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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The effect of metal salts on quantification of elemental and organic carbon in diesel exhaust particles using thermal-optical evolved gas analysis" *by* Y. Wang et al.

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Review report (acp-2010-440) (#2) Title: The effect of metal salts on quantification of elemental and organic carbon in diesel exhaust particles using thermal-optical evolved gas analysis Authors: Y. Wang, A. Chung, and S. E. Paulson

Reviewer: "General comments: Metal salts have long been suspected to catalyze EC oxidation in the thermal analysis of EC and OC, but there has not been a systematic investigation. This work has filled in this gap. The authors did a systematic study on the comparative catalytical behaviors of 13 metal salts in the quantification of EC and OC in diesel exhaust particles using thermal/optical transmittance methods. They

have clearly shown that metals reduce the oxidation temperature of EC and enhance the charring of OC. The experiments are well designed. I only have a few minor points for authors to consider in their next revision of the manuscript

Specific comments 1. Figure 1 shows the thermogram in the form of normalized FID signal versus elapsed analysis time. In the ambient sample, OC dominates while in the combined ambient+diesel particle sample, EC dominates due to the larger carbon loading from the preload diesel particles. It is difficult to tell from the normalized thermogram how the OC evolution patter changes when ambient particles and diesel particle co-exist on the filter. It will be helpful to include in this figure the normal thermograms, i.e., absolute FID signal as a function of elapsed analysis time and the transmittance variation curves. The normal thermograms will allow a better visual comparison of the OC evolution patterns in the He stage and eyeball whether the thermograms are additive."

» We agree with the reviewer and will replace the normalized FID curves with the absolute FID curves in the new version, with minor changes to the figure legend and text (see figure below).

Reviewer: "2. Section 3.1: The authors discuss in this section the effect of ambient aerosols on thermal analysis of diesel particles. They report that the weighted EC/OC ratio of the ambient+diesel particle mixture sample would be 3.72; however my calculation using the information given leads to a value of 2.51 (see the table below for my calculation). Please check."

» We thank the reviewer for the careful check; it should be 2.51 based on the data in the table and text. This will be corrected based on re-analysis of the thermograms in the new version.

Reviewer: "3. In the discussion of effects on EC/OC ratio (page 16955, 1st paragraph), the authors are right in pointing out that POC and EC likely have different absorption coefficients of the monitoring laser. The correct speciation of OC and EC in ther-

mal/optical methods depends on one of the following two assumptions: (1) pyrolytically-generated EC evolves before native EC evolves in the analysis or (2) pyrolytically-generated EC and native EC have the same apparent light absorption coefficient (σ) at the monitoring light wavelength (Yang and Yu, EST, 2002, v36,5199-5204). The work by Yang and Yu is relevant here and can strength the authors' argument on why EC/OC is shifted despite the use of transmittance-based charring correction."

» Yes, the work by Yang and Yu could support our study. We plan to include their study in the new version, so that it will reads: "A complication arises from the differences in the absorption cross section of POC vs. EC (Yang and Yu, 2002); POC is usually, more absorbing than EC (e.g., (Subramanian et al., 2006)). This situation can lead to a delayed split point and an underestimate of EC because early evolving EC does not bring the transmission signal back up sufficiently to compensate for the POC that evolves later."

Reviewer: "4. Towards the end of the manuscript, the authors discussed the atmospheric implication that metal salts cause early EC oxidation, which then causes underestimates of EC in ambient samples. This important atmospheric implication should be mentioned in the abstract, since many readers of this journal are interested in measurements of ambient EC and OC."

» This is an excellent suggestion, thank you. We plan to add a sentence to the abstract so that it will read: "The resulting EC/OC ratio is reduced by 0-80% in the presence of most of the salts, although some metal salts increased reported EC/OC at low metal to carbon ratios. The result implies that EC/OC ratios of ambient aerosols quantified by TOEGA may have variable low biases due to the presence of metals. In general,**********"

Reviewer: "We do note that the low bias caused by metals on the reported EC/OC ratio does not appear to arise entirely from depression of the EC oxidation temperature (it does not correlate well with this parameter) but rather from a combination of effects in-

cluding dynamics of formation and evolution of pyrolized carbon and, likely, differences in the absorption cross section of pyrolized carbon compared to the absorption cross section of the native EC."

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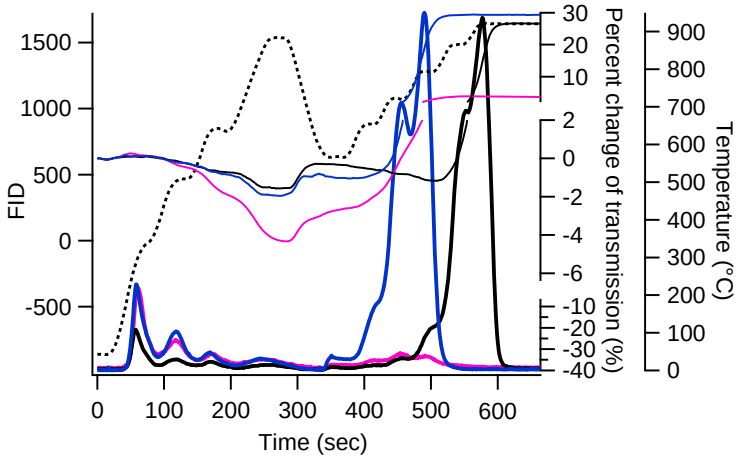
FID
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1000
500
0
-500
Percent change of transmission (%)
30
20
10
2
0
-2
-4
-6
-10
-20
-30
-40
Temperature (°C)
900
800
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
Time (sec)

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