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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal variations and spatial distribution of carbonaceous aerosols in Taiwan" *by* C. C.-K. Chou et al.

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We are very grateful to the comments from both reviewers. We'll revise this manuscript according to their kind suggestions. The followings are our point-to-point responses to the respective comments.

To Reviewer 1,

1. The EC tracer method is simple and easy to use. Therefore it enjoys widespread applications. However, it is important to be aware of the fact that the real situation may be fairly complicated. As Yuan et al., 2006 pointed out 'In comparison, the method that uses EC as a tracer for primary carbonaceous aerosol sources to derive SOC overestimated SOC by 70–212% for the summer samples and by 4–43% for the winter

samples. The overestimation by the EC tracer method resulted from the inability of obtaining a single OC/EC ratio that represented a mixture of primary sources varying in time and space.' The author has discussed that _ is a source-specific parameter and varies from one source to another. It is also worthwhile to note that it is season-specific as well. According to Figure 2 in Yuan et al., 2006 this parameter had a factor of two variations (summer 0.41; winter 0.88; spring 0.73; autumn 0.70). It seems more reasonable to extract a parameter (OC/EC)primary from a certain season and use it for that season at the site, rather than to take the annual mean (OC/EC)primary for the year as a whole. It may be advisable for the author to work out a new table similar to Table 1, listing linear regression results (slope and intercept) for the relationship between primary organic carbon and elemental carbon for each of four seasons at seven stations. It would be more scientifically sound to calculate SOC for each season using a season-specific parameter (OC/EC)primary.

R: We agree with this comment. Ideally, the (OC/EC)p should be derived from measurements of specific season and specific site. However, in practice, such a task is usually subject to the number of samples. Thus, the approach of data analysis depends on the constraints of each study. In the HK study, for instance, Yuan et al. (2006) lumped their data from all the stations together to derive "season-specific" (OC/EC)p because the sources of aerosols were changed with seasonal meteorological conditions, particularly in summertime (Dr. Z. Yuan, personal communication). On the contrary, in this study, we assumed that the primary emission profiles of OC and EC were not season-dependent and, in turn, used the year-round dataset of each site to derive "site-specific" (OC/EC)p. In this context, the spatial distribution of SOC presented in this paper was more representative than the seasonality, which could have been biased to some extent. Nevertheless, in response to the reviewer's comments, we applied season-specific minimal OC/EC ratios measured at the respective stations to calculate the seasonal SOC concentrations (Castro et al., 1999). The SOC levels presented in the discussion paper and those calculated using season-specific(OC/EC)min were compared in Table S1-S2. Obviously, applying season-specific (OC/EC)min did

not alter the spatial distribution and seasonal pattern of SOC presented in the paper although this method tends to give higher SOC concentrations. Thus, the results of the "seasonal variations and spatial distribution" of SOC discussed in this paper are warranted, and the bias due to using season-independent parameters should be rather limited in our case. We'll publish the intercomparison work as supplemental material of this paper.

2. Here it is said that 'In urban areas, the POA are believed to be mostly from the exhaust of vehicles, whereas biomass burning was suggested as the predominant POA source on global scale (Hallquistetal., 2009). ' However, biomass burning was not mentioned elsewhere in the text. There are some previous studies concerning biomass burning in this part of the world. Even in urban and coastal sites of Taichung, Chio et al., 2004 pointed out 'Vehicle emissions was the most important source of PM10 at the urban site, followed by crustal materials, secondary aerosols, biomass burning, industrial emissions and marine spray. There was a similar pattern of sources at the coastal site, . . .Although biomass burning and secondary aerosols were not main sources during clean air quality periods, they were the influential sources causing the increase of PM10 to "episodic" levels at both sites.' There are several more previous studies presented details on biomass burning contributions from either rice straw burning in the agricultural area in Taiwan (Yang et al., 2006; Lee et al., 2008) or long-range transported biomass burning emission from Indochina (Lin et al., 2009). I would like to comment that as a paper on carbonaceous aerosols in Taiwan the biomass burning contributions from either local emission or long-range transported need to be taken into account. Why not leave it open and new insights may come soon from this rich data set when the data evaluation continues, as this manuscript is based on general statistical analysis and little attention has been paid to episodic cases, let alone the application of air mass back trajectory analysis.

R: Indeed, biomass burning is among the major sources of carbonaceous aerosols. However, as the reviewer's comment, its impacts in Taiwan were significant for specific

"episodes" only. In terms of annual averages, the influences of biomass burning are rather limited in Taiwan. Nevertheless, we agree that it could be an important source of aerosols in the central and southern Taiwan during the harvest seasons. We'll add this into the discussion of seasonal variations in the revised paper. Regarding the long-range transport of biomass burning aerosols from Indochina, the aerosols were mostly in the free troposphere over Taiwan (Lin et al., 2009, and personal communication) and, therefore, we presumed that the influences were negligible at our ground-level stations.

3. Here it is said 'Instead, the spatial distribution of SOC was characterized by a north-south contrast.' This 'north-south contrast' shows up suddenly in 'Conclusion', without a proper discussion in 'Results and Discussion' sections.

R: Thanks for the comment. We'll add this into the "Results and Discussion" in the revised paper.

4. Figure 6 could be improved by using different colors for four seasons.

R: Thanks for the comment. We'll color the figures in the revised paper.

5. P7081, line 6; 'in the aerosol field', what does it mean?

R: Here "the aerosol field" means the space of aerosols' characteristics. To avoid misunderstanding, we'll delete the "field" in the revised paper.

6. It would be nice to give an exact number of the samples on which this manuscript is based.

R: Thanks for the comment. We'll tabulate the sample number in the revised paper.

To Reviewer 2

1. One of the most important questions which I could not understand is that "Are SOCs observed in Taiwan dominated by local sources or by effects of long-range transport from China?" The authors stated that the SOC precursors were mainly from local an-

thropogenic sources, whereas they also concluded that the Asian outflow (from China?) may affect the observed levels of aerosols. If the aerosols were transported from upwind source regions, the estimation of SOC using the EC-tracer method has huge uncertainties and is even invalid. This is because the primary OC/EC ratio used to estimate secondary OC is valid ONLY when carbonaceous particles are emitted from local sources (here, around each sampling site). Also if the emissions of biogenic precursors contributed to SOC (P.7096, L12-13), then the EC-tracer method cannot be used. With respect to the possible contributions of biogenic sources, how do the authors explain the Figures 7 and 8 that show relationships between SOC and anthropogenic tracers? Overall the discussions on SOC sources are not systematic and are difficult to follow.

R: Thanks for this comment, which allows us to make the following clarification. (1). The results of this investigation showed clearly that the "spatial distribution of SOC observed in Taiwan" was dominated by local sources, as depicted in Figure 8. As indicated by the reviewer, EC-tracer method presumes that the aerosols are emitted from local sources. In this context, the application of EC-tracer method in this study is warranted. (2). In the discussion on the seasonal variation of air pollutants, it was inferred that long-range-transport of aerosols, particularly from China, could result in the shift of peak PM season from winter to spring in the northern Taiwan. This inference is based on our previous work (Lin et al., 2005), in which significant influences of long-range-transport events upon the air quality in North Taiwan was reported. However, the influences of long-range-transport were significant in some episodes only. In terms of seasonal and annual means, the influences should be limited. Shift of seasonal peak from winter to springtime doesn't mean the long-range-transport becoming the major source. Considering the substantial local emissions, as indicated by the summer measurements, the enhanced long-range-transport was actually playing the role of "key minor" in the seasonal patterns of carbonaceous aerosols in the northern Taiwan. (3). The reviewer argued that EC-tracer method cannot be used in case of biogenic SOC. We'd like to make clarification. The basic assumption of EC-tracer method

is on the estimate of POC, and the SOC is actually the difference between TOC and POC. In this context, the precursors of SOC can be either anthropogenic or biogenic. The EC-tracer method itself cannot provide any information for the sources of SOC. In case where the precursors are mostly from anthropogenic, the estimated SOC levels are expected being highly correlated with key pollutants like nitrate and EC. Figure 8c depicts the correlation between SOC and nitrate; indeed the SOC correlated with EC as well. Nevertheless, the correlation with R2 of $\sim$0.6 cannot exclude the contribution from biogenic sources. The conclusion drawn from the figures is that "the SOA were mostly produced by oxidation of anthropogenic precursors". The contribution of biogenic sources was inferred for the observed summer maxima of SOC at 5 of the 7 stations. However, in terms of annual means, the anthropogenic emissions were still the predominant contributors of SOA precursors in Taiwan.

2. Estimation of primary OC/EC ratios: (1) The ratio may change depending on season. If not, the authors should at least show the results of the ratios in each season. Also, are the data with rainfall events (which may contain lower OC/EC ratios) excluded? This may also affect the uncertainties of the ratios. (2) The authors note that significant ïĄć values in several sites are due to non-combustion sources. Is there any possibility that the offset is caused by field blanks (e.g., VOC artifacts)? These blanks are different from laboratory blanks and are not mentioned in the manuscript.

R: (1). This is also the major concern of reviewer 1. We have used seasonal (OC/EC)min as season-specific primary OC/EC of each site to estimate the SOC, and compared with the previous results presented in the discussion paper. It was found that applying season-specific (OC/EC)min did not alter the spatial distribution and seasonal pattern of SOC presented in the paper although this method tends to give higher SOC concentrations. Thus, the results of the "seasonal variations and spatial distribution" of SOC discussed in this paper are warranted, and the bias due to using season-independent parameters should be rather limited in our case. We have listed the seasonal (OC/EC)min of each site for PM10 and PM2.5 in Table S1 and S2, re-

spectively. (2). Indeed, the data did not include any rainy event because the sampling cannot be con ducted on rainy days. On rainy days, wet deposition of water soluble OC will be enhanced significantly and the formation of SOC could be suppressed even more than on cloudy days. Thus, the annual and seasonal means of aerosols, and also the OC/EC ratio should have been overestimated to a certain degree. We'll identify this point in the revised manuscript. (3) Thanks for the comment. Indeed, VOC adsorption is a potential source of the offset. The field blank levels were around 5-10 % of the total measured OC in this study. Unfortunately, we did not use denuders to remove the interferences due to VOCs. We'll clarify this in the revised paper.

3. Experimental methods: Several basic information are missing. For example, the authors should describe the number of data in each category, and definitions of "spring", "summer", "autumn," and "winter" periods in the text or tables.

R: Thanks for the comments. We'll add these information into the revised manuscript.

4. P.7087, L.24-25: "The causes of. . ., likely due to uncertainties in the sampling and statistics processes." I could not understand the meaning.

R: Over there, we are discussing the negative offset value observed in PM2.5 of Taipei. The negative offset is significant in terms of statistics; however, which is certainly meaningless in physics. The most plausible cause could be the negative sampling artifacts, i.e. the evaporation loss. However, the loss should be a common issue for all the stations. Besides, the selection of samples for the regression analysis is also a source of uncertainties. For instance, using the lowest 15% (OC/EC) ratio as the criterion will shift the offset approaching zero. We'll clarify this in the revised paper.

5. P.7088, L.24: "the SOC concentration in Hualien was comparable with those in the western Taiwan" Is there any possibility that SOC in Hualien is just photochemically aged transported from a long distance?

R: Thanks for the comment. Indeed, in addition to the local biogenic sources, long-

range-transport could contribute to the SOC in Hualien as well. We'll revise the paper accordingly.

6. Figure 6: (1)Actually, the data are not shown as mass concentrations but as "normalized" concentrations. How did the authors derive them? Why did they use these values? (2)Also only the values for PM10 are shown, because "the carbonaceous aerosols were mostly confined in the fine mode. (P. 7090, L.23)" However, significant fractions of mass were also found in the coarse mode particularly for OC as seen in Table 2. In fact, the authors have discussed possible contribution of sea-salt and dust (P.7091, L.11) (without showing the authors' data). The authors' statement seems to be inconsistent and not systematic. (3)Are all the difference discussed in the text statistically significant? In table 3, "the standard error" values are shown in parentheses. Are they standard deviations or 1-sigma values? The values seem to be too small considering that the individual data points show large variability as shown in Figures 2 and 3. (4)The authors have mentioned that the decreased concentrations of aerosols in fall are due to "meteorological conditions that favored dispersion of air pollutants." However, none of the meteorological parameters (wind speed, wind direction, temperature, RH, etc.) is shown in the manuscript. I cannot understand what the "meteorological conditions" are and how they affect the concentrations of aerosols. This point is true for descriptions in L.22-29, in P. 7091: they are only speculation because the authors have not shown their original meteorological data.

R: (1) In Figure 6, the seasonal variations of 6 species at 7 stations were compared. The seasonal means of each species at a specific station were normalized by their respective seasonal maxima. For example, at the Cape Fuguei, the seasonal maximum of EC occurred in spring and decreased by 35% in autumn. Thus, the "normalized concentrations" were 1 and 0.65 for spring and autumn, respectively. This approach allows the readers to compare the seasonality of each species among the seven stations easily. (2) In the discussion paper (p. 7091), it was mentioned that the seasonal minima of POC, SOC, and EC in the northern Taiwan occurred consistently in the fall

season, whereas the total PM10 concentration reached the minima in summertime. Thus, there must be some non-carbonaceous species increased in autumn. Indeed, our previous study showed the increases in the dust and sea salt in the northern Taiwan during northeasterly monsoon period that starts from autumn. Here we cited the paper Chou et al. (2008) and, therefore, did not present the published data again. (3) The seasonality of PM2.5 was not illustrated in the discussion paper because the seasonal patterns of carbonaceous species in PM2.5 were consistent with those in PM10. Nevertheless, the data were tabulated in the paper and were ready for readers who are interested to see the details. (4) In the tables, the "standard error" of each mean was listed, which can be used to calculate approximate confidence intervals for the mean. In the figures, "standard deviation" of each data point were plotted, which were used to show the distribution of the measurements. The apparent small values of the "standard error of mean" benefited by the relatively large sample numbers. However, it doesn't mean that the measurements distributed within such a narrow range. (5) Thanks for the comment. The original meteorological data were illustrated in Figure S1. Obviously, strong surface winds favored dispersion of air pollutants in autumn.

7. P.7089,L.25: "For instance, : : : (14% vs. 11% for PM10; 18% vs. 16% for PM2.5)." Are the differences of these numbers statistically significant? The comparison should be statistically strict.

R: Thanks for the comment. Indeed the differences were just apparent and not significant statistically. The comparison was used to demonstrate the SOM did not exhibit the urban-rural contrast as did the POM and EC. Thus, in the revised paper, we'll correct the description as "SOM content in the aerosols in the Metropolis Taipei was comparable with that measured at the Cape Fuguei, the northern rural station. The differences are not significant statistically."

8. P.7095,L.16-17: ": : : the reduced amount of diesel vehicles in the eastern Taiwan" The authors have not shown any supporting material (e.g., emission inventory, etc.). Again, it lacks scientific rigor.

R: Thanks for the comment. The official emission inventory of air pollutants in Taiwan will be cited in the revised paper.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C4721/2010/acpd-10-C4721-2010-supplement.pdf

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