

Interactive comment on “The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides” by T. E. Kleindienst et al.

T. E. Kleindienst et al.

kleindienst.tad@epa.gov

Received and published: 24 August 2012

General response to both anonymous reviewers:

The authors wish to thank the two reviewers for their insight and critical thinking in evaluating the manuscript on photooxidation of naphthalene and the evolution of chemical tracers during the formation of secondary organic aerosol. The reviewers' comments have been examined by all five authors and the comments, herein, represents their collaborative response. All comments have been carefully considered and where ap-

C6148

propriate changes and other revisions have been made to the text, tables, and figures. In some cases, the reviewers may have misinterpreted the manner in which experiments or analyses were conducted or how the measurements were made. We have sought to explain these aspects in better detail in the paper and point these out below in our response. By-and-large, virtually all the recommended changes have been implemented, as well as other changes we initiated involving clarifications and additions to the text. (See end of this response for the modifications.) These changes have resulted in a paper that has far more clarity and is also more precise and consistent than the original version and for this we again thank the reviewers.

Note: By convention here and throughout, an initial incomplete paragraph at the top of a page will be considered Paragraph 1.

General comments: In this work, the authors extend their work in quantifying mass fractions of SOA tracers to naphthalene and its methyl analogs. They conducted laboratory smog chamber experiments in a flow mode to quantify phthalic acid and methyl analogs and their mass fractions in SOA. The data obtained in this work allows the estimation of SOA contributions from naphthalene and its methyl analogs, which could be important SOA precursors in urban environments. This set of data is an important addition to the knowledge database of significant SOA precursors and will help us to move closer to a more quantitative understanding of SOA and their precursors. I recommend the publication of this work. My review comments are largely minor and on clarification of experimental details. The specific comments are given below for the authors to consider in their next revision.

Specific comments:

1. Page 12178, Lines 9-19: In the experiments to examine the interference of phthalic anhydride, how was phthalic anhydride introduced to the chamber for measurements? What concentration levels were tested? What were filter sample collection duration and sampling flow rates? What was the chamber RH in these experiments? In the abstract

C6149

(Lines 15-17), the use of in-line denuders was mentioned for these experiments, but this experimental detail was not described in the manuscript text. Please provide more details about these experiments so that readers can assess the extent of artifact in measuring phthalic acid in the presence of phthalic anhydride in their own systems.

Response: We probably should have introduced the topic better in the manuscript. We presumed to form phthalic anhydride in-situ during the photooxidation of naphthalene, primarily in the presence of NO_x according to the work of Wang et al., 2007. The reviewer's comment suggests that we may have introduced phthalic anhydride as a neat compound into the chamber to test uptake. In fact, we did not do this since it would have been difficult to regulate the amount added and there would have been significant chamber mixing problems, in addition to other potential experimental shortcomings. Thus, we should have given added detail to the experimental design for the putative formation of phthalic anhydride. Additional details and improved clarity of how the experiment was conducted have now been included in the revised experimental section, as requested. The abstract (lines 15-17) have now been rewritten to make clearer the distinction between phthalic anhydride formed during reaction and phthalic acid detected in denuder samples. The use of the denuders was handled by reference to Kleindienst et al. (2004, 2009). Other experimental details have already been included in the Table 1 entry for ER479. The RH was 30% as now given in the caption for Table 1. The experimental section now includes added details as seen at the end of Paragraph 3 on p.8.

2. Was gas-phase phthalic anhydride measured during the experiments? This information would be useful considering phthalic acid is mechanistically linked to phthalic anhydride.

Response: In general, gas-phase phthalic anhydride could not be measured given the analytical tools available to us and could only be inferred from phthalic acid detected during the denuder collection of chamber effluent from a supplementary experiment ER479. Thus, it is difficult to unambiguously link mechanistically the gas-phase ph-

C6150

thalic anhydride concentrations to phthalic acid concentrations in the aerosol. In addition, on occasion early in our experimental program (2000-2002) in unpublished data, we found evidence that was consistent for phthalic acid detected in organic-extractable denuder samples of ambient atmospheres. Whether this was due to the uptake of phthalic anhydride is unknown and was never pursued. We have now made clear in the text that our measurement of phthalic acid is only a proxy for gas-phase phthalic anhydride. Of course, since we could not measure phthalic anhydride directly, it is largely untenable to determine its gas-phase concentration. We have made these points in the revised text in the last sentence of Paragraph 3 on p.8.

3. As the authors have mentioned, the plausible formation pathway of phthalic acid is from the heterogeneous hydrolysis of phthalic anhydride involving aerosol liquid water. For such a reaction, one would expect the hydrolysis is sensitive to in-situ pH condition on the particles. In the experiments in this study, ammonium sulfate is used as seed aerosols and it seems that aerosol acidity as an experimental parameter was not investigated. For many ambient particles, the in-situ pH is likely more acidic than the ammonium sulfate particles used in this study. Can the authors comment on how aerosol acidity might affect the mass fraction yields of phthalic acid, based on available literature information and their own observations (if any)? A few sentences in the discussion or the summary section would help readers to appreciate the potential uncertainties in using the mass fraction data reported in this work.

Response: We appreciate the comment and are currently trying to understand the effect of aerosol acidity, that is from acidic sulfate aerosol, as part of our present experimental program. At this point, we have seen increases in SOA produced by naphthalene photooxidation in the presence of acidic sulfate aerosol, but these findings were considered outside the scope of the present work. A consideration of the shortcomings and uncertainties of the approach is found in the discussion and handled by reference.

4. The mass fraction values are determined using both authentic standards of phthalic acid and the surrogate standard of cis-ketopinic acid (KPA) (Table 4). I expect that

C6151

phthalic acid quantified using the two approaches would differ by a constant factor (i.e., the GCMS calibration response factor ratio) among different sets of experiments. But this factor varies from 0.57 to 3.84 (Table 4). Can the authors elaborate on this non-constant factor between the two sets of "phthalic acid" values?

Response: We appreciate the reviewer's diligence in evaluating the data. However, we believe the reviewer's expectation for the data consistency may perhaps be higher than that achievable by this analysis, especially using the five-ion approach and scaling to the total ion chromatograph to obtain the concentrations. For example, occasionally when the sensitivity of the instrument deteriorates due to progressive source contamination, poor internal standard sensitivities will increase variations in the tracer concentrations. This is a possible explanation for the variation noted by the reviewer. Overall, this is not a major problem but occasionally can be seen in a specific dataset. In addition, there can be variations in the measurement of the aerosol mass, as well. Doing the calculation that the reviewer has performed simply places the values in the worst possible light using realistic data for tracers, (e.g., KPA tracer value for ER459-1 as one example). We take the reviewer's concern seriously and have added a comment in the Results regarding the possibility of outliers from the analysis. Of course, this will be a problem with any experimental study where different methods are used to measure the same metric laying bare possible inconsistencies. We have always acknowledged that uncertainties in the approach can be high and have always referred to the resultant SOA attribution masses as estimates (see Kleindienst et al., 2007). On the other hand, other research groups have applied the laboratory data from this approach to their own field measurements with some success to achieve realistic SOA source attribution.

5. How was OM determined? Was OM determined to be the total aerosol mass minus the mass due to ammonium sulfate? Please provide this information in the paper.

Response: OM was determined by gravimetric means as discussed on p. 12,171 line 4. For all of these experiments, approximately 1 (micro)g m⁻³ of ammonium sulfate seed aerosol was used. The ammonium sulfate seed was a negligible fraction of the total

C6152

organic aerosol mass collected but was nonetheless subtracted from the measured gravimetric mass. In general, the seed aerosol mass was estimated using SMPS volume data before the laboratory irradiation began. The aerosol mass corrected for the 1 (micro)g m⁻³ is now mentioned in the text immediately after the gravimetric mass text at the top of p.8.

6. Table 3: There are multiple data entries for each experiment. Please explain in a table note why there are more than one data entries for one experiment.

Response: In Table 3, footnote "d", has been expanded and should cover the explanation sought by the reviewer. Differences represent minor variations in the flow-mode operation of the chamber and leading to some variation between collection periods of the same nominal conditions.

7. The mass fraction of phthalic acid in SOA from naphthalene in presence of NO_x is given to be 0.023 in the abstract, but this value is listed to be 0.0199 +/- 0.0084 in Table 4. And an average mass fraction of 0.0193 was used to estimate SOA for ambient data (page 12185, line 13). Please check and report consistent data.

Response: We have now made the abstract and Table 4 consistent.

8. The mass fraction used for estimating SOA in ambient samples is 0.0199, obtained from the naphthalene photooxidation experiments in the presence of NO_x. However, the OM/OC ratio used (1.954) is the average value obtained in experiments for both with NO_x and without NO_x cases. Please revise and use consistent data.

Response: We have now used the experiments with NO_x present in reporting the mass fraction and the OM/OC values.

9. It will be helpful and convenient for readers if the authors can include in Table 3 the average OM/OC values obtained in the naphthalene, 1-MN, and 2-MN experiments.

Response: For the methylnaphthalenes, there are only single measurements for OM/OC under specific types of experiments and an average would have no meaning

C6153

per se. For naphthalene, we have included the individual OM/OC values in the table and have chosen to give the averages in the text only, given that Table 3 is already complex and the values in the text at the top of p.12 and in abstract should be sufficient for the discerning reader.

10. Page 12172 - Line 27, authors mentioned "The use of the five-ion-to-TIC calibration factor. . .", Please specify which five ions of phthalic acid were chosen for quantification.

Response: The five ions used in the phthalic acid analysis are now specified in the text. In general order of decreasing intensity, they are m/z 295, 221, 311, 339, and 351 and given as the respective fragments and adducts of (M-15), (M-89), (M+1), (M+29), and (M+41). Again, in some cases the intensity order varies, especially between laboratory and field samples, although where there is variation, retention time is an additional constraint. This information is found in the text at the bottom of p.9 and continuing on p.10 both for phthalic acid and the methylphthalic acid isomers.

11. The authors report two mass fractions of SOA for phthalic acid in terms of quantification by both authentic standards and KPA in both presence and absence of NOx scenario. For the previous SOA tracer mass fraction data from the authors' team, only a single-valued mass fraction of SOA for isoprene, α -pinene, β -caryophyllene and toluene was given (Kleindienst et al., 2007). Can the authors make a clear recommendation whether the mass fraction determined in the presence of NOx (i.e., 0.0199 ± 0.0084) for phthalic acid is more applicable to ambient samples?

Response: We now make such a recommendation for ambient samples in the abstract and at the bottom of p.1.

Minor comments:

1. Page 12164, Line 25, suggest replacing "other PAHs tested" with "methylnaphthalenes as well".

Response: Suggestion accepted and found at the top of p.2.

C6154

2. Page 12166, the sentence "It appears that . . . emission rates." (Lines 14-17) is difficult to understand. Please re-phrase.

Response: Suggestion accepted. The third paragraph on p.3 has been largely rewritten to improve clarity.

3. Page 12172, Line 8, experimental method, please specify the temperature and duration for derivatization or give a reference from which this information can be found.

Response: The BSTFA derivatization is sufficiently aggressive that at room temperature the reaction is generally complete within an hour although the allowed reaction period is 2 h. The details are the same as those described in Jaoui et al. (2004), Anal. Chem. 76: 4765-4778, which is now given in the first sentence of the final paragraph on p.8.

4. Page 12175, Line 4, the average OM/OC value was reported 1.93 here, but the value reported on page 12185, Line 14 was 1.954. Please check data and remove the inconsistency.

Response: Recommendation accepted.

5. Page 12179, line 20: please provide one or more references for ". . . mainly through diesel exhaust emissions".

Response: The sentence has been changed to read: "Polycyclic aromatic hydrocarbons have been found to be emitted from the combustion of fossil-fuels, for example, through diesel exhaust emissions (Schauer et al. 1999)." This sentence is found in the final paragraph of p.16. Schauer et al. (1999) was already in the reference list.

Technical Corrections:

Page 12170, Line 29: 8 Lmin-1 Page 12172, Line 2-3: improves the chromatography of tracer peaks that might otherwise tail considerably Page 12172, Line 10: extraction

Page 12179, Line 5: "during the weekend with peak values from the 10:00-15:00 h

C6155

time period” is redundant, as the same information is given in the next sentence. Page 12183, line 25: the “Hu et al., 2008” reference is missing in the references section.

Response: Technical corrections made.

Additions to text and references.

The following text was added:

“These trends are similar to the findings of Stone et al. (2009) for composite SOA.” This sentence refers to the observation by Stone et al. (2009) that weekend SOA attribution masses were higher than weekday mass and is also seen in this work as shown in Figure 4. The sentence appears toward the end of the second paragraph on p.16. The Stone et al. (2009) reference has been added.

Hu et al. (2008) was missing as noted by Reviewer 2 and has now been added.

Shakya and Griffin (2010) has now been added.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12163, 2012.