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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Determination of Primary combustion source organic carbon-to-elemental carbon (OC/EC) ratio using ambient OC and EC measurements: Secondary OC-EC correlation minimization method" *by* Cheng Wu and Jian Zhen Yu

Anonymous Referee #2

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Generally Comments

Typically the EC tracer method, when used in estimating the secondary organic carbon (SOC), relies on three conditions– 1) the relatively constant $(OC/EC)_{pri}$ over the period of study; 2) the random nature of SOC formation relative to EC; and 3) a subset of dataset without significant SOC contributions. The $OC/EC_{10\%}$ or OC/EC_{min} essentially utilize the subset in Condition #3 to derive the $(OC/EC)_{pri}$ if it does have an unique value. Any deviations from the conditions as well as measurement uncertainties will

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lead to bias in determining $(OC/EC)_{pri}$. In some environments where SOC dominates, the third condition is generally impossible to be met. This study, through an extensive test, shows that the third condition is not necessary in calculating $(OC/EC)_{pri}$, if an algorithm, i.e., minimum R^2 (MRS), is used looking for $(OC/EC)_{pri}$ that yields SOC least correlated with EC. Without further examinations, the reviewer thinks that MRS is probably mathematically rigorous for any datasets satisfying the first two conditions and, additionally, with sufficient size and accuracy. It can perform better than $OC/EC_{10\%}$ or OC/EC_{min} most of the time because Condition 3 is fortuitous, as described by the authors.

While the reviewer agrees that MRS should be used instead of $OC/EC_{10\%}$ or OC/EC_{min} in calculating SOC, particularly for a large dataset which can support meaningful correlation analysis, MRS does not solve fundamental problems in the EC tracer method. The $(OC/EC)_{pri}$ is by no means constant, as it varies with source contributions from day to day and season to season. SOC is likely correlated with EC because in urban areas many SOC precursors originate from the same combustion sources as EC. This paper demonstrates that when Conditions 1 and 2 are in doubt, MRS produces erroneous results. MRS results are also sensitive to measurement uncertainty that impacts the correlation coefficients. These limitations, however, are not emphasized adequately in the abstract, which sounds almost like MRS has tackled all these issues. These issues, still, can only be solved by using multivariate or chemical mass balance analysis with additional markers.

Specific Comments

Abstract: Please describe the assumptions of MRS, datasets that are suitable for MRS analysis, and potential errors while in the same time shortening the abstract. Just saying MRS is better than $OC/EC_{10\%}$ or OC/EC_{min} is not meaningful because all the three could be very wrong in some cases.

Line 97-102: While using simulated data is insightful, it offers no proof. The authors

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may explore if there is a true “proof” from mathematical or statistical derivations that MRS will yield true $(OC/EC)_{pri}$ if SOC is indeed random and the dataset is big enough. This may also answer the question- how big is big? MRS does not seem suitable for a dataset with only dozens of points.

Line 116-118: How good are the K-S statistics? In other words, how well did the pseudorandom number generator reproduce the statistics in the original dataset?

Line 126: Eqs. (4)-(5) do not work for all datasets. They are probably asymptotes when datasets are large enough in size.

Line 136: Mention here that the case with combustion-related SOC is discussed later.

Line 151-152: The results of log-normally distributed $(OE/CC)_{pri}$ should be summarized in the text if possible.

Line 220-222: It is not clear if f_{EC1} was varied from sample to sample in a single test or only varied from test to test. If the former, how could you make sure EC1 and EC2 are highly correlated?

Line 284-286: Since POC and SOC are not directly measured, what is the meaning to simulate their measurement uncertainty?

Line 384: How were the six subsets selected?

Line 360-362: Emphasize that this only happens when measurement uncertainties are small.