**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Positive sampling artifact of carbonaceous aerosols and its influence on the thermal-optical split of OC/EC" *by* Y. Cheng et al.

Y. Cheng et al.

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First, we would like to acknowledge Dr. Subramanian for his attention to our paper. After considering the comments and suggestions carefully, we provide replies as follows.

(1) Page 13743, bottom: Subramanian et al. (2006) did not suggest criteria to choose the peak inert mode temperature - that likely was Conny et al. (2003). Rather, we suggest that biases are likely present in all temperature protocols! Subramanian et al. demonstrate that the peak inert mode temperature affects the OC/EC split, particularly that too high of a peak inert mode temperature underestimates EC due to premature EC evolution (also shown by Chow et al. 2001) and that too low a peak inert-mode temperature (550 C as in IMPROVE) would overestimate EC due to non-light-absorbing, less-volatile OC (attributed in the current manuscript to Schauer et al. 2003).

Reply: (1)As pointed out in the comment, Subramanian et al.(2006) found that too high of a peak inert mode temperature would result in the premature EC evolution, while too low of a peak inert mode temperature would induce OC charring into non-light-adsorbing carbon. The premature EC evolution could be demonstrated by the increase of transmittance signal in the He-4 step. Moreover, Schauer et al. (2003) found that too low of a peak inert mode temperature would cause the OC not completely evolving, which could be demonstrated by the decrease of transmittance signal at the start of the He-O2 mode. These two biases should be avoided when choosing a temperature protocol, and a criterion to choose the peak inert mode temperature based on the transmittance signal was suggested. As a result, the criterion was mainly drawn from the results of Subramanian et al. (2006), though it was not stated by the paper directly. It seems that we should make a more clear description about the process of getting the criterion in the revised version of the paper. We are considering change the paragraph about the criterion in Page 13743 to: "According to the results from Subramanian et al. (2006) and Schauer et al. (2003), it is suggested using the following criterion to choose the peak inert mode temperature. . . . . .". (2)We agree with the comment that Subramanian et al. (2006) found that OC charring into non-light-adsorbing carbon for a temperature protocol such as IMPROVE. But the OC not completely evolving due to too low a peak inert mode temperature was indeed reported by Schauer et al. (2003). We decide to change the corresponding content in Line 24, Page 13743 to "OC not completely evolving (Schauer et al. 2003) or pyrolyzing into non-light-adsorbing carbon (Subramanian et al. 2006)" in the revised version of the paper.

(2)Page 13746, Lines 10-17: Non-light-absorbing carbon will not affect the reflectance signal. The increase in the reflectance signal while the transmittance signal remains flat indicates that the transmittance signal is saturated, while light-absorbing carbon is evolving from the top of the filter (perhaps EC and some charred OC), and light-absorbing carbon within the filter (perhaps charred OC) remains behind; in other words, premature evolution of EC.

Reply: We agree with the comment about the explanation for the increase of the reflectance signal. But, we still think that the IMPROVE-A protocol is suitable for the Beijing samples for two reasons. First, the transmittance signal remains flat, indicating that the loss of EC shouldn't be significant. Second, if we reduce the peak inert mode temperature of the current protocol, for example to the 550 used in the IMPROVE protocol, the influence of non-light-adsorbing carbon would be considerable (Subramanian et al. 2006).

(3) Page 13750, lines 16-19: Subramanian et al. (2004) showed that for a sampling volume of 24 m3, the Q-QBQ OC was effectively the same as the particulate OC determined by the denuder system. Thus, the authors' interpretation on lines 18-19 that this finding of Subramanian et al. (2004) indicates that "QBQ OC underestimated the positive artifact even for a sampling volume of 24m3" is incorrect. The authors' finding of a significant intercept (i.e. QBQ underestimating the positive artifact) is more similar to the 4-6 hour samples in Subramanian et al., for sampling volumes of 4-6 m3 (not surprising, given the low sampling volumes in the present study). The Cabada et al. (2004) reference cited in Table 2 is for 4-6 h samples (the intensive sampling period of the Pittsburgh Air Quality Study). The authors are mixing up statements and results from Subramanian et al. (2004) that refer to 24-h samples and 4-6h samples, for example the statement on Page 13751, lines 9-12. Please be more careful/specify the data subset.

Reply: It should be pointed out that, as shown in Table 3 and Figure 5, "underestimation" and "overestimation" are based on the comparison between different OC estimations (such as (Q-QBQ)-OC) and DQ-OC. As a result, "QBQ-OC underestimated the positive artifact" means (Q-QBQ)-OC was higher than DQ-OC. Subramanian et al. (2004) showed that, for the 24h samples, the (Q-QBQ)-OC was almost the same as the sum of NVOC (DQ-OC) and SVOC collected by the denuded backup CIG filter, indicating that (Q-QBQ)-OC was higher than DQ-OC. So it is reasonable to say that "according to Subramanian et al., QBQ-OC underestimated the positive artifact for a

C2293

sampling volume of 24m3" in this paper.

(4) Page 13751: In section 3.2.2, the authors should look at the QBT-OC results from Subramanian et al. (2004). It is likely that the QBT OC is exposed to a higher concentration of semi-volatile OC due to volatilization from the particulate OC on the upstream Teflon filter. The difference in "positive artifact" between the bare quartz (undenuded) OC and the QBT OC is likely due to this difference in gas-phase SVOC concentrations to which each filter is exposed (altering the equilibrium concentration of adsorbed gas-phase SVOC on each filter), rather than the adsorptive capacity of the quartz filter, with or without particles. I believe Turpin et al. (Atm. Env. 1994) did a calculation to suggest that the quartz filter surface area is significantly higher than the surface area provided

Reply: The comment mixed up the QBT-OC and positive artifact-contributed QBT-OC. As shown in Page 13749, it is assumed that (1) QBT-OC is from both the gaseous organics passing through the front filter (positive artifact contributed) and the evaporated particulate OC (negative artifact contributed); (2) OC determined by the denuded QBT (D-QBT) provides an upper limit of negative artifact-contributed OC, since the removal of gaseous organics enhances the evaporation of particulate organic carbon; (3) thus, the positive artifact-contributed QBT-OC is calculated as the difference between QBT-OC and (D-QBT)-OC. The overestimation of positive artifact by QBT-OC was attributed to the collection of evaporated particulate OC by the QBT, as discussed in Line 17~23, Page 13751. The overestimation of positive artifact by positive artifact-contributed QBT-OC was attributed to the difference in the adsorption properties of the loaded filter (BQ) and the filter without particle loading (QBT), as discussed in Line 1~5, Page 13752. Moreover, we will consider the calculation of Turpin et al. in the revised version of the paper.

(5) For the regression analysis on Page 13752, I would caution the authors that assuming HeOx carbon as "PC+EC only" works only if there is no non-light-absorbing OC in the HeOx phase, which is possible with the IMPROVE protocols, particularly if there is a strong influence of wood smoke or other heavy organic matter. I would also like to

C2294

see some statistical significance tests on the difference between kPC_undenuded and kPC_denuded.

Reply: We agree with the comment that assuming He-O2 carbon as "PC+EC" works only if there is non-light-absorbing OC in the He-O2 mode, and we will add this assumption in the revised version of the paper.