Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-805-AC1, 2016

Atmospheric Chemistry and Physics Discussions
Open Access

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

Ibrahim M. Al-Naiema and Elizabeth A. Stone

betsy-stone@uiowa.edu

Received and published: 21 December 2016

Anonymous referee #1 general comments: "The authors selected 2,3-dihydroxy-4-oxopentanoic acid (DHOPA), phthalic acid derivatives, nitroaromatic compounds, and furandiones as the candidates of anthropogenic secondary organic aerosol (ASOA) tracer to test them based on a field observation campaign. Secondary organic aerosol is believed to affect climate, visibility, and human health. A tracer-based approach is hopeful technique to identify aerosol sources. Currently DHOPA is an only established tracer of ASOA, therefore additional ASOA tracers would be helpful for better understanding. The authors collected gas and particle offline samples in November, 2015 at a site in Iowa City, United States. The authors analyzed sample extracts em-

Printer-friendly version

Discussion paper

ploying TMS-derivatization gas chromatography-mass spectrometry. The authors studied source specificity, consistent detectability, atmospheric stability, and partitioning to the aerosol phase for each candidate to conclude that DHOPA, phthalic acid, and 4-hydroxy-3-nitrobenzyl alcohol will be used as ASOA tracers. The manuscript is well written and will provide new physical insight into the atmospheric chemistry, but the following comments should be addressed before publication"

Response to referee #1 general comments: We agree with the referee's summary of our manuscript. We thank the referee for the valuable comments regarding the manuscript. Specific comments are addressed point-by-point below.

Referee #1 comment 1 – Page 3, line 22: "Is November the suitable season to study the validity of ASOA markers? Discussion on observation period would be necessary."

Response to referee #1 comment 1: We agree that it is important to justify the timing of this field study. To clarify this, the following text has been added to the introduction page 3, line 15: "November was chosen for this study because, in a prior study at this site, biogenic SOA tracers were detected in this month (Jayarathne et al., 2016) and aromatic SOA tracers have a less pronounced seasonal variation than those that are biogenic (Shen et al., 2015; Ding et al., 2012; Lewandowski et al., 2008).

Referee #1 comment 2 – Page 4, line 14: "Ketopinic acid would have lower polarity than DHOPA. 13C-Labeled adipic acid or deuterated tartaric acid might be better internal standards for DHOPA. Discussion on the internal standard of DHOPA would be necessary."

Response to referee #1 comment 2: It is important that the internal standard match the analyte in physical properties, such as solubility, volatility, and reactivity, so that the internal standard can properly normalize out any deviations arising during the extraction, GC analysis, and derivatization process, respectively (Zhang et al., 2009). Ketopinic acid was selected as an internal standard, because of the precedence set by founding studies of the SOA tracer method (Kleindienst et al., 2007; Kleindienst et al., 2009). Using a DHOPA standard and ketopinic acid internal standard, we show that the extraction efficiency for DHOPA was 98.7 ± 1.8% (n=3) and thus demonstrate the effectiveness and suitability of ketopinic acid as an internal standard for DHOPA. To clarify this in the text, the following text is added to page 4 line 17: "The use of KPA as internal standard for DHOPA builds upon prior work by Kleindienst et al. (2007)."

Referee #1 comment 3 – Page 4, line 17-18: "The power of sonication is missing."

Response to referee #1 comment 3: The sonicator we use has a power of 137 W. This information has been added at page 4 line 19: "Filters were extracted sequentially with three 10 mL portions of acetonitrile using ultrasonication (Branson 5510, 137 W) for 15 minutes at 60 sonics per minute."

Referee #1 comment 4 – Page 8, line 31: "Is 4M-PhA the product of naphthalene photooxidation? It would be produced by the reaction of an isomer of methylnaphthalene."

Response to referee #1 comment 4: We thank the referee for bringing this to our attention. There is no evidence that 4M-PhA would produce from naphthalene; instead it is produced from methylnaphthalene.

The following text has been removed from page 8 line 30: "Together, the relative high concentration detected in the particle phase relative to other tracers, and the high correlations with DHOPA suggest that PhA and 4M-PhA are useful SOA tracers for naphthalene photooxidation." The new text reads: "Together, the relative high concentration detected in the particle phase relative to other tracers, and the strong correlations with DHOPA, suggesting PhA and 4M-PhA as useful SOA tracers for naphthalene and methylnaphthalene photooxidation, respectively." Referee #1 comment 5 - Page 9, line 8-10: "The definition of M is missing. If M indicates the molecular mass of derivative, [M-NO2-CH3]+ and [M-NO2-CH3-Si(CH3)3]+ would be measured at m/z of M-61 and M-134, respectively."

Response to referee #1 comment 5: We thank the referee for bring this point to our attention. There were some typos with the reported numbers, and M refers to the molecular ion for the trimethylsilylated ester.

The following text has been removed from page 9 line 8-10: “Save for nitroguiacols, nitromonoaromatics mass spectra included mass fragments of [M-57]+ (loss of NO2 and CH3) and [M-129]+ (loss of (Si(CH3)3) for the singly and doubly derivatized analytes, respectively. Nitroguaiacol isomers had a fragment at [M-42]+ 10 (loss of NO2)..”

The new text reads: Nitromonoaromatic mass spectra (Table S2) included mass fragments with m/z [M-60]+ (from the loss of NO2 and CH3), where M is molecular ion for the trimethylsilylated ester. Save for nitroguiacols and 4-methyl-5-nitrocatechol, other nitromonoaromatics mass spectra included a mass fragment of [M-15]+ (loss of CH3).

Referee #1 comment 6 - Page 9, line 10: “[M-NO2]+ fragment would be measured at m/z of M-46 if M is the molecular mass of derivative. According to Table S2, [M-NO2]+ fragment would be observed for methylnitrophenol isomers rather than nitroguaiacol isomers.”

Response to referee #1 comment 6: We thank the referee for pointing out this typographical error. This error has been corrected in our response to comment 5.

Referee #1 comment 7 - Page 24, Figure 4: “The chromatographic peaks of 4NP and 4M-2NP are overlapped. These fragment signals might be interfered each other. Discussion on these interferences would be necessary in text.

Response to referee #1 comment 7: We thank the referee for pointing this out. To clarify that we have investigated the possible interferences from the co-eluting nitromonoaromatic peaks, the following text has been added at page 9 line 19: “The mass spectra for the co-eluting peaks (Figure 4, Table S2) indicates that potential interferences for the 4NP-D4, 4NP, and 4M-2NP are not appreciably strong (< 1%), and thus interferences are expected to be negligible. There is potential for 4M-3NP to interfere with detection of 4M-2NP, because the former shows a relatively strong signal for m/z 210 (at 38%

of the base peak signal) that is used to quantify the latter; however 4M-3NP was not detected in this study, so no interference is expected.

Works Cited

Ding, X., X.-M. Wang, B. Gao, X.-X. Fu, Q.-F. He, X.-Y. Zhao, J.-Z. Yu and M. Zheng, 2012. Tracer-based estimation of secondary organic carbon in the Pearl River Delta, south China. Journal of Geophysical Research-Atmospheres 117.

Jayarathne, T., C. M. Rathnayake and E. A. Stone, 2016. Local source impacts on primary and secondary aerosols in the Midwestern United States. Atmospheric Environment 130, 74-83.

Kleindienst, T. E., M. Jaoui, M. Lewandowski, J. H. Offenberg, C. W. Lewis, P. V. Bhave and E. O. Edney, 2007. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. Atmospheric Environment 41 (37), 8288-8300.

Kleindienst, T. E., M. Lewandowski, J. H. Offenberg, M. Jaoui and E. O. Edney, 2009. The formation of secondary organic aerosol from the isoprene plus OH reaction in the absence of NOx. Atmospheric Chemistry and Physics 9 (17), 6541-6558.

Lewandowski, M., M. Jaoui, J. H. Offenberg, T. E. Kleindienst, E. O. Edney, R. J. Sheesley and J. J. Schauer, 2008. Primary and secondary contributions to ambient PM in the midwestern United States. Environmental Science & Technology 42 (9), 3303-3309.

Shen, R. Q., X. Ding, Q. F. He, Z. Y. Cong, Q. Q. Yu and X. M. Wang, 2015. Seasonal variation of secondary organic aerosol tracers in Central Tibetan Plateau. Atmospheric Chemistry and Physics 15 (15), 8781-8793.

Zhang, Y. X., J. J. Schauer, E. A. Stone, Y. H. Zhang, M. Shao, Y. J. Wei and X. L. Zhu, 2009. Harmonizing Molecular Marker Analyses of Organic Aerosols. Aerosol Science and Technology 43 (4), 275-283.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-805, 2016.

Printer-friendly version

Discussion paper