Manuscript number: acp-2010-423

Title: Improved Measurement of Carbonaceous Aerosol in Beijing, China: intercomparison of sampling and thermal-optical analysis methods

We thank the anonymous referees for their valuable comments and suggestions on our submitted paper. We have considered the points raised and revised our manuscript accordingly. We are now detailing our responses and the changes that we have made.

1. Comments of reviewer #1:

This is a carefully conducted study of positive and negative sampling artefacts of OC and a valuable contribution to the discussion of how to sample carbonaceous aerosols with minimum artefacts, which is highly relevant in the atmospheric "Carbon community". It should certainly be published after a few points are addressed.

(1) The answer to the other questions in the Review guidelines is generally: "yes", but I suggest a few changes (given in the order of appearance in the text). The MS should also be checked again for grammar and typos. e.g. Fizt, 1990 should be Fitz, Waston et al. should be Watson et al., "light adsorption" changed to "light absorption" (occurs several times in the text) and in some cases, "form" should be "from".

Changes made: We have checked the text and made the corrections accordingly.

(2) A list of abbreviations would help to make the MS more easily accessible.

Changes made: We would add an Appendix describing all the abbreviations.

(3) The title is not quite appropriate. Of course the study was conducted in Beijing, but what is new in the study is the analysis of the artefact. I suggest changing the title to stress the artefacts, because these are more interesting to the scientific community. The thermal-optical analysis methods should stay in the title, too.

Changes made: The title have been changed to "Improved Measurement of Carbonaceous Aerosol: evaluation of the sampling artifacts and inter-comparison of the thermal-optical analysis methods".

(4) p. 15677: the semi-continuous OC/EC analyzer is not an in-situ instruments, as the particles are collected on a filter just as in all other filter-based methods. A true in-situ

instrument would be a photoacoustic spectrometer, which measures the absorption properties of particles in their airborne state.

Changes made: Only AMS and ATOFMS were kept as the examples for the in-situ instruments. The semi-continuous OC/EC analyzer has been removed.

(5) The last sentence of the second paragraph on p.15677 could benefit from a little more explanation – it is not obvious why Chinese aerosols are so special.

Changes made: We have rewrote that part and explained why the inter-comparison of thermal-optical methods is necessary for China: "The inter-comparison of different protocols could provide important information about the thermal and optical properties of carbonaceous aerosol which greatly depend on its source (Schauer et al., 2003a; Hitzenberger et al., 2006; Reisinger et al., 2008). However, few studies based on samples collected in China were available.".

(6) p. 15679 lines 19/20: why does the instrument allow "more accurate and precise control of sample temperature"? Compared to what other instrument? There are also other commercial instruments that allow simultaneous recording of reflectance and transmittance.

Changes made: The sentence has been changed to "The quartz and CIG filters were analyzed using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA), which allows more accurate and precise control and monitoring of the sample temperature comparing with its previous version".

(7) p. 15681, lines 11/12: please give the first reference for Eatough's work with the CIG/CIF.

Changes made: The reference (Tang et al., 1994) has been added.

(8) p. 15681, last line: please check sentence.

Changes made: The sentence has been changed to "The degradation was still significant when 250℃was used".

(9) p. 15684, discussion on "early split": is there a reason why the early split is observed so frequently in China compared to other regions?

Our response: We have suggested a possible explanation: "The evolution of brown carbon at high temperature (such as 800℃) in the inert mode is the most likely factor

that caused “early split” occurring at relatively low temperature for Beijing aerosol.”.

(10) p. 15685, lines 22 till the end: Are there other indications for the presence of brown carbon than the discrepancy between the methods? Of course brown carbon would give large discrepancies between thermal methods, but I am not sure whether the discrepancy alone should be used to infer the presence of brown carbon. The statement in the abstract, however, is sufficiently cautious.

Our response: We have shown the presence of brown carbon in a follow-up paper: “Cheng, Y., He, K. B., Zheng, M., Duan, F. K., Du, Z. Y., Ma, Y. L., Tan, J. H., Zhang, X., Weber, R. J., Bergin, M. H., Russell, A. G.: Light absorption by elemental carbon and brown carbon in Beijing. Submitted to Environmental Science & Technology.”

Briefly, we measured the light absorption spectra over wavelength range of 250 to 800nm for the $PM_{2.5}$ aqueous extracts using a UV-Visible Spectrophotometer and Long-Path Absorption Cell. The absorption spectra has the brown carbon spectra characteristic of sharply increasing absorption with decreasing wavelengths ($\sigma_{abs} \sim \lambda^{-7}$), similar to that recorded in water soluble humic-like substances (HULIS) extracted from the ambient aerosol in Amazonian biomass burning plumes (Hoffer et al., 2006).

(11) p. 15686, line 16: please clarify what is meant by “breakthrough sensitive to CIG filter”.

Changes made: The sentence has been changed to: “Only breakthrough that can be adsorbed by quartz filter is discussed here, while breakthrough that can be adsorbed by CIG filter is discussed separately in Sect. 3.2.4.”.

(12) p. 15692: please differentiate more clearly between (sample or backup) filter and filter used as denuders.

Changes made: The first sentence of this section has been changed to “As discussed in Sect. 2.3.2, the maximum temperature (200℃) used for the analysis of CIG backup filters,……”. We think the readers would clearly know that results from CIG backup filter would be discussed. Moreover, we do not mention “CIG denuder” throughout the paper.

(13) p. 15693 (and earlier text on this topic): oxidation of OC’s during sampling: the possible oxidation of OCs on the filter during sampling is discussed, but could some

oxidation also occur during the He-mode by oxygen-containing other aerosol material?

Our response: We agree that a fraction of OC (even native EC) might be oxidized in the He mode by oxygen-containing materials in aerosol (such as minerals). However, it can not explain the difference in the carbon evolution pattern between the denuded and un-denuded quartz filter, because the denuded and un-denuded filter should contain the same amount of oxygen-containing materials that could oxidize OC (such as minerals). As a result, we suggested that the difference in the carbon evolution pattern between the denuded and un-denuded quartz filter was due to the reaction artifact.

(14) p. 15694, line 2/3: "inconclusive" seems too cautious. From the data shown in the MS, I think it would be justified to say that the CIG filter method should not be used in China.

Changes made: We have clearly stated that "it seems that the CIG filter might not be suitable for the assessment of negative artifact in China". However, we do not use the term "the CIG filter can not be used in China", because there might be more effective activated carbon denuder in the future.

2. Comments of reviewer #2:

This paper focuses on positive and negative sampling artefacts of OC. Furthermore the influence of the peak inert temperature on the OC-EC split was investigated. The study was well conducted and is a useful contribution to the discussion about carbonaceous aerosols. The manuscript should be published after a few corrections.

(1) p. 15673, line 2: it should be clarified in the introduction that only in $PM_{2.5}$ aerosols the carbonaceous fraction mainly consists of EC and OC. In PM_{10} aerosols carbonates may constitute an important carbonaceous fraction as well. This makes the analysis and attribution to the different fractions even more complicated.

Changes made: The first sentence in the introduction has been changed to "Carbonaceous aerosol, a major component in $PM_{2.5}$, consists of organic carbon (OC) and elemental carbon (EC).".

(2) p. 156679, lines 19-20: the mentioned instrument is more accurate than ……? Please clarify.

Changes made: The sentence has been changed to "The quartz and CIG filters were analyzed using a DRI Model 2001 thermal/optical carbon analyzer (Atmoslytic Inc., Calabasas, CA), which allows more accurate and precise control and monitoring of the sample temperature comparing with its previous version".

(3) p. 15685, lines 25-32: it is a bit risky to deduce brown carbon from the larger discrepancy between EC values defined by different temperature protocols only. Is there data about the influence of biomass burning on the ambient aerosol available?

Our response: Data about the influence of biomass burning is not available at present. However, we have demonstrated the presence of brown carbon in a follow-up paper: "Cheng, Y., He, K. B., Zheng, M., Duan, F. K., Du, Z. Y., Ma, Y. L., Tan, J. H., Zhang, X., Weber, R. J., Bergin, M. H., Russell, A. G.: Light absorption by elemental carbon and brown carbon in Beijing. Submitted to Environmental Science & Technology." Briefly, we measured the light absorption spectra over wavelength range of 250 to 800nm for the $PM_{2.5}$ aqueous extracts using a UV-Visible Spectrophotometer and Long-Path Absorption Cell. The absorption spectra has the brown carbon spectra characteristic of sharply increasing absorption with decreasing wavelengths ($\sigma_{abs} \sim \lambda^{-7}$), similar to that recorded in water soluble humic-like substances (HULIS)

extracted from the ambient aerosol in Amazonian biomass burning plumes (Hoffer et al., 2006).

(4) p. 15694, lines 2-3: it should be stated clearly that the CIG filter is not suitable for the assessment of negative artefacts in China.

Changes made: We have clearly stated that "it seems that the CIG filter might not be suitable for the assessment of negative artifact in China".

That is all of our responses to the comments from referees. We appreciate referees very much for their constructive comments.

Sincerely yours,

Cheng Yuan and He Kebin