

# ***Interactive comment on “Evaluation of Anthropogenic Secondary Organic Aerosol Tracers” by Ibrahim M. Al-Naiema and Elizabeth A. Stone***

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Anonymous referee #2 general comments: “This paper describes analytical methods and a test ambient study to evaluate the applicability of a range of compounds to be used as tracers for SOA produced from anthropogenic aromatic VOCs. I offer the following comments and suggestions to help improve the manuscript.”

Response to referee #2 general comments: We thank the referee for the careful review and suggestions to improve the manuscript. We address the specific questions and comments point-by-point below.

Referee #2 comment 1 – Abstract: “The title’s focus of “anthropogenic” SOA tracers is

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focused away from “anthropogenic” and toward “aromatic” derived SOA tracers in the abstract. Maybe “aromatic” should also be included somehow in the title.”

Response to referee #2 comment 1: As suggested by the referee, the title for this paper has been revised to reflect the aromatic origin of the investigated tracers. The new title of the manuscript is: “Evaluation of Anthropogenic Secondary Organic Aerosol Tracers from Aromatic Hydrocarbons”

Referee #2 comment 2 – Page 4, line 32: “different derivatization condition was used for nitromonoaromatics, but the reasoning for a different method is not discussed. Please describe why alternate method was applied.”

Response to referee #2 comment 2: To clarify why we used a different derivatization conditions for nitromonoaromatics the following text has been added to Page 5 line 5: “The different silylation protocol used for nitromonoaromatics yielded more symmetrical peak shapes and higher intensities, compared to the derivatization method used for levoglucosan and phthalic acid isomers that resulted in asymmetrical nitromonoaromatic peaks with low intensities.” Referee #2 comment 3 – Page 5, line 4: “update Al-Naiema et al., in review if possible.”

Response to referee #2 comment 3: We thank the referee for pointing out this point. This manuscript is currently in revision at Atmospheric Environment and we anticipate being able to update this soon.

Referee #2 comment 4 – Page 5, line 24: “assuming activity coefficient =1 introduces some large potential errors. Knowing something about the classes of interest and the greater aerosol mixture could help justify this assumption, or help to assume an alternate activity coefficient. Optionally, a lower and higher value could be incorporated in the final table to show a range of resulting partitioning values.”

Response to referee #2 comment 4: We thank the referee for his valuable suggestion. Activity coefficient ( $\zeta$ ) for atmospheric organic compounds in the literature ranges

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from 0.3-3.0 (Seinfeld and Pankow, 2003). We followed the referee's suggestion and included the upper and lower Fp values for the compounds of interest. A new column has been added to Table S1 in the supplement. As indicated in Table S1, the calculated fractions in the particle phase show no significant changes in FP for phthalic acid isomers and furandiones when moving from an activity coefficient of 0.3 to 3.

The following text has been removed from the Supplement: "Table S1: Parameters used to calculate gas-particle partitioning by absorption theory. The activity coefficients were assumed to equal one, subcooled vapour pressures were obtained from the Estimation Programs Interface suite (EPA, 2012). The vapour pressure values were corrected for average ambient temperature during sample collection (282 K) using Clausius-Clapeyron equation, then the corrected values were used to calculate the partitioning coefficient, expressed as fraction in the particle phase (FP).

The new text reads: "Table S1: Parameters used to calculate gas-particle partitioning by absorption theory at three different values of activity coefficients (zeta), each of 0.3, 1, and 3 (Seinfeld and Pankow, 2003), representing the upper, middle, and lower range of calculated fraction in the particle phase (FP), respectively. Subcooled vapour pressures were obtained from the Estimation Programs Interface suite (EPA, 2012). The vapour pressure values were corrected for average ambient temperature during sample collection (282 K) using Clausius-Clapeyron equation, then the corrected values were used to calculate the partitioning coefficient, expressed FP."

Referee #2 comment 5 - Page 7, line 17: "Regarding, "DHOPA accounted for 0.0079  $\pm$  0.0026 of secondary OC mass", is that a fraction or percentage?

Response to referee #2 comment 5: We thank the referee for bring this point to our attention. These numbers represent the mass fraction of DHOPA to the total OC formed from toluene photooxidation. The following text has been removed from Page 7, line 17: "The contribution of toluene SOA to OC was estimated based on the SOA-tracer method introduced by Kleindienst et al., (2007), where DHOPA accounted for 0.0079

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$\pm 0.0026$  of secondary OC mass from toluene.” The new text reads: “The contribution of toluene SOA to OC was estimated based on the SOA-tracer method introduced by Kleindienst et al., (2007), where the DHOPA mass fraction of secondary organic carbon (SOC) from toluene was  $0.0079 \pm 0.0026$ .”

Referee #2 comment 6 - Page 7, line 18: “SOC has not been defined previously.”

Response to referee #2 comment 6: We thank the referee for bringing this to our attention to this point. SOC is now defined at page 7 on line 23, with the revised text provided in response to referee #2 comment 5.

Referee #2 comment 7 - Page 11, Line 9: “Be sure to define all abbreviations before use in main text (e.g. FD and MFD here).”

Response to referee #2 comment 7: We thank the referee for pointing out this important point. The following text has been removed from Page 11, Line 23: “The relative rate of hydrolysis for FD and, MFD are 6 times higher than DFD and DMFD (Trivedi and Culbertson, 1982).”

The new text reads:” The relative rate of hydrolysis for 2,5-furandione (FD) and, 3-methyl-2,5-furandione (MFD) are 6 times higher than dihydro-2,5-furandione (DFD) and dihydro-3-methyl-2,5,-furandione (DMFD) (Trivedi and Culbertson, 1982).

Referee #2 comment 8 - General: “Would be useful to have another figure, maybe in Supplement that incorporates other daily metrics from Nov4-17 such as T, RH, OC, EC, PM2.5, and any other supporting info.”

Response to referee #2 comment 8: We thank the referee for his suggestion. While PM2.5 measurements are not available for this study, the rest of the suggested information are included to Table S4 in the supplement.

Referee #2 comment 9 - General: “With an understanding of the amount of work devoted to developing and testing new methods, the ambient results would be much more meaningful with a longer sample period, and a contrast with different seasons

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or different locations. However, I think the results provided on new methods and a test-case ambient example are sufficient to highlight good candidate tracers, but solid conclusions should be reserved for longer sample periods, various seasons (especially summer), and additional environments.”

Response to referee #2 comment 9: We thank the reviewer and agree that the number of the tested samples provide some limitations, taking the seasonal and diurnal variations of the SOA tracers. We are in the process of testing these tracers using longer time period, and in different seasons, time of the day, and locations to understand the value of applying these compounds to trace anthropogenic SOA in different environments.

The following text has been added to the conclusion, Line 28: “Given the limited time and geographic distribution for the samples analyzed in this study, further investigation is needed to realize the value these compounds as tracers of anthropogenic SOA more broadly.”

#### Works Cited

EPA: Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11 or insert version used. United States Environmental Protection Agency, Washington, DC, USA., in, 2012.

Seinfeld, J. H. and J. F. Pankow, 2003. Organic atmospheric particulate material. Annual Review of Physical Chemistry 54, 121-140.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-805/acp-2016-805-AC2-supplement.pdf>

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	OC ( $\mu\text{g m}^{-3}$ ) Average $\pm$ SD	EC ( $\mu\text{g m}^{-3}$ ) Average $\pm$ SD	Average daily Temperature ( $^{\circ}\text{C}$ )	RH (%)
11/4/2015	1.76 $\pm$ 0.10	0.14 $\pm$ 0.02	14	87
11/5/2015	0.66 $\pm$ 0.05	0.11 $\pm$ 0.02	15	85
11/6/2015	1.12 $\pm$ 0.07	0.11 $\pm$ 0.02	7	72
11/7/2015	2.28 $\pm$ 0.12	0.25 $\pm$ 0.02	5	68
11/8/2015	1.95 $\pm$ 0.11	0.26 $\pm$ 0.02	5	68
11/9/2015	2.90 $\pm$ 0.15	0.38 $\pm$ 0.03	5	65
11/10/2015	3.01 $\pm$ 0.16	0.26 $\pm$ 0.02	6	70
11/11/2015	1.95 $\pm$ 0.11	0.13 $\pm$ 0.02	11	81
11/12/2015	1.07 $\pm$ 0.07	0.03 $\pm$ 0.02	6	74
11/13/2015	1.56 $\pm$ 0.09	0.18 $\pm$ 0.02	4	57
11/14/2015	2.12 $\pm$ 0.12	0.13 $\pm$ 0.02	8	66
11/15/2015	9.65 $\pm$ 0.49	0.81 $\pm$ 0.04	10	59
11/16/2015	1.37 $\pm$ 0.08	0.10 $\pm$ 0.02	9	72
11/17/2015	1.23 $\pm$ 0.08	0.05 $\pm$ 0.02	13	95

Table S4: Daily measurements of organic carbon (OC), elemental carbon (EC), ambient temperature and relative humidity (RH), in Iowa City, IA from Nov 4 - Nov. 17, 2011.

Fig. 1.

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