Atmos. Chem. Phys. Discuss., 9, S562–S564, 2009
www.atmos-chem-phys-discuss.net/9/S562/2009/

Atmospheric
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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.

Anonymous Referee #2

Received and published: 4 March 2009

This is an important, well-written paper that should be published in ACP. It describes a smog chamber study of secondary organic aerosol (SOA) production from naphthalenes under high and low NOx conditions. SOA production from polycyclic aromatic hydrocarbons has not previously been studied and is not currently included in atmospheric models. The results demonstrate that napthalenes have high SOA yields (˜ 50% at atmospherically relevant conditions), much higher than single ring aromatics. Similar to other compounds, the yields are NOx dependent, with higher yields at low NOx conditions. There is some variation with yield with structure (some of which seems

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counter-intuitive, see comments below). The paper presents fits of the yield data for use in chemical transport models.

The paper also presents some simple model calculations to assess the relative importance of different classes of SOA precursors (light aromatics, PAHs, and n-alkanes). This analysis suggests that PAH are a very important class of SOA precursors in urban environments, contributing two to three times more SOA than light aromatics. Therefore including PAHs in atmospheric models may help explain the large amounts SOA observed in urban environments and smog chamber studies with real emissions. The modeling also illustrates the interplay between reactivity, emissions, and yield in determining the relative importance of a different SOA precursor. The modeling is a very nice piece of analysis that helps frame the issues.

I only have a few comments that the authors should consider when revising the manuscript.

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 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 – 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.

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 pre-

cursors 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 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).

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?

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

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