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Comment

## ***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.**

**Anonymous Referee #2**

Received and published: 13 July 2012

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

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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 (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.

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

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

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uncertainties in using the mass fraction data reported in this work.

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 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?

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.

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.

7. The mass fraction of phthalic acid in SOA from naphthalene in presence of NO<sub>x</sub> 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.

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<sub>x</sub>. However, the OM/OC ratio used (1.954) is the average value obtained in experiments for both with NO<sub>x</sub> and without NO<sub>x</sub> cases. Please revise and use consistent data.

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.

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.

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 NO<sub>x</sub> scenario. For the previous SOA tracer mass fraction data from the authors’ team,

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only a single-valued mass fraction of SOA for isoprene,  $\alpha$ -pinene,  $\beta$ -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 NO<sub>x</sub> (i.e.,  $0.0199 \pm 0.0084$ ) for phthalic acid is more applicable to ambient samples?

Minor comments:

1. Page 12164, Line 25, suggest replacing “other PAHs tested” with “methylnaphthalenes as well”.
2. Page 12166, the sentence “It appears that ... emission rates.” (Lines 14-17) is difficult to understand. Please re-phrase.
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.
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.
5. Page 12179, line 20: please provide one or more references for “... mainly through diesel exhaust emissions”.

Technical Corrections:

Page 12170, Line 29: 8 Lmin<sup>-1</sup> 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 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.

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

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