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Atmospheric
Chemistry
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Discussions

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.

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We thank reviewer 2 for the helpful comments. Changes have been made to address the issue of IVOC definition. We have also addressed the issues of effects of methyl substitution on SOA yields, and emission inventories of PAHs. Please see our response below.

1. IVOC definition in intro (line 20). The paper states that CMU group calls semivolatile compounds as IVOC. This is not quite right (see Donahue et al. AE 2009 for definitions). The CMU group uses the term IVOCs to refer to low volatility organic that are not semivolatile but exist exclusively in the vapor phase in the atmosphere (e.g. C-12 to

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C-20 n-alkanes); napthalenes are at the most volatile end of this category. Therefore, from an atmospheric perspective, IVOCs are really just low volatility VOCs, but they have largely been overlooked in inventories and models so they have been given a special name 8211; IVOC. In addition, from a measurement perspective, one typically must use different techniques to measure IVOCs (sorbents) compared to traditional VOCs (canisters). So there is an operational reason to name them different things.

To be consistent with the literature, we now refer to all 2-ring PAHs and n-alkanes considered here as IVOCs. We refer to other semivolatile organic compounds, those that are distributed between gas- and particle-phases, as semivolatile OCs (SVOCs).

2. The modeling compares SOA production from different classes of precursors (PAH, n-alkanes, and light aromatics). The work also mentions some other classes that need study such large aldehydes. However, a challenge as one considers higher MW precursors is that the vast majority of these emissions (IVOCs and SVOCs) from motor vehicles and other sources have not been speciated. Diesel, in particular, is a real problem. For example, Figure 3 in the Schauer 1999 EST paper on diesel exhaust shows that only about 4% of the semivolatile vapor emissions have been speciated (the other 96% is reported as UCM). About 2% of the semivolatile vapors are PAH vapors such as those considered here and about 1% is n-alkanes. Therefore the modeling presented in the paper only accounts for a very small fraction of the IVOC emissions from a diesel engine. (Note that Schauer semivolatile vapors as material collected on denuder/filter/PUF sampling train, this includes things like naphthalene which are not technically semivolatile). Although aromatics likely have much higher yields than the "UCM" (which is presumably a complex mix of branched and cyclic hydrocarbons), the UCM is the dominant component of the IVOC emissions (at least from diesel vehicles) and therefore may also be an important SOA precursor. The paper is careful to state that the modeling only considers three classes of precursors, but I think that it is important to provide this broader perspective. The UCM creates substantial challenges for SOA modeling and experiments. (I see that reviewer #1 also raised some concerns

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with the modeling from the perspective of traditional SOA precursors. It is challenging to strike the right balance on this, but this sort of framing analysis can be very insightful).

We agree with both reviewers that the chemical composition of diesel exhaust is still relatively unknown, and can be highly variable (similar to biomass burning). Here we use the emission profile from Schauer et al. (1999) because the engine used has a similar toluene/particle mass ratio as the one used in Robinson et al. (2007). It is therefore easier to compare the “known” SOA source (light aromatics) with PAHs studied here and n-alkanes. 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. Nonetheless, once analytical techniques allow for more complete speciation of gas-phase diesel emissions, SOA production from these IVOCs can be estimated from SOA yields measured in this study. We have added the following sentence to the manuscript to address this concern:

“Only a small fraction of the compounds present in diesel emissions are speciated in Schauer et al. (1999b), but considering only these three classes of compounds, PAHs are estimated to account for up to 54% of the SOA formed in the first 12 h of diesel exhaust photooxidation, representing a potentially large source of atmospheric SOA.”

3. At low NOx the yields are fixed with naphthalene giving the highest yield followed by 1-MN, and then 2-MN. This is opposite to carbon number which seems interesting. Given that the compounds have similar chemical structure one might have expected the opposite trend with the largest molecules producing the highest yields. The data indicate that this is not the case. This should be pointed out in the manuscript. Any ideas why?

We cannot conclude from our experiments that there is a dependence of SOA yield on carbon number under either NOx conditions. Under low NOx, only 2 carbon numbers (C10 and C11) were studied. Under high NOx, SOA yield of 1,2-DMN is lower than those of 1- or 2-MN, which are higher than that of naphthalene. While the volatility of oxidation products can depend on their molecular weights, the branching ratios of ring-retaining versus ring-opening pathways are also dependent on the degree of substitution by methyl groups. For example, for alkanes, fragmentation is favored over isomerization for methyl-substituted alkanes (Lim and Ziemann, ES&T 2009). This would suggest that radicals from 1-MN and 2-MN are more likely to decompose than those from naphthalene under low NOx, where ring-opening is not the dominant pathway. As a result, it is likely a combination of these two effects (increasing MW vs increasing decomposition) that ultimately determines the SOA yields. The dependence of SOA yields on the number of methyl groups is also unclear for single-ring aromatics. More study with other methyl-substituted aromatic compounds (single-ring and PAHs) is warranted.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1873, 2009.