AUTHORS’ COMMENTS

The authors would like to thank both reviewers for their helpful comments and suggestions. All comments are addressed below. Reviewer comments are in plain text and our responses are in italics.

Response to Reviewer 1

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 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 agree that beside the source type there are many parameters that can have an influence on the processing pathways, extent of aging and partitioning. When using actual emission sources, not only parameters like the VOC/NO_x *ratio will vary but also the emissions of these sources show a day-to-day variability. These variabilities within a single source can influence the mass spectral fingerprint and therefore its position in the PCA model resulting in a decrease in clustering performance of the sources. However, the good clustering of the duplicate scooter experiments indicate that, although the second experiment was performed at a concentration five times higher than the first experiment, the partitioning did not have a major effect on the PCA clustering. Additionally, the two α-pinene experiments were performed at different VOC/*NO_x *ratios and with different types of aging (Table 1.) and cluster fairly well.*
The models shown in this manuscript are based on the results of laboratory studies on real emission sources which are not identical to the results that can be expected during all ambient conditions. This will be addressed in the introduction which will be changed to:
In this paper, we describe the properties of fresh and aged SOA from the gas phase emissions of a log wood burner, a Euro 2 diesel car without emission abatement devices and a Euro 2 scooter. Mass spectral features of SOA are depending on many parameters like VOC/NO_x *ratio, concentration and temperature. Therefore, the models shown in this manuscript, based on the results of laboratory studies on real emission sources, are not necessarily identical to the results that can be expected during all ambient conditions.*

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 alert mass spectra).

Parameters like NO_x*, organic aerosol concentration and the OA O:C ratio are described in Table 1. There was no instrumentation available to measure VOC and OH concentration. Although differences in OH exposure can be expected between the different experiments the change in O:C ratio was very similar for the different photo-oxidation experiments. All experiments were performed without seed particles.*

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., 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.

The authors agree that achieving an average fingerprint of a highly variable source like wood burning is difficult and only possible when many burners, wood types and burning conditions are tested. This will be addressed in the text. Because of the averaging effect of the long sampling time (~1 hour) fluctuations in burning conditions should be reduced compared to the variability of experiments with shorter sampling times. Additionally, PCA uses all the information in the organic mass spectrum and therefore reduces the effect of the variability of single ions. SOA fingerprinting will also present a challenge with variability similar to what is seen with wood burning, and the authors are interested in applying this method to SOA systems and datasets to see what can be learned from this method.

Other approaches that have 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).

This will be added to the introduction. The modified part will read:

Although other techniques, like organic tracers, PMF and modeling can supply information about different POA and SOA sources (Kleindienst et al., 2007; Lewandowski et al., 2008; Schwartz et al., 2010; Farina et al., 2010; Andreani-Aksoyoglu et al., 2008), the high time resolution of the AMS in combination with the ability to measure quantitatively the major fraction of PM_1 *OA, AMS data could supply important information for the quantification of SOA from different sources.*

Were the experiments conducted with seed aerosols? It seems that they were not – heated filter page 29061. Presumably that removed the refractory component of emissions (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 a-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 a-pinene). How would that influence the composition of the mass spectra?

All experiments where conducted without seed aerosol and no nucleation was observed in the smog chamber before the lights were switched on. The use of a non-reactive seed aerosol could lead to an early condensation of semi-volatiles and might therefore slightly increase the heterogeneous reaction over the duration of the experiment. Based on the rapid increase in OA concentration by SOA formation, the gas phase reactions are expected to be faster and therefore dominating the mass spectral features.

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.

Particle number was chosen to show the different rates of nucleation of the different experiments. The organic concentrations were normalized to the maximum concentration during each experiment to compare different experiments with different concentrations. The % organic axis label has been changed to % of maximum OA concentration. The SOA concentration after 5 hours, when the reference spectra were taken, is found in Table 1.

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 OC.

The OA concentration after 5 hours of aging was < 75 µg/m^3 for all experiments and 6 experiments were in the range of 4 - 20 µg/m^3. This indicates that the variability between experiments was typically less than one log-bin in the volatility basis set framework. The influence of the nucleation and increase in OA concentration on the O:C ratio is discussed starting line 29 at page 29065. The observation that the source with the highest O:C ratio had the largest fraction of small ions could be explained by the higher degree of oxygenation needed for smaller molecules to reduce their vapor pressure enough to partition to the particle phase. However, neither increased fragmentation of more oxygenated molecules nor variations in OH concentrations for the different experiments can be excluded as possible causes for this observation and therefore further investigations are needed.

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

The fraction of precursor mass that was consumed could not be determined since there was no available gas phase instrumentation to monitor precursor species. However, the increase in OA concentration, shown in Fig. 2, indicates that the SOA formation rate was larger than the wall loss rate indicating ongoing photo-oxidation during the experiments.

Response to Reviewer 2

1) The application of principal components analysis to mass spectra data is not new, thus the title should be revised.
Principal component analysis has been used on mass spectral data but to our knowledge PCA has not been used for the discrimination of SOA spectra and therefore in our opinion the title is appropriate.

2) The paper appears to be written for AMS users. Attention to information pertinant to the larger community should be included and/or emphasized.
It is true that a fraction of the text is rather specific to the AMS measurements but this was the main instrument used here. Conceptually, such experiments could also be done with other instruments, which is now emphasized in chapter 3.4:
Principal component analysis was applied on the AMS spectra to improve the separation of the four different types of SOA produced in the smog chamber. This approach could also be applied to data from other instruments or data from a set of instruments.

3) The abstract is ackwardly written with too many details.
The abstract has been simplified and will read:
Organic aerosol (OA) represents a significant and often major fraction of the non-refractory PM_1 *(particulate matter with an aerodynamic diameter* $d_a < 1\mu m$*) mass. Secondary organic aerosol (SOA) is an important contributor to the OA and can be formed from biogenic and anthropogenic precursors. Here we present results from the characterization of SOA produced from the emissions of three different anthropogenic sources. SOA from a log wood burner, a Euro 2 diesel car and a two-stroke Euro 2 scooter were characterized with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) and compared to SOA from α-pinene.*
The emissions were sampled from the chimney/tailpipe by a heated inlet system and filtered before injection into a smog chamber. The gas phase emissions were irradiated by xenon arc lamps to initiate photo-chemistry which led to nucleation and subsequent particle growth by SOA production.
Duplicate experiments were performed for each SOA type, with the averaged organic mass spectra showing Pearson's r values > 0.94 for the correlations between the four different SOA types after five hours of aging. High-resolution mass spectra (HR-MS) showed that the dominant peaks in the MS, m/z 43 and 44, are dominated by the oxygenated ions $C_2H_3O^+$ *and* CO_2^+*, respectively, similarly to the relatively fresh semi-volatile oxidized OA (SV-OOA) observed in the ambient aerosol. The atomic O:C ratios were found to be in the range of 0.25 - 0.55 with no major increase during the first five hours of aging. On average, the diesel SOA showed the lowest O:C ratio followed by SOA from wood burning, α-pinene and the scooter emissions. Grouping the fragment ions revealed that the SOA source with the highest O:C ratio had the largest fraction of small ions.*
The HR data of the four sources could be clustered and separated using principal component analysis (PCA). The model showed a significant separation of the four SOA types and clustering of the duplicate experiments on the first two principal components (PCs), which explained 79% of the total variance. Projection of ambient SV-OOA spectra resolved by positive matrix factorization (PMF) showed that this approach could be useful to identify large contributions of the tested SOA sources to

SV-OOA. The first results from this study indicate that the SV-OOA in Barcelona is strongly influenced by diesel emissions in winter while in summer at SIRTA at the southwestern edge of Paris SV-OOA is more similar to alpha-pinene SOA. However, contributions to the ambient SV-OOA from SOA sources that are not covered by the model can cause major interference and therefore future expansions of the PCA model with additional SOA sources is recommended.

4) SOA may also result from accretion reactions and oxidation reactions that occur in the aerosol phase. Review the following for more information: Chacon-Madrid et al., Functionalization vs. fragmentation: n-aldehyde oxidation mechanisms and secondary organic aerosol formation, PCCP, 2010 and related papers.
SOA formation and properties can indeed be influenced by accretion and heterogeneous reactions. The sentence in the manuscript will be modified to read "This bulk organic property can change by condensation of SOA, accretion reactions and heterogeneous chemistry. In addition, molecules in equilibrium between the particle phase and the gas phase can evaporate, oxidize in the gas phase and condense again as more oxidized species".

5) It is said that the "properties of fresh and aged SOA. . ." will be described. The composition emphasis is on the aged SOA with very little discussion of the fresh SOA composition.
The properties of the fresh SOA is described by the temporal evolution of the O:C ratio (Fig. 4.) and the dynamics in the fCO_2 *vs.* fC_2H_3O *graph (Fig. 5.). Additionally, all data points from the fresh SOA are included in the SOA separation graphs (Fig. 7, 8 & 10.). A more detailed comparison of the fresh and more aged SOA within one SOA source was considered out of the scope of this manuscript.*

6) It's not clear why the authors discuss the details of the UMR mass spectra. I think the authors made a point that HR spectra are needed to differentiate SOA sources. Inclusion of both spectra in the discussion and PCA analyses is confusing as written.
The PCA section starts with the UMR mass spectra since the application of PCA on UMR data first was the legitimate progression. The authors made the decision to include the graph and details of the UMR data because this could be of interest of the large group of Q-AMS and aerosol chemical speciation monitor (ACSM) users. Only the statement that HR data was necessary to differentiate these SOA sources without a more detailed description was found inappropriate.

7) Please describe the 4 PCA models with more detail. More description will inform the reader of the critical differences between model 2, 3 and 4. Were models run with fresh SOA spectra or only aged? At what point in the 10 hr experiment were the spectra collected? or what time span was averaged?
The PCA models using averaged spectra (Avg UMR and Avg HR) were based on the averaged mass spectra after five hours of aging. These spectra were averaged after five hours over an average time period of 16 minutes. The ten hour data was not used as averaged spectrum but all data points were used individually.
The text describing the four different models will be extended to include this information in Section 3.4.1.

8) What components make up the PCs? What differences in the PCs do you observe? Can you say that the PCs represent the unique aspects of the spectra that constitute a specific SOA type? More details are needed here.

The coordinate of the mass spectrum at PC1 is the sum of the products of the normalized ion signals and the loading of the specific ions on PC1 (calculated as the PCA model). The loading plots (Fig. 9a and SI-1) show which ions have a positive or negative contribution to the first two PCs where Fig. 9b - 9d show the ions colored according to m/z, number of carbon and number of oxygen, respectively. Fig. 9b shows that the larger fragments have a positive contribution to PC1. Additionally, ions with high carbon numbers and no oxygen have in general a positive contribution to PC1 where the ions with two oxygen atoms have a negative contribution to PC1 (Fig. 9c-d). For PC2 there was no general correlation observed between m/z, number of carbon or number of oxygen and the value on PC2.