

Interactive comment on “A new method to discriminate secondary organic aerosols from different sources using high-resolution aerosol mass spectra” by M. F. Heringa et al.

Anonymous Referee #1

Received and published: 22 December 2011

Review of “A new method to discriminate secondary organic aerosols from different sources using high-resolution aerosol mass spectra” Author(s): M.F. Heringa et al. ACP manuscript # MS No.: acp-2011-845

The identification of the sources of secondary organic aerosol (SOA) is an important and very challenging problem. Our current understanding of the sources of SOA is largely based on chemical transport models and receptor models using molecular tracers for different types of SOA. In this paper they attempt to differentiate sources of SOA using HR-AMS data. HR-AMS data have been widely used to separate ambient organic aerosol into primary and secondary components. HR-AMS analysis has also

C13573

been used to separate primary organic aerosol into source classes, but HR-AMS analysis has only separated SOA into more and less oxygenated components which do not appear to have any link to sources.

This paper describes a study that differentiates between four different classes of secondary organic aerosol (SOA) using HR-AMS data: SOA formed from α -pinene, SOA formed from diesel engine exhaust, SOA formed from 2-stroke gasoline motor scooter exhaust, and SOA formed from woodsmoke. To do this they have conducted smog chamber experiments to characterize the SOA formation from each of these precursors. The chamber experiments have been described in previous publication. The new contribution of this paper is that they have analyzed and compared the high resolution aerosol mass spectra measured to identify mass spectral signatures for each of these different types of SOA. They report results from several different techniques, including grouping ions based on their elemental composition and principal component. They demonstrate that they can differentiate between the different types of SOA formed in the smog chamber. They compare results from chamber to ambient measurements made in two European cities.

This is an important topic of interest to ACP readers. It is a very challenging problem and this paper takes an important step forward, but inevitably there are outstanding questions and challenges. The paper is well written and I recommend it be published in ACP after the authors address the following comments:

A major challenge with SOA is that its properties depend on so many different parameters: precursor composition, organic aerosol concentration, oxidant concentrations, seed aerosol type and concentration, VOC/NO_x ratio, etc. In this paper they are trying to differentiate between SOA formed from different precursors (sources), which is only one (but certainly an important one) parameter that SOA composition depends on. To rigorously do this requires that all of the other parameters that influence SOA formation should be held constant across the set of experiments. This is very difficult to do experimentally (especially with emissions from actual sources) and I suspect that

C13574

differences in experimental conditions may influence the results. How can we be confident that the differences identified by the authors are not due to some other parameter besides precursor composition? The authors need to provide some discussion to alert readers to this problem and limitations of the data. The authors need to list key values for experimental conditions that likely influence HR-AMS mass spectra. I would think that this table would include: precursor concentrations, seed concentrations, organic aerosol concentration, average oxidant concentration, extent of oxidation, and VOC/NO_x. The authors then need to describe what is known about how these different parameters effects of these different parameters on AMS mass spectra (e.g. there are multiple studies that show how changes in organic aerosol concentration / partitioning alter systematically aerosol mass spectra).

A similar concern to the previous one is that source emissions can be highly variable, especially biomass burning emissions. Not surprisingly AMS BBOA spectra show a lot of variability. Chamber aging experiments (e.g. Hennigan et al. ACP 2010) have shown a wide variability in SOA production and composition. How robust are the measures proposed here given that variability? E.g. for BBOA m/z 60 is thought to be a pretty robust indicator for BBOA, 44 for SOA, 57 HOA. It seems like we need to identify similar robust features for SOA. These questions cannot be addressed with the current dataset which only includes information for one source, but the authors need to at least point out this challenge to the reader.

Other approaches that have been used to classify SOA by source are receptor models with organic tracers and chemical transport models. The paper should include a sentence or two in and some references to alert readers to these other approaches and what they have found (Schauer and others have recently published papers on the organic tracer approach for SOA, Pandis and others have published papers on transport modeling approaches).

Were the experiments conducted with seed aerosols? It seems that they were not – heated filter page 29061. Presumably that removed the refractory component of emis-

C13575

sions (BC). Did any POA condense in the chamber when the exhaust was cooled as it mixed with chamber air? Some of the induction of observed in scooter and α -pinene photo-oxidation could have been due to lack of seed (see e.g. Kroll et al. chamber work on isoprene, or Pathak et al. work on α -pinene). How would that influence the composition of the mass spectra?

Figure 2 – presents particle number. A more useful parameter to present is particle mass (or OA) in chamber, since this influences partitioning and AMS mass spectrum. It is not clear what % organic refers to? This suggests there were seed particles in the experiments.

Figure 4 – O:C depends on lots of parameters. Were the OA concentrations in these experiments the same? Could that have influenced the O:C ratio? It would be useful to present the data in a way that tries to isolate what is influencing O:C (beyond precursor composition). It is clear that time since lights on is not strongly influencing O:C.

Figure 4 – this shows at most modest increases in OA with additional time. Was there significant photo-oxidation occurring in chamber after 1 hour? I.e. was there the potential for more chemistry. What fraction of the precursors mass was consumed during the experiment?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29055, 2011.

C13576