

Interactive comment on “Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs)” by A. W. H. Chan et al.

A. W. H. Chan et al.

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We thank reviewer 1 for the insightful comments. Changes have been made to address the issues raised. In particular, an analysis of SOA production from aromatics and PAHs over longer timescales is added. Please see our responses below.

A. I fear that the SOA production estimates in section 5 are biased towards the importance of PAHs. The light aromatics react slower with OH than the PAHs and therefore, the relative importance of PAHs is higher after a shorter reaction time. After 12 hours, the longest reaction time considered in Tables 4 and 5, the removal of light aromatics is not complete, so I would at least add a column with a significantly longer reaction

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time to show what happens when the chemistry is complete.

We agree with the reviewer that in short timescales (e.g. 3 hours employed in the Robinson et al. (2007)), SOA production from PAHs is favored over that from light aromatics, not only owing to the higher SOA yields from less volatile PAHs, but also to the faster reaction rates with OH radicals. This has been noted in the manuscript in Section 5.1. A reaction time of 12 hours was chosen in Tables 4 and 5 for the maximum duration of photooxidation in the atmosphere before nighttime chemistry occurs (which is not considered in this work). Also, in this study, the SOA yields were measured over the course of at most 20 hours. The role of aging is uncertain over longer timescales. Assuming these measured yields still apply, light aromatics are expected to dominate SOA formation over longer timescales (much greater than 12 hours) owing to higher emissions. The analysis in this manuscript only represents urban environments where the photochemical age is short and NO_x concentrations are high. To better represent longer photochemical ages, we have included an estimate of SOA production from these compounds assuming complete reaction. (See response to the next comment)

B. The problem is more complicated than that, because after a certain reaction time, the NO_x levels can no longer be assumed to be high and the SOA yields are higher than near the sources. A paper from the same group (Henze, ACP 2008) studied the relative importance of low-NO_x versus high-NO_x pathways for light aromatics and found that the majority of the SOA from these compounds was formed through the low-NO_x pathway. Again, this indicates that the production estimates in tables 4 and 5 may be biased towards PAHs. I do not suggest that the authors do a full model calculation of PAH oxidation in the atmosphere, but to bracket the actual atmospheric importance, it would be very good if the calculations in tables 4 and 5 would be rerun with the low-NO_x yields.

We have added an estimate of SOA production from diesel exhaust and wood burning for much longer photochemical ages in Tables 4 and 5, respectively. Here we assume that reaction with OH is the only sink for all gas-phase hydrocarbons (ignoring deposi-

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tion and nighttime chemistry). To account for the difference in SOA formation from light aromatics between high- and low-NO_x pathways, we use the branching ratios calculated by Henze et al. (2008) for benzene, toluene and *m*-xylene. Because naphthalene has a similar OH rate as *m*-xylene, we use the same branching ratio for naphthalene. For all other PAHs, we assume they all react under high-NO_x as a conservative estimate. For *n*-alkanes, since their low-NO_x yields are not known, they are not included in this part of the analysis. The results are presented in Tables 4 and 5, and the following paragraphs have been added to Sections 5.1 and 5.2 to discuss the significance:

Section 5.1: “To estimate the SOA production from diesel exhaust over longer timescales (> 12 h), we assume that the reaction time is sufficiently long that all of the hydrocarbon has been consumed by reaction with OH radicals (ignoring nighttime chemistry and deposition of gas-phase hydrocarbons). This also allows for the air mass to be transported away from the sources, where the NO_x levels are lower and aromatic compounds are expected to produce SOA at higher mass yields (Henze et al, 2008, Ng et al., 2007b). To account for the difference in SOA formation from light aromatics between high- and low-NO_x pathways, we use the branching ratios calculated by Henze et al. (2008) for benzene, toluene and *m*-xylene. Because naphthalene has a similar OH rate as *m*-xylene, we use the same branching ratio for naphthalene. For all other PAHs, we assume they all react under high-NO_x as a conservative estimate. For *n*-alkanes, since their low-NO_x yields are not known, they are not included in this part of the analysis. We caution readers that this is a zeroth-order estimate to compare SOA formation of light aromatics and PAHs over longer timescales. Multi-generation oxidation chemistry and aerosol aging will play an as yet undetermined role beyond the timescale over which these SOA yields were measured. Nonetheless, over very long timescales, the contribution of PAHs to overall SOA production is about half that of light aromatics (see Table 4).”

Section 5.2: “Assuming the SOA yields do not change, PAHs contribute a comparable amount of SOA to light aromatics over very long timescales.”

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C. In many studies the amount of SOA formed in an air mass is related to that of an inert tracer such as CO or acetylene. The emissions from Schauer, which the authors use as input for their calculations, do not give CO but they do give acetylene. It would be of interest to relate the amount of SOA formed from PAHs to the amount of acetylene emitted and compare that ratio to the results of field studies. For example, deGouw (JGR 2005) gives values for SOA versus acetylene in urban air. The comparison needs to be done carefully, as the field data only give information on average SOA formation in an urban plume (Diesel and gasoline vehicles), whereas the current study gives information on these separate sources.

This is a very good idea. As noted in the manuscript, the analysis considers only single sources derived from emission studies. To assess the overall significance of PAH oxidation, we must consider the relative contributions of diesel and gasoline exhaust, biomass burning, cooking operations and other primary sources to an urban plume. Because the emissions can be highly variable even for one type of source (e.g. diesel), it is difficult to carry out such analysis to properly estimate SOA production for a typical urban plume. Alternatively, we have looked at emission inventories of gas-phase compounds compiled by the EPA. The EPA National Emission Inventory (NEI) includes emissions of single-ring aromatics (benzene, toluene, xylenes) and naphthalene. The emission factor for naphthalene is an order of magnitude less than the single-ring aromatics. Based on these numbers, we estimate that the contribution of naphthalene to total SOA production from the United States will be small compared to that of light aromatics. However, naphthalene is the only gas-phase PAH that is included in this inventory. As shown in the diesel example, emissions of other PAHs can also produce a significant amount of SOA. To assess the atmospheric importance of our results, we will also study the chemical composition of the SOA produced by PAHs and identify the important aerosol-phase products. We will then look for chemical signatures in urban SOA and compare to our chamber study.

Line 3–7: I would not say that semi-volatiles were previously assumed to be inert. It

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was not until the work of Robinson (Science 2007) that their emissions were positively identified.

This sentence has been removed from the abstract.

Line 21: Do we really know that PAHs account for a large fraction of semi-volatile emissions?

From the available literature, PAHs account for a significant fraction of the *identified* semivolatile emissions. As noted by reviewer #2, a large fraction of the emissions is not resolved under the analytical technique employed. Without knowledge of the chemical composition of the UCM, it is difficult to properly account for SOA formation of oxidation of diesel exhaust. However, among the classes of compounds considered in this analysis (PAHs, light aromatics, *n*-alkanes), PAHs are likely the most reactive and therefore produce significant amounts of SOA upon photooxidation.

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