (1.6 on non-haze days and 2.1 on haze days). These results indicate that $\sim 0.4 \mu\text{m}$ mode EC is fresh soot particles while EC in the $\sim 0.9 \mu\text{m}$ mode is aged with extra OC coating. The sulfate/EC ratio is also much higher in the droplet mode, about 2.5 times that in the condensation mode (Table 3), supporting that addition of sulfate through in-cloud processing could cause growth of the EC particles from the condensation mode to the droplet mode."

Lines 198-203: "EC, OC, and sulfate shared similar size distribution characteristics at the two suburban/rural locations, but their size distributions were distinct from those at the urban locations in that the most significant mode was the droplet mode (MMAD: 0.7-1.1 μm). The droplet-mode EC accounted for 63% of the total EC mass in the BG samples, 81% in the HKUST winter samples, and 58% in the HKUST summer samples.

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70-80% of sulfate and 45-74% of OC were in the droplet mode at the suburban and rural sites.”

Lines 226-228: “While the OC/EC ratios in the condensation mode (1.8-2.3) are almost equal to those in the droplet mode, they are much higher than the OC/EC ratios (0.8-0.9) in the freshly emitted 0.4 μm EC in the urban samples (Table 3).”

Comment 3 2.5 Modal characteristics of EC at the suburban and rural locations. The authors attribute the difference in the size distributions of EC to aerosol aging, which are related with locations of each sites. If so, the authors should show trajectories or local wind fields to clarify the “upwind” and “downwind” relationships among three sites: BG, GZ, and HKUST.

Author Response:

We have now added two wind vector maps of the PRD region (Figures 1b and 1c) to illustrate the upwind and downwind relationships among the three sites. These two maps are generated for a typical summer sampling day (3 Jul 2006) and a winter sampling day (10 Jan 2008) by HKUST MM5 model based on local surface wind observations (Fung et al., 2005). The maps clearly show that the prevailing southeast wind places the BG site downwind of the Guangzhou urban area while the HKUST site is upwind of the PRD region. In winter, the north and northwest wind affects the region and places HKUST in downwind of the PRD region. The following text is added to the manuscript.

Lines 83-88: “In summer, the prevailing southeast monsoon places the BG site downwind of the GZ urban area while the HKUST site is upwind of the PRD region. In winter, the northwest monsoon affects the region and places HKUST in downwind of the PRD region. The upwind and downwind relationships among the three sites are demonstrated in two wind vector maps of the PRD region generated by MM5 model based on local surface wind observations (Figs. 1b and 1c) (Fung et al., 2005).”

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Comment 4 On the other hand, the authors say that local biomass burning is a significant source at the BG site (p.23036, l.16-22) without showing any evidence, which indicates that the influence of urban sources in GZ was insignificant in BG. These descriptions are very confusing and seem to be inconsistent.

Author Response:

We would like to clarify that “local biomass burning is significant at BG” does not mean the influence of urban source must be insignificant at this site. Both sources could be significant at the same time. We have re-worded the relevant text to clarify this issue and to avoid possible confusion (Lines 424-429):

“At the BG site, local biomass burning emissions were a significant aerosol source in addition to transported urban emissions from upwind urban areas. During the measurement periods, the average K^+ concentration was $0.25 \mu\text{g m}^{-3}$ at BG versus $0.08 \mu\text{g m}^{-3}$ in GZ, indicating that BG was more influenced by biomass burning emissions. One episodic biomass burning event nearby occurred during July 23-25, leading to a spike (703 Mm^{-1}) in the average $\sigma_{\text{ext,obs}}$ at BG (Garland et al., 2008).”

Comment 5 I cannot understand why the authors show (maybe averaged?) results from five “scattered” sites in GZ. Do they intend to say that the GZ results are spatially representative for urban GZ? Were the samples obtained simultaneously at five sites in each period? From Table 1, the answer may be “No.” The authors should provide more descriptions on this point, because they only say that “they are monitoring stations scattered around the city.” This information can be related with the conclusion: how representative the contribution of EC-containing particles to light extinction is in time and space?

Author Response:

The five stations in GZ are close to each other. They are within a radius of 7.5 km in the urban area of Guangzhou. All the five stations are close to roadside. Samples at

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different sites were not collected simultaneously. Due to the close distances between the stations and the similar site characteristics, aerosol samples collected at these five sites are similar in chemical and physical properties. Therefore we grouped the samples from these five stations together and assign them as GZ urban samples. The following text has been revised to better explain the five urban sites.

Lines 74-77: “The five urban sites are meteorological monitoring stations set up by the Guangzhou (GZ) local meteorology administration and they are within a radius of 7.5 km in the GZ urban area (23o18’03”N, 113o15’50”E).”

Lines 159-163: “Despite the different locations of the five monitoring stations, our results show that the EC size distributions were very similar among the five sites. This similarity may be explained by the fact that GZ is highly urbanized and all the five sites are close to roadside and consequently heavily influenced by vehicular emissions.”

Comment 6

P.23025, l.12-16: With regard to the way of splitting TC into OC and EC, the authors just mention the PMF and only refer to Yu and Yu [2009]. Because the determination of the EC mass may affect the results, the authors should show more details about the determination of the EC mass instead of using the laser correction (reproducibility in PMF, uncertainties, etc.).

Author Response:

More details on using PMF to apportion EC and OC are now included in the manuscript (Lines 109-119 and text given below). We wish to note that EC and OC are operationally defined. Different thermal methods are known to give different EC and OC concentrations. It is difficult to estimate uncertainties of EC and OC determination as the true EC and OC concentrations for any ambient samples are variable and dependent on the analytical methods for their determination.

Lines 109-120: “Instead, positive matrix factorization (PMF2, version 4.2) has been

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used to apportion the evolved C peaks (OC1-OC4 and EC1-EC5) in the thermograms to OC and EC. The method details are presented in our previous paper (Yu and Yu, 2009). Compared with apparent EC (AEC, the sum of EC1-EC5, i.e., the amount of carbon that is released from the filter substrate during the second stage of analysis in O₂/He atmosphere), the PMF-resolved EC accounts for 77% of AEC and the PMF-resolved OC is 112% of apparent OC (AOC, the sum of OC1-OC4) in the GZ urban samples. In the HKUST samples, the PMF-resolved EC is 79% of AEC and PMF-resolved OC is 115% of AOC. In the BG samples, the PMF-resolved EC is 81% of AEC and PMF-resolved OC is 107% of AOC. It is expected that AEC would overestimate actual EC while AOC would underestimate actual OC since pyrolytically generated EC from charring of OC appears as part of AEC.”

Comment 7 P. 23030, l.18-28: “Influence of organic materials . . .” I think these descriptions are wrong. Chemical and physical characteristics of EC and other aerosols in “urban,” or “suburban/rural” in this work are not necessarily the same as those reported by Saxena et al. Influence of organics on water uptake of particles depends on many factors (e.g., water-solubility of organics, properties of particle surfaces, etc.). The authors have not shown even RH from their measurements. Without these detailed descriptions, the authors can say almost nothing here.

Author Response:

We agree with the referee that influence of organics on water uptake of particles is much more complicated. We may be over-interpreting the data in trying to say something on the direction of influence of OM on water uptake by the particles.

In the revised manuscript, we deleted the following text: “Saxena et al. (1995) reported that for two nonurban locations, organics enhanced water absorption and accounted for 25-40% of the total water uptake in the RH range of 80-88%, while for an urban location in Los Angeles, the net effect of organics was to diminish water absorption of the inorganics by 25-35% in the RH range of 83-93%. We note that neglecting the

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influence of OM on water uptake likely leads to underestimation of the amount of water absorbed by the particles for the suburban/rural samples and overestimation of water uptake for the urban samples.”

The revised text now reads (Lines 256-263): “Less is understood about the hygroscopic properties of organic aerosols or inorganic/organic aerosol mixtures. Depending on whether the hydrophobic or the hydrophilic fraction dominates, organics could either enhance or diminish water absorption by inorganics (Saxena et al., 1995). In the original IMPROVE formula (Malm et al., 1994) and the revised IMPROVE formula (Pitchford et al., 2007), water uptake by OM is not considered by setting water growth factor as 1. We here adopt the same treatment for OM and do not consider influence of organic materials on water uptake in our calculations.”

Comment 8 In figure 3, only one case for MAE, MSE, and MEE in HKUST (from only two-days sampling) and this is not mentioned in the figure caption. Are the dependences on size “general” characteristics? How about the GZ and BG samples and their differences compared to the HKUST samples (slopes etc.)?

Author Response:

This one case is shown to demonstrate the general trend and order of magnitude of the three EC-normalized light extinction efficiency parameters as a function of particle size and chemical composition. The calculated values are also compared with values obtained experimentally or derived using different approaches (Andreae et al., 2008; Cheng et al 2008) to demonstrate our calculation approach is reasonable.

(1) The following paragraph is added to better explain the objectives of Figure 3. Lines 304-320: “For the purpose of demonstrating how optical characteristics of EC-containing particles change as the size and chemical composition change over the course of atmospheric aging, the HKUST sample collected on February 5-6, 2008 was used as an example for the calculation of the three light extinction efficiency parameters. Figure 3 shows MAE, MSE, and MEE values of EC-containing particles of different

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sizes relevant to this example. In this sample, the size distribution was dominated by the droplet mode (MMAD: $0.82 \mu\text{m}$) and the modal concentrations for EC, OC, and ammonium sulfate in the droplet mode were 2.1, 3.7, and $15.6 \mu\text{g m}^{-3}$, respectively. The absorbed water was estimated using AIM2 to be $9.0 \mu\text{g m}^{-3}$ (Clegg et al., 1998). The droplet mode particles are grown from freshly-emitted EC particles through vapor condensation and cloud processing. It is reasonable to assume that the $0.82 \mu\text{m}$ particle (particle (d) in Fig. 3) is of a spherical core-shell structure with EC being the core and sulfate and OM making up the outside spherical shell. When this particle is stripped of OM, sulfate, and water, the diameter of the EC core left behind is estimated to be $0.35 \mu\text{m}$. We denote this “naked” hypothetical EC particle as particle (b) (Fig. 3). Particle (c) is a $0.43 \mu\text{m}$ condensation-mode particle consisting of the EC core and OM coating, but without sulfate coating, approximating an EC particle in the condensation mode that has been aged in the atmosphere to acquired organic coating but has not participated in cloud-processing.”

(2) Calculations are also carried out on other samples from GZ, BG and HKUST. The MAE, MSE and MEE dependences on size (e.g., slope) are not general characteristics, but change with particle composition. The composition of particles determines the refractive index (n) and the density of particles, which in turn affects extinction coefficients. For example, when there is more fraction of OM than the above case, the slope of MAE versus size becomes slightly larger and the slope of MSE versus size decreases. The following paragraph is added to elaborate on calculation results for samples other than the one shown in Fig.3:

Lines 344-346: “The above calculation is based on one HKUST sample. Calculations on other samples from GZ, BG and HKUST show that the “naked” EC particles have a size range of $0.3\text{-}0.35 \mu\text{m}$ and MEE of $10.3\text{-}14.2 \text{m}^2\text{g}^{-1}$. The MAE and MSE of the droplet mode particles (particle d) range from 45 to $88 \text{m}^2\text{g}^{-1}$, apparently dependent on particle size and chemical composition.”

(3) The caption of Figure3 has been revised to: “Figure 3. EC-normalized mass scatter-

ing efficiency (MSE), mass absorption efficiency (MAE) and mass extinction efficiency (MEE) of four types of EC-containing particles, taking chemical composition of the HKUST sample collected on February 5-6, 2008 as example.”

Comment 9 The authors mostly use single values for any results without showing any uncertainties. As long as they are averages, they have variability (e.g., ± 1 sigma). The authors should show these uncertainties or variability. e.g., contribution of water content to particles $10 \pm ?\%$ for GZ samples (p.23030, l.16-17), contribution of EC-containing particles to the observed light extinction ($76 \pm ?\%$) (p.23037, l.6-7), etc.

Author Response:

Now all average values in the manuscript text and Table 1 are presented together with standard variation, in the form of average $\pm \sigma$. Comment 10 Technical Comments: Figures 4 and 5: X-axis is not in the right order of time: x-axis in HKUST runs from 2008 to 2007. I suggest the authors to plot each category in different frames.

Author Response: The order of HKUST sampling time was corrected to run from 2007 to 2008. We plotted all sample groups in one frame to make visual comparison of extinction coefficients easier.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23021, 2009.

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