



# **Evolving mass spectra of the oxidized component of organic aerosol: results from aerosol mass spectrometer analyses of aged diesel emissions**

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# **Evolving mass spectra of the oxidized component of organic aerosol: results from aerosol mass spectrometer analyses of aged diesel emissions**

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## Abstract

The species and chemistry responsible for secondary organic aerosol (SOA) formation remain highly uncertain. Laboratory studies of the oxidation of individual, high-flux SOA precursors do not lead to particles with mass spectra (MS) matching those of ambient aged organic material. And, the complexity of real organic particles challenges efforts to identify their chemical origins. We have previously hypothesized that SOA can form from the atmospheric oxidation of a large suite of precursors with varying vapor pressures. Here, we support this hypothesis by using an aerosol mass spectrometer to track the chemical evolution of diesel exhaust as it is photochemically oxidized in an environmental chamber. With explicit knowledge of the condensed-phase MS of the primary emissions from our engine, we are able to decompose each recorded MS into contributing primary and secondary spectra throughout the experiment. We find that the SOA MS becomes increasingly oxidized as a function of time, eventually reaching a final MS that closely resembles that of ambient aged organic particulate matter. This observation is consistent with the idea that lower vapor pressure, semi-volatile organic emissions can form condensable products with fewer generations of oxidation, and therefore, they form relatively less oxidized SOA very quickly.

## 1 Introduction

Based on available emissions profiles and laboratory-generated yield curves, secondary organic aerosol (SOA) has been estimated to comprise around 60% of the global burden of organic aerosol (OA) (Kanakidou et al., 2005). However, a recent global mass balance calculation for the removal of volatile organic compounds (VOCs) from the atmosphere suggests that this estimate underpredicts SOA production rates by as much as an order of magnitude (Goldstein and Galbally, 2007). Data from several sources support the higher values (Zhang et al., 2007; Volkamer et al., 2006; de Gouw et al., 2005). For example, inexplicably high mass loadings of SOA in photochemically

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young air masses in Mexico City indicate that SOA can be the dominant component of OA there, even locally, at certain times of day (Salcedo et al., 2006). The oxidation chemistry of the high-flux VOCs that have traditionally been considered as SOA precursors cannot explain these observations, which indicates that SOA remains a relatively poorly characterized contributor to atmospheric aerosol.

The deficits in our knowledge of SOA precursors and formation mechanisms are underscored primarily by two facts. First, ambient measurements indicate that SOA concentrations downwind of anthropogenic sources are considerably higher than current models predict (Volkamer et al., 2006). This discrepancy has been documented in studies of major urban areas in North America, Europe, and Asia (de Gouw et al., 2005; Johnson et al., 2006; Heald et al., 2005). Second, chamber studies of the oxidation of the precursors included in these models yield product aerosol with mass spectra (MS) dissimilar to those observed in field campaigns (Alfarra et al., 2006). SOA formed from first-generation products of VOCs like  $\alpha$ - and  $\beta$ -pinene, m-xylene, and trimethylbenzene is not that found in ambient aged organic material (Alfarra et al., 2006; Bahreini et al., 2005).

Taken together, these two facts call into question our understanding of the chemical nature of SOA. In response, efforts have been made to speciate ambient OA (Schauer et al., 1999; Rogge et al., 1993; Williams et al., 2006). However, these efforts are challenged by the complexity of the samples, which have been shown to contain tens of thousands of compounds (Hamilton et al., 2004), with the molecular identity of the majority of the organic mass still unknown. Molecular-level approaches confirm that SOA is the product of complicated, uncontrolled radical chemistry that results in compositionally complex particles; the identities of the individual compounds are unlikely to unambiguously indicate its origin. Consequently, there is a need for physically meaningful parameterizations that will allow this chemistry to be efficiently and accurately incorporated into atmospheric chemistry models.

Due to this need, investigations of the chemical nature of bulk SOA are also underway. Recent advancements in aerosol mass spectrometry have yielded a wealth of

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information about the composition of ambient particles. However, the time-averaged sampling necessary to generate acceptable signal and the high-energy ionization methods standard to mass spectrometry, when combined with the complexity typical of atmospheric organics, result in spectra that cannot be deconvolved to a molecular level. Still, considerable progress has been made in determining the properties of OA based on its total signal. For example, laboratory studies have confirmed the formation of “oligomeric” oxidation products with masses several times those of the reactants (Kalberer et al., 2004). Combined thermal desorption and aerosol mass spectrometry provides insight into the vapor pressures of particle constituents (Chattopadhyay et al., 2001). And, several mathematical methods for the analysis of bulk spectra, informed by existing knowledge of atmospheric organic chemistry, can classify organic material by source, functionality, and oxidation state (Bahreini et al., 2005; Marcolli et al., 2006; Zhang et al., 2005a; Lanz et al., 2007).

Zhang et al. (2005b) have convincingly applied such a method to ambient data collected during the Pittsburgh Air Quality Study. Their approach, employing a custom principal component analysis (CPCA), mathematically deconvolves the organic MS from an Aerodyne quadrupole aerosol mass spectrometer (Q-AMS) into two time-invariant factors: hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA). These two factors combine to explain 99% of the variance in the Pittsburgh data set. Additionally, they show the temporal trends of HOA to be strongly correlated with those of elemental carbon, NO, and CO, indicating that HOA is associated with primary emissions; OOA is similarly correlated with sulfate, suggesting that it constitutes SOA. Preliminary results from other locations have shown similar success using this approach (Zhang et al., 2007; Kondo et al., 2007). Interestingly, the OOA component derived from the CPCA method is not the MS of SOA formed in chamber experiments, suggesting that these experiments are not accurately reproducing either the species or the chemistry involved in ambient SOA formation. This points to the need for laboratory SOA experiments carried out under more atmospherically relevant conditions.

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In response, we have exposed the entire exhaust (vapors and particles) of a diesel generator, without explicit knowledge of its molecular composition, to atmospheric oxidants in an environmental chamber. The goal of this paper is to use AMS data to investigate the chemistry of SOA formation from UV-initiated oxidation of this exhaust.

5 A unique advantage of these experiments is that we know the spectrum of the primary organic aerosol (POA) because it is monitored prior to the initiation of chamber chemistry. With this knowledge, we are confident that we can remove the POA spectrum from the total organic MS with high fidelity. In these experiments, SOA was formed rapidly and in high concentrations. Here, we carefully consider the the MS of this SOA.  
10 We track the evolution of the MS in time and discuss what that evolution suggests about the species and chemistry driving SOA formation. We compare this MS to the OOA MS derived from the CPCA method to reconcile the time-dependence observed in our SOA with the time-invariant OOA component used to describe ambient data. And, we evaluate the atmospheric relevance of our experiments by comparing the composition  
15 of our oxidized OA to that of ambient aged OA.

## 2 Methods

The experiments discussed here have been described in detail in a companion publication. (Weitkamp et al., 2007<sup>1</sup>). Briefly, several experiments were conducted to observe UV-initiated oxidation chemistry of diesel exhaust in the Carnegie Mellon University smog chamber. The chamber (described in detail in Huff Hartz et al., 2005; Presto  
20 et al., 2005) is comprised of a 10 m<sup>3</sup> Teflon bag filled with clean, dry air. The bag is suspended in a temperature-controlled room banked with UV lights. In these experiments, small amounts of exhaust from a single-cylinder diesel generator (Yanmar) operated under several engine loads were added to the chamber. After injection of the

<sup>1</sup>Weitkamp, E. A., Sage, A. M., Pierce, J. R., Donahue, N. M., and Robinson, A. L.: Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber, Environ. Sci. Technol., in review, 2007.

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exhaust, the UV lights in the chamber were turned on to initiate oxidation. The chamber was held at  $23^{\circ}\text{C}\pm 1^{\circ}\text{C}$  and  $\sim 5\%$  relative humidity. The evolution of the resulting aerosol was observed for several hours.

In each experiment we observed significant particle growth after illumination – in most cases the wall-loss corrected particle mass roughly doubled after a few hours. We observed ten times more SOA than we expected based on oxidation of volatile aromatic precursors such as trimethyl benzene (Weitkamp et al., 2007<sup>1</sup>). Our conclusion, discussed elsewhere, is that oxidation of semi-volatile gas-phase species is responsible for this mass increase (Robinson et al., 2007).

Here we wish to explicitly consider the chemical nature of the SOA that was formed. Toward this end, the composition of the non-refractory portion of the diesel particulate matter was monitored using a Q-AMS (Aerodyne Research, Inc.). The Q-AMS alternated between operating in mass spectrum (MS) scanning mode and in particle time-of-flight (PToF) mode every fifteen seconds (Jayne et al., 2000; Jimenez et al., 2003). The sample averaging time was five minutes, and the vaporizer temperature was  $600^{\circ}\text{C}$ .

The AMS data were analyzed using the standard fragmentation table with corrections applied for particle mass appearing at a mass-to-charge ratio ( $m/z$ ) of 28 and for increased gas-phase  $\text{CO}_2$  concentrations when necessary (Allan et al., 2004a,b). The particle mass appearing at  $m/z=28$  is calculated by subtracting the gas-phase  $\text{N}_2^+$  signal from the total signal recorded at  $m/z=28$  and attributing the difference to condensed-phase  $\text{CO}^+$ . This approach is supported by data collected in PToF mode that show a bimodal size distribution at  $m/z=28$ ; the smaller mode matching the time of flight of air sampled prior to the experiment and the larger mode tracking signal from the diesel emissions at less ambiguous masses. When it is observed, the particle signal at  $m/z=28$  appears early in the experiment, but is small enough to be indistinguishable from noise at later sampling times. The gas-phase  $\text{CO}_2$  concentration is set using chamber air sampled through a hepa filter at the end of the experiment. Signal appearing at  $m/z=44$  during this sampling period is attributed entirely to gas-phase

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CO<sub>2</sub> and taken to be representative of concentrations throughout the experiment. CO<sub>2</sub> concentrations varied from 350 to 640 ppm in the experiments discussed here. All spectra presented here are normalized by total organic mass to facilitate comparisons among experiments and methods.

- 5 Additional information about particle size distributions was obtained from a scanning mobility particle sizer (SMPS, TSI 3080) and about concentrations of gas-phase organics from a proton transfer reaction mass spectrometer (Ionicon).

## 2.1 Decomposition of Organic MS

10 The MS recorded by the Q-AMS are time- and spatially-averaged composite spectra of a complex mixture of hundreds of chemical compounds, which are further complicated by the fragmentation characteristic of the high-temperature vaporization and electron-impact ionization of organic species. The deconvolution of these spectra into individual chemical components is an overwhelmingly difficult task, and we instead aim to glean, as others have, the information that we can about the chemical evolution of the SOA  
15 that is formed from the bulk spectra.

We use two methods to decompose the bulk organic MS into reduced and oxidized components. The first is our residual analysis method, described below, and the second is the CPCA method of Zhang et al. (2005a). In our residual analysis method, we exploit the advantage provided by the controlled nature of smog-chamber studies: it is  
20 a batch process with a known POA MS. Using this primary MS (MS<sub>POA</sub>) and assuming that the chemical composition of the POA remains constant throughout the experiment, we can obtain the MS of the secondary material (MS<sub>residual</sub>) that is formed during the experiment by subtracting the known MS<sub>POA</sub> from the observed total spectrum at time  $t$ :

$$25 \quad \text{MS}_{\text{residual}} = \text{MS}_t - f_{57} \text{MS}_{\text{POA}} \quad (1)$$

where  $f_{57}$  is the maximum fraction of MS<sub>POA</sub> that can contribute to MS <sub>$t$</sub> . This method defines MS<sub>POA</sub> as the MS recorded prior to the initiation of oxidation at time  $t=0$ . It is

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assumed to be an invariant and known component of the total MS at each subsequent time  $t$ .  $f_{57}$  is calculated as:

$$f_{57} = \frac{m_{m/z=57}(t)}{m_{m/z=57}(t_o)} \quad (2)$$

where  $m_{m/z=57}$  is the mass appearing at a  $m/z=57$  in the organic MS. The use of  $m/z=57$  is in agreement with the identification of  $m/z=57$  by Zhang et al. (2005a) as the single best tracer for HOA based on a combination of its intensity and unique source ( $C_4H_9^+$ ) in the MS of combustion exhaust. Values of  $f_{57}$  exceeding one sometimes occur in the first few samples after the chamber lights are turned on and are attributed to incomplete mixing in the chamber. The residual analysis method of apportioning organic mass between primary and secondary material is in good agreement with independent wall-loss estimates from SMPS data, as shown below.

Beyond its well-documented correlation with anthropogenic POA, our choice of  $m/z=57$  is purely phenomenological: it is the first MS peak to reach zero when we progressively increase the fraction of  $MS_{POA}$  that is subtracted from the observed total MS (Zhang et al., 2005a; Canagaratna et al., 2004). Ambient data suggest that attributing all of the signal at  $m/z=57$  may overestimate the contribution of POA. Application of the CPCA method in field campaigns has found that oxidized organic material has a signal at  $m/z=57$  that is between 2% and 6% of that at  $m/z=44$ . In our experiments, we find that reducing the amount of  $MS_{POA}$  subtracted from  $MS_t$  to meet this criterion results in only a slightly less oxidized  $MS_{residual}$ ; the change in  $f_{57}$  is on the order of 1%.

We have also applied the CPCA method of Zhang et al. (2005a) to data from these experiments. This method deconvolves observed organic mass spectra into two factors: HOA and OOA. These component MS are determined iteratively, starting from an initial guess based on the time series of the organic mass appearing at representative peaks ( $m/z=57$  and  $m/z=44$ , respectively, for HOA and OOA) that is refined based on the results of multiple multivariate linear regressions. The MS observed at any time during an experiment can be expressed as a linear combination of the resulting HOA

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and OOA spectra for that experiment.

Both apportionment methods provide insight into the chemical processes occurring in the chamber. However, there is a fundamental difference: the two factors (HOA and OOA) in the factor analysis method are, by definition, constants, with a time-evolving mixing term that describes the time evolution of the overall mass spectrum; on the other hand, in the residual analysis method  $MS_{POA}$  is a constant, fixed at its initial value, but  $MS_{residual}$  can and does evolve in time.

### 3 Results and discussion

In each of the experiments discussed here, the MS of the condensed phase changes with time. The fractions of the total organic mass appearing at  $m/z=44$  ( $CO_2^+$ ) and 31 ( $CHO^+$ ), two masses that are indicative of oxidized material, increase with time, while the fractions appearing at masses associated with reduced organic material, such as  $m/z=57$  ( $C_4H_9^+$ ) and 71 ( $C_5H_{11}^+$ ), decrease (Zhang et al., 2005a). From the increasingly oxidized nature of the condensed-phase material and accompanying observations of increases in its mass, we conclude that substantial amounts of SOA are formed from the oxidation of diesel emissions (Weitkamp et al., 2007<sup>1</sup>).

#### 3.1 Decomposition of organic MS

Using the residual analysis method in Eqs. (1) and (2), the decomposition of the organic mass into primary and residual components in three different experiments is shown by the solid lines in Fig. 1. The three experiments vary in both initial mass concentrations of primary aerosol and engine loads. Each experiment, however, shows the same trend. Within 15 minutes of the initiation of oxidation, the primary MS fraction begins to diminish. Within 1 h, the primary MS only accounts for 70% of the observed organic mass. The primary MS fraction continues to decline throughout the experiments, though at a slowing rate, until, after 3 h, only between 30 and 60% of the observed

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mass can be identified as primary.

As in all static chamber experiments, uncertainties in the wall loss rates limit our accuracy. Direct observation of wall loss in these experiments is confounded by concurrent SOA production. Using an inverse model, we have independently estimated wall losses in the chamber during these experiments (Pierce et al., 2007<sup>2</sup>). The inverse model allows us to explicitly calculate the primary mass in the chamber. With this we can apportion the mass between primary and new (secondary). We can directly compare this apportionment to the MS-based apportionment. The agreement is reasonable, as shown in Fig. 1. Discrepancies that do exist suggest that the residual analysis method and wall-loss model estimates of the POA/SOA split converge as aerosol mass increases. At lower aerosol masses, the residual analysis method may underestimate the primary fraction of the organic mass. In the following section, our detailed analysis focuses on the third, highest mass ( $68 \mu\text{g m}^{-3}$ ) experiment where the two approaches are in excellent agreement. Here, we are confident that the residual MS reflects the composition of the SOA that is formed. We will then show that these results are consistent with our observations from and hence generalizable to the other experiments.

Implicit in our use of a single MS peak as a scaler for the entire  $\text{MS}_{\text{POA}}$  is the assumption that the initially recorded MS accurately represents the chemical composition of the condensed fraction of the primary emissions throughout an experiment. This assumption excludes consideration of spectral changes due to both repartitioning of primary emissions and condensed-phase chemistry. The first exclusion we can validate based on our observations that the  $\text{MS}_{\text{POA}}$  from the engine used in these experiment varies little between experiments and changes negligibly in the absence of light. Over the conditions of these experiments (initial mass concentrations of 5 to  $80 \mu\text{g/m}^3$ , as mea-

<sup>2</sup>Pierce, J. R., Engelhart, G. J., Weitkamp, E. A., Pathak, R. K., Pandis, S. N., Donahue, N. M., Robinson, A. L., and Adams, P. J.: Constraining particle evolution from wall losses, coagulation, and condensation-evaporation in smog- chamber experiments: optimal estimation based on size distribution measurements, in preparation, 2007.

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sured by the SMPS assuming spherical particles with a density of  $1\text{ g cm}^{-3}$ ), changes in partitioning do not appear to affect the basic features of the averaged  $\text{MS}_{\text{POA}}$ .

The second assumption is more difficult to evaluate. Ambient observations of molecular-marker decay and laboratory studies of the heterogeneous reactions in organic particles suggest that condensed-phase primary organics are oxidized under atmospheric conditions (Robinson et al., 2006; Rudich et al., 2007). However, in their analysis of OA in Pittsburgh, Zhang et al. (2005b) show a strong correlation between OOA and sulfate concentrations, indicating that the OOA signal is primarily due to SOA, not oxidized POA. Here, we have assumed an invariant  $\text{MS}_{\text{POA}}$ , but we acknowledge that small changes in this spectrum due to, for example, heterogeneous processing, could affect the apportionment of organic aerosol between primary and residual components. We can estimate the potential effects of heterogeneous oxidation by assuming that it is dominated by OH chemistry. With an OH uptake coefficient of unity, 100 nm particles with a density of  $1\text{ g cm}^{-3}$  and a mean molar mass of  $150\text{ g mol}^{-1}$  would have a lifetime with respect to OH oxidation on the order of 2 days in our experiments. Therefore, at the conclusion of a 5-h experiment, no more than 12% of the POA should be oxidized. This estimate is in line with the discrepancy observed between the results of the residual analysis method and the wall-loss model estimates for the lower mass experiments in Fig. 1. Accounting for this oxidation would increase the fraction of the material identified as primary, and decrease the fractional contribution of oxidation marker peaks, such as  $m/z=44$ , to the  $\text{MS}_{\text{residual}}$ , but it would not change either of our fundamental conclusions. A large amount of SOA is formed from oxidized diesel emissions and the MS of that SOA, whether it is represented by our entire residual or only a portion of it, is changing as a function of time.

### 3.2 Evolution of $\text{MS}_{\text{residual}}$

The time-dependent evolution of the  $\text{MS}_{\text{residual}}$  is demonstrated by the results of a typical experiment shown in Fig. 2. In Fig. 2a, the organic mass measured by the Q-AMS

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is apportioned between primary and residual components as discussed above. The MS of the grey portion is  $MS_{POA}$ . The MS of the green portion is  $MS_{residual}$ ; this spectrum evolves in time as indicated in Figs. 2b and c. According to this apportionment, secondary material begins to form immediately after the chamber lights are turned on and accounts for over 10% of the total organic mass within 15 minutes. After 5 hours, the  $MS_{residual}$  accounts for approximately 40% of the suspended organic mass.

One of the most straightforward indicators of the oxidation state of organic aerosol is the mass appearing at  $m/z=44$  (Zhang et al., 2005a). Signal at this mass is the canonical indicator for OOA. The  $CO_2^+$  fragment appearing at this mass is formed in electron-impact mass spectrometers from the dehydration of carboxylic acid groups and in the degradation of pyrolyzable material on the Q-AMS vaporizer surface. Figure 2b shows the percentage of the mass in the  $MS_{residual}$  appearing at  $m/z=44$  as a function of time. This simple metric shows the residual becoming progressively more oxidized over the course of the experiment. The percent of the  $MS_{residual}$  appearing at  $m/z=44$  increases by a factor of three, from 4% to 12%, during this five-hour experiment. The combination of the residual becoming more oxidized (Fig. 2b) and the decreasing fractional contribution of  $MS_{POA}$  (Fig. 2a) means that the organic particles are becoming increasingly oxidized with time.

Figure 2c shows the evolving oxidation of the residual fraction of the organic mass in more detail. Six residual spectra are shown at one-hour intervals starting 15 min after the initiation of oxidation. These times are designated by the colored lines and circles in Figs. 2a and b, respectively; the earliest spectrum is shown in red at the top of the column and the last in purple at the bottom. Two features of the time series of these  $MS_{residual}$  are readily apparent. The first is that the basic structure of the residual spectrum emerges quickly, being established only 15 min into the experiment. The dominant peaks in the first  $MS_{residual}$  remain dominant throughout the experiment. The second is that the ratio of the height of the peak at  $m/z=44$  to that at  $m/z=43$  (the 44:43 ratio) steadily increases throughout the experiment. In the early spectra,  $m/z=43$  is the strongest peak, whereas in the later ones it is  $m/z=44$  (and  $m/z=18$ , which is set

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equal to  $m/z=44$  in the fragmentation table used here [Allan et al., 2004a,b](#)).

Single-precursor SOA experiments display the exact opposite behavior to that observed here ([Zhang et al., 2006](#)). In those experiments, terpenes are oxidized with ozone, presumably leading to products whose composition does not evolve in time.

5 Increased precursor oxidation simply increases the total product mass, and the most oxidized SOA is observed to condense first, at the lowest aerosol loadings. This is presumably because the most highly oxidized material generally has the lowest vapor pressure; therefore, it condenses earlier, at the lower OA concentrations. This difference between our current results and the single-precursor experiments strongly suggests that the chemistry occurring in the diesel experiments involves a suite of precursors that form condensable products after varying numbers of oxidation reactions. Therefore, the diesel SOA is presumably becoming progressively more oxidized through continuing oxidation of semi-volatile gas-phase species.

15 The spectra shown in Fig. 2 are expressed in terms of percentage of the total organic signal, so the relative increase in signals at  $m/z=44$  and 18 (almost 20% of the total organics) must be counterbalanced by corresponding losses elsewhere. These losses are spread out, appearing as small relative decreases at most masses greater than  $m/z=62$ . The progressive changes observed in the  $MS_{\text{residual}}$  over the course of this experiment are shown in the difference spectrum in Fig. 3. This spectrum shows the cumulative changes occurring at each  $m/z$  ratio relative to the initial  $MS_{\text{residual}}$  at  $t=0.25$  hrs, shown in red in Fig. 2c. The height of a bar indicates the change in the percent contribution at that  $m/z$  ratio and the color of the bar indicates the time elapsed.

20 For example, the mass appearing at  $m/z=44$  is shown in Fig. 2b to increase from 4% to 14% of the total organic mass between  $t=0.25$  and  $t=5.25$  h; this 10% change is indicated by the purple bar at  $m/z=44$  in Fig. 3.

25 Masses in Fig. 3 that show the same color progression shown in Fig. 2c are changing systematically with oxidant exposure. Masses that are increasing in importance with time are shown as positive; those that are decreasing are negative. Examples of masses of increasing and decreasing importance are  $m/z=44$  and 91, respectively.

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The negative signal at later times (shown in blue and violet) at  $m/z=28$  is a result of imperfect apportionment of the signal at that mass between the dominant  $N_2^+$  ion and the small particle signal corresponding to  $CO^+$ . Inaccuracy in this correction limits the our certainty in the absolute percentages calculated in the residual spectra, but has no effect on the observed trends. Overall, this spectrum shows a characteristic typical of increasingly oxidized organic material: as long carbon chains become more functionalized with oxidation, they are increasingly fragmented by electron impact ionization, and signal in their MS shifts to smaller masses. Hence, small masses become increasingly dominant as oxidation progresses.

The results shown in Figs. 2 and 3 are typical of those observed in all three experiments. The variations among the  $MS_{POA}$  and the final  $MS_{residual}$  in the three experiments are compared in Fig. 4. All three  $MS_{POA}$  show patterns characteristic of samples dominated by long alkyl chains. Similar spectra have been observed for fuel and lubricating oil in laboratory studies and for fresh vehicle emissions in New York City chase studies (Canagaratna et al., 2004). This pattern is also characteristic of the HOA-component of ambient spectra analyzed using the CPCA method of Zhang et al. (2005a). It is worthwhile to note, that 2 to 4% of the mass in our  $MS_{POA}$  appears at  $m/z=44$ . Engines are oxidizing devices, so a modest contribution to  $MS_{POA}$  at  $m/z=44$  does not seem unreasonable. This indicates that there is some oxidized or pyrolyzable material in our primary fraction that is not found in analyses of ambient emissions (Zhang et al., 2005a; Canagaratna et al., 2004). The modest variations among our primary spectra are due, most likely, to changing engine loads, initial mass concentrations, and inlet temperatures, but these variations have not been systematically explored.

Figure 4b shows the final  $MS_{residual}$ , averaged over the last five sampling periods (25 minutes) of each experiment. Each spectrum has the same basic structure, dominated by the peaks at  $m/z=18$  and 44. All show that the 44:43 ratio exceeds one, though not by as much as in spectra of aged organic material from field studies downwind of Vancouver or in the OOA component of the total spectrum in Pittsburgh (Alfarra et al.,

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2004; Zhang et al., 2005b). Our data suggest that this ratio continues to increase with time, but our ability to explore this evolution further is limited by loss of mass to the chamber walls. The high mass experiment shown in the bottom panel of Fig. 4b was the longest of the three and shows a correspondingly larger mass fraction at  $m/z=18$ , 43, and 44.

### 3.3 Analysis method comparison

The residual analysis method is uniquely suited to laboratory studies, because it requires explicit knowledge of  $MS_{POA}$ . This knowledge, however, provides us with some confidence in attributing our  $MS_{residual}$  to the SOA being formed in the experiment. Ambient conditions do not easily accommodate measurements of a representative  $MS_{POA}$ , making it necessary to mathematically deconvolve ambient organic MS. Zhang et al. (2005b) have used their CPCA method convincingly to apportion organic aerosol between two components: an oxidized component (OOA) that closely tracks processes associated with SOA formation and a reduced component (HOA) that is well correlated with markers for primary emissions. We can combine the results of these two analysis methods to gain greater insight into SOA formation.

Figure 5 shows the results of the CPCA method for the same experiment analyzed using the residual method in Figs. 2 and 3. This method describes the total MS observed at any time as a linear combination of the OOA MS (shown in pink) and the HOA MS (in grey) shown in Fig. 5a. While the OOA MS is similar to the final  $MS_{residual}$  from our residual method (see Fig. 2c), there are key differences. Most significantly, the 44:43 ratio in the OOA spectrum is less than one. In fact, the OOA MS more closely resembles the  $MS_{residual}$  earlier in the experiment. The HOA spectrum is very similar to our primary spectrum, which is shown again in Fig. 5b for reference. Both the HOA MS and  $MS_{POA}$  display the picket-fence pattern characteristic of primary emissions from fossil-fuel combustion. However, there are again important differences. Most notably, our  $MS_{POA}$  shows a significant  $m/z=44$  signal, while the HOA signal at  $m/z=44$  is nearly zero. The correction performed for particle mass at  $m/z=28$  was highly uncer-

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tain, so these data were not used in the CPCA method.

Figure 5c, shows how the factor analysis method apportions the mass among OOA and HOA. The apportionment is very similar to that obtained from the residual analysis method (see Fig. 2a), but the amount of OOA determined by the CPCA method is greater than the fraction of material attributed to the residual by a relatively constant offset of 10 to 15%. This offset is due to the partial oxidation we observed in the primary emissions: the CPCA method apportions 15% of the initial MS to OOA. The HOA/OOA division thus lies about 15% below the primary/residual division, in agreement with our observation that the primary emissions in this experiment had 2% of their organic mass at  $m/z=44$ .

The quality of the fit result obtained with the CPCA method is shown in Fig. 5d. This is expressed as the ratio of the absolute residual of the least-squares fit to the total organic mass as a function of time and shows that the reconstruction of the total MS from only two component spectra becomes increasingly poor as the experiment progresses. Even at its worst, this ratio is less than 10% of total organic mass, suggesting that these two components reproduce more than 90% of the variation in the recorded spectra, but the systematic increase suggests a trend in these data that is not being captured by this approach.

In order to further investigate this trend, we divided the data into three 105-min sections (designated early, middle, and late) and applied the CPCA method to each section individually. This division allows us to exploit the mathematical rigor of the CPCA method while permitting some time-dependent variation in the resulting components. The three OOA components calculated using this approach are shown in Fig. 6, alongside the results of the residual analysis method, which have been averaged over the same time periods. The early OOA MS shown in Fig. 6a, is nearly identical to the OOA MS determined from analysis of the entire dataset (shown in Fig. 5a). However, analysis of the data collected later in the experiment produces a more oxidized OOA component (as measured by the 44:43 ratio). Analyzing the data in this piecewise fashion reveals that the 44:43 ratio in the OOA MS increases from approximately 1:1

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to more than 2:1 over the course of the 5-h experiment. The HOA spectra remain relatively constant over time except for a 2% increase in the fraction of the HOA mass appearing at  $m/z=43$  between the middle and late segments. Reassigning this entire increase in the late HOA  $m/z=43$  mass to the late OOA MS would decrease the final 44:43 ratio to 1.4:1. This ratio is still considerably larger than the ratio determined using the CPCA method either at earlier times or on the entire dataset.

These piecewise components are better able to reconstruct the observed MS over the course of the experiment. The largest error in any of the three time periods is 3.5% of the organic mass, again at the end of the last time period. Even with this piecewise approach, there remains a generally increasing trend in the residual ratio over time, both within a single time period and over the course of the experiment. This suggests that further subdivision of the data would continue to show the OOA component becoming progressively more oxidized with time, similar to the results from our residual analysis shown in Fig. 2c.

When viewed using the piecewise approach, the results of the CPCA and the residual analysis agree qualitatively. Both methods show the secondary aerosol becoming progressively more oxidized with time. Both also give MS that are dominated by peaks at  $m/z=18$  ( $\text{H}_2\text{O}^+$ ), 29 ( $\text{CHO}^+$ ), 43 ( $\text{C}_2\text{H}_3\text{O}^+$  and  $\text{C}_3\text{H}_7^+$ ), and 44 ( $\text{CO}_2^+$ ). The MS determined by the two methods differ most notably by the percentages of their total mass located at  $m/z=44$ , which indicate that the OOA component is more oxidized than the final, averaged residual. This difference is likely attributable to the oxidized material that is included in the  $\text{MS}_{\text{POA}}$  according to the residual analysis but attributed to OOA in the CPCA.

Our conclusion from both of these analyses is that the MS of the oxidized component formed from oxidation of diesel emission is evolving in time. This is chemically intuitive: relatively low vapor pressure, gas-phase species should require little oxidation before condensing, whereas more volatile species will require more oxidation and, consequently, more time before they begin to condense under atmospheric conditions. Therefore, we expect and observe different mass spectra from SOA formed earlier and

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later in this experiment. However, this result appears to run counter to the successful application of the two-component CPCA to ambient data, which describes recorded MS as a linear combination of two time-invariant component spectra and captures the evolution in the total organic MS using a time-dependent mixing term.

The piecewise application of the CPCA method suggests a source for this incongruity. When applied to the entire dataset, the method resulted in an OOA component remarkably similar to that of the earliest one-third of the experiment. In a chamber experiment, this is the period with the highest mass loading. The latter two time periods, when evaluated independently of this early period show more oxidized OOA components. Because the fit strives to minimize the difference between the recorded and reconstructed MS, it inherently weights periods of high signal where that difference will be the largest. In the atmosphere, this will have the opposite effect: as SOA formation continues with time, the organic aerosol concentration increases. Consequently, the fit will be weighted toward later times, resulting in a highly oxidized OOA component. Moreover, our batch experiments have a well-defined  $t=0$  and chemistry that evolves unambiguously, while field measurements are always complicated by mixing of parcels with differing ages. Even relatively small error ratios (absolute residual to total organic mass), such as the 10% which is typical of the fits resulting from application of this method to ambient data, may mask trends that elucidate SOA formation chemistry. Recent work that builds on the CPCA method by increasing numbers of components considered and parallel work using positive matrix factorization to describe ambient organic MS show that including more than one oxidized component MS frequently improves the fit<sup>1</sup> (Lanz et al., 2007).

### 3.4 Comparison with ambient measurements

Efforts to understand SOA formation have traditionally focused on the particle-forming potential of a few high-flux, reactive species. Results from laboratory oxidation studies of these species are neither qualitatively nor quantitatively congruous with ambient observations. We have shown here and elsewhere the similarity between the component

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MS observed in our laboratory studies and those calculated from ambient data (Robinson et al., 2007). But the larger question is whether the condensed-phase organic material we study in the lab is chemically representative of that found in the atmosphere. Figure 7 strongly suggests that it is. The figure compares the *total* final MS of the suspended aerosol in smog chamber at the end of an experiment (top MS) to the MS of aged material collected downwind of Vancouver, Canada (middle MS) (Alfarra et al., 2004). The laboratory MS is from the experiment with the lowest initial mass concentration (shown in blue in Fig. 1), as this experiment was most representative of ambient aerosol loadings. The bottom spectrum in Fig. 7 is the difference between the top two. A few peaks stand out in this difference spectrum. Most notably, the ambient aerosol is more oxidized than ours, with a higher 44:43 ratio and less mass at higher  $m/z$  ratios. However, its most striking characteristic is the absence of major differences outside of those expected from incomplete oxidation. The inset at the top right of the figure shows that our aerosol is increasingly oxidized with time, and there is no indication that this oxidation has stopped at the end of the experiment. Therefore, with continued oxidant exposure, we would expect the chemical composition of our laboratory aerosol to further converge toward ambient observations.

## 4 Conclusions

Upon exposure to atmospheric oxidants, gas-phase emissions from a diesel generator react to form substantial amounts of SOA. This chemistry is reflected in changes to the MS of the organic aerosol with increasing oxidant exposure time, and its results can be isolated when the MS of the primary emissions is known. Our analyses reveal that the chemical composition of the SOA formed in these experiments is not constant in time. As an experiment progresses, the SOA (and also, consequently, the total OA) becomes increasingly oxidized. This evolution appears as a progressive shift of signal in the MS over time from higher masses characteristic of unsubstituted hydrocarbons to the smaller masses that indicate more highly functionalized species, and as the in-

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creasing dominance of the  $\text{CO}_2^+$  fragment at  $m/z=44$  with time. At the end of each of our experiments, the residual MS, which is the MS of the non-primary organic mass, closely resembles the oxidized component of organic material that has been observed in several field studies. Additionally, the MS of the total aerosol appears to be asymptotically approaching that of ambient aged organic aerosol.

Our results support the hypothesis that the species in an air mass that are responsible for SOA formation change as a function of time. The precursors of early-forming SOA give rise to condensable organics that are considerably less oxidized than those which contribute to later SOA formation, illustrating that vapor pressure has a controlling influence on SOA composition. This influence is only partially captured by considering a compound's oxidation state; molecular weight is also important. Large, saturated semi-volatile species with low vapor pressures may contribute significantly to ambient SOA concentrations. We attribute this SOA formation pattern to the presence of relatively reduced, but low vapor-pressure species that form condensable products. These species can contribute to rapid, early SOA formation with very high efficiency.

Overall, the experiments described here form SOA with two features consistent with ambient observations. Both features have been difficult for earlier chamber experiments to match. First, SOA is formed rapidly, quickly reaching a mass loading comparable to the primary organic aerosol mass. Second, the mass spectrum of the SOA is quite highly oxidized and matches the mass spectrum of ambient OOA after a few hours. Both of these features suggest that these experiments may be a good model for OOA formation processes in the atmosphere.

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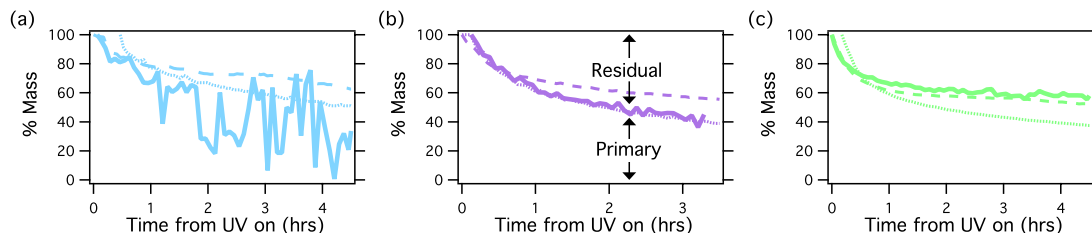
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**Fig. 1.** Results of the organic mass apportionment from the residual analysis method for three experiments: **(a)** low ( $6.5 \mu\text{g m}^{-3}$ ), **(b)** medium ( $10.2 \mu\text{g m}^{-3}$ ) and **(c)** high ( $68 \mu\text{g m}^{-3}$ ) initial aerosol mass concentrations. Masses are reported from SMPS data assuming spherical particles with a density  $1.0 \text{ g cm}^{-3}$ . Results from an inverse wall-loss model are also shown. Dotted lines assume wall loss rates to be independent of particle size while dashed lines explicitly incorporate a size-dependence (Pierce et al., 2007<sup>2</sup>).

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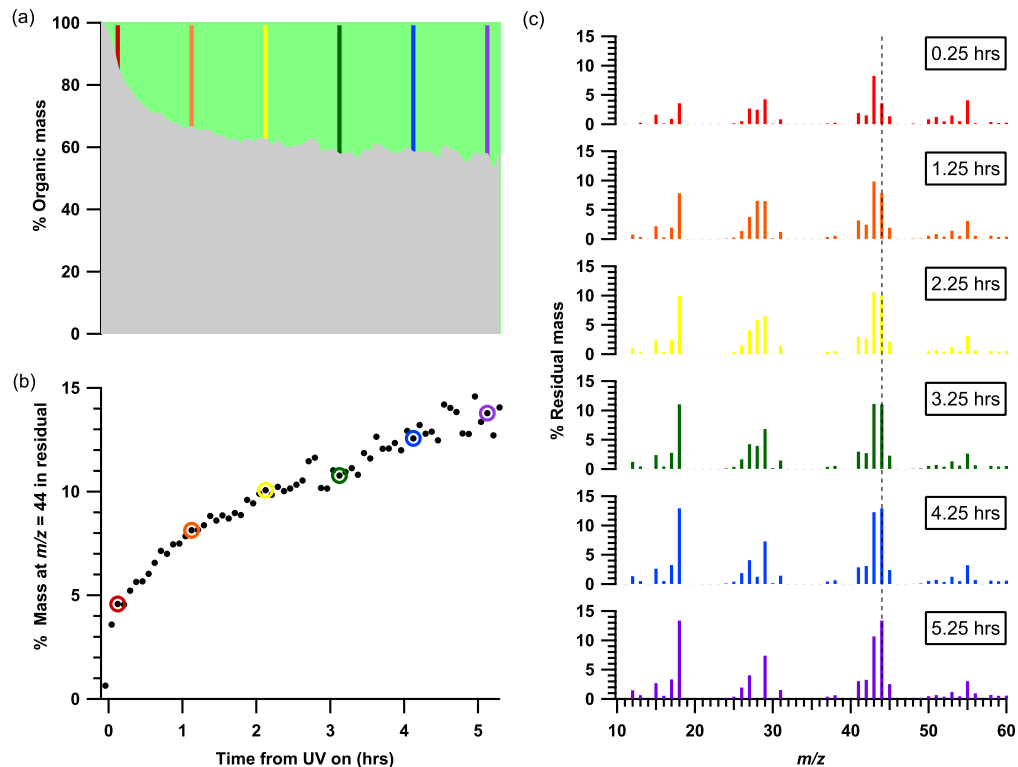
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**Fig. 2.** Results of residual analysis. **(a)** Apportionment of organic signal among primary (grey) and residual (green). The MS of the grey portion is constant and is shown in Fig. 4; the evolving MS of the green portion is shown to the right. The colored lines indicate the times for which residual spectra are shown. **(b)** Percent of the residual MS mass appearing at  $m/z=44$  as a function of time. The colored circles indicate the times for which residual spectra are shown. **(c)** Changes in the residual MS with time starting at 0.15 h after the initiation of oxidation (top, red) and shown every hour until 5.25 h (bottom, purple). The dashed line marks  $m/z=44$ .

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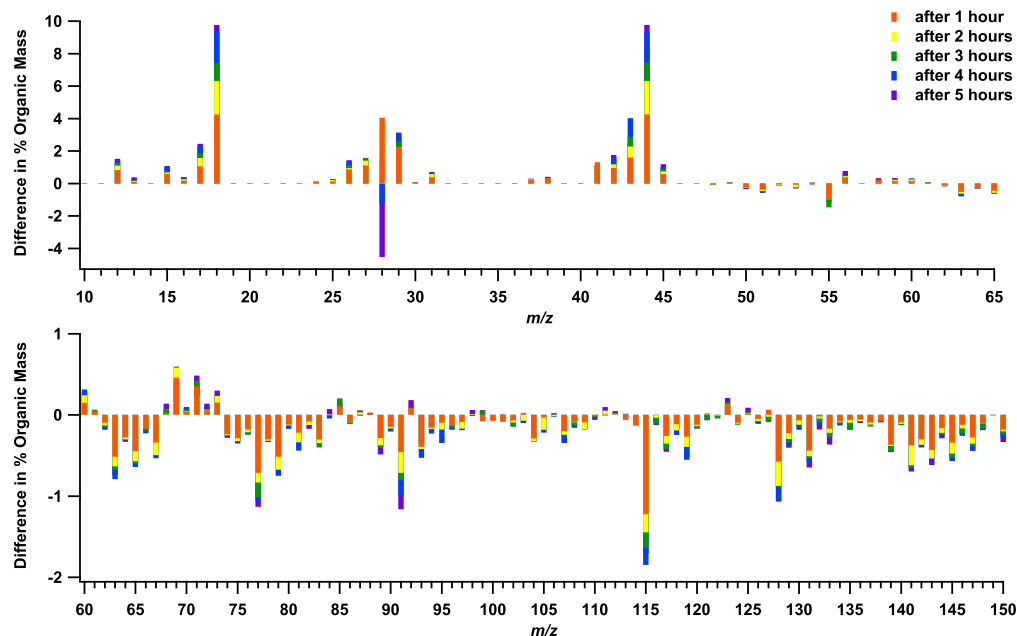
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**Fig. 3.** Detailed evolution of the residual MS as a function of time during a typical experiment. The cumulative changes occurring at each  $m/z$  ratio relative to the initial  $MS_{\text{residual}}$  at  $t=0.25$  h (in red in Fig. 2c are shown). The height of a bar indicates the change in the percent contribution at that  $m/z$  ratio and the color of the bar indicates the time elapsed.

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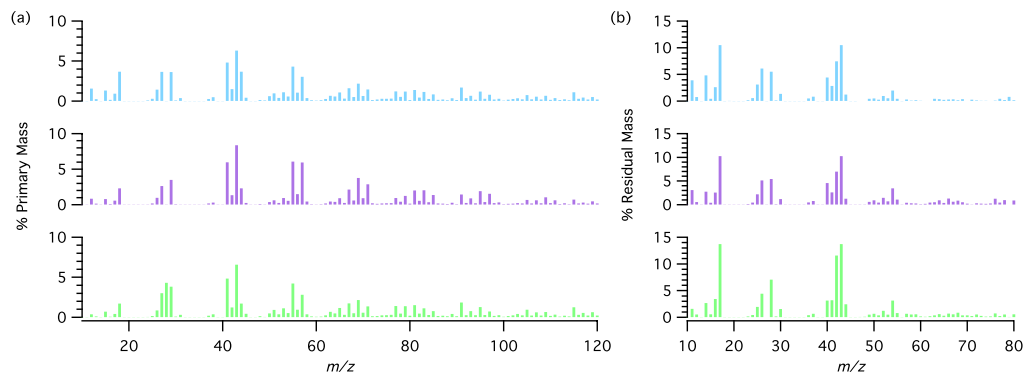
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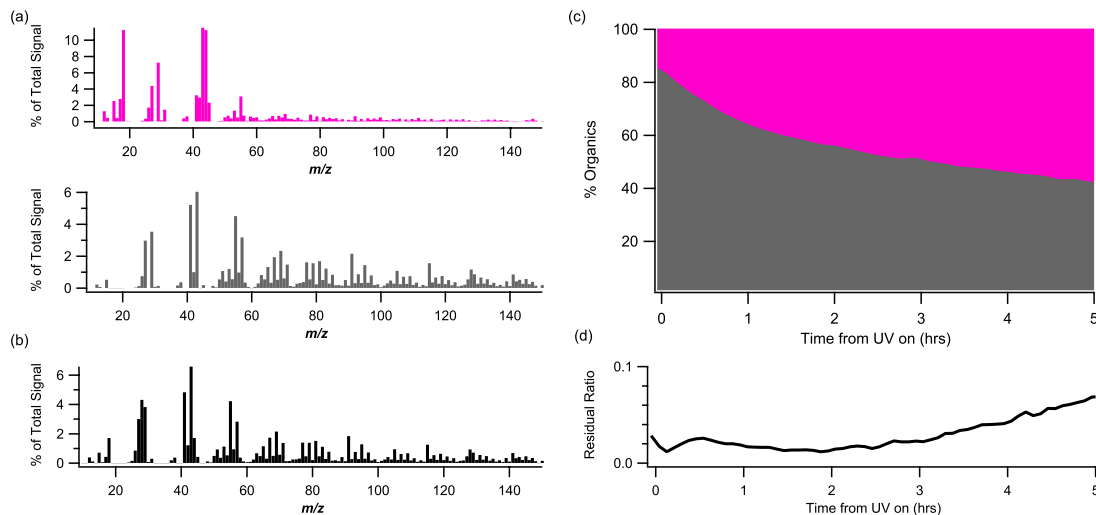


**Fig. 4.** Variations in the **(a)** primary and **(b)** residual spectra among experiments. Colors correspond to the three experiments shown in Fig. 1.

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**Fig. 5.** Results of the CPCA method for the experiment shown in Figs. 2 and 3. **(a)** The OOA (top, pink) and HOA (bottom, grey) spectra found for this experiment. **(b)** The primary spectrum measured prior to the initiation of oxidation in the chamber for this experiment. **(c)** The HOA/OOA split for the experiment shown in 2. **(d)** The ratio of the absolute residual of the two factor fit to the the organic mass.

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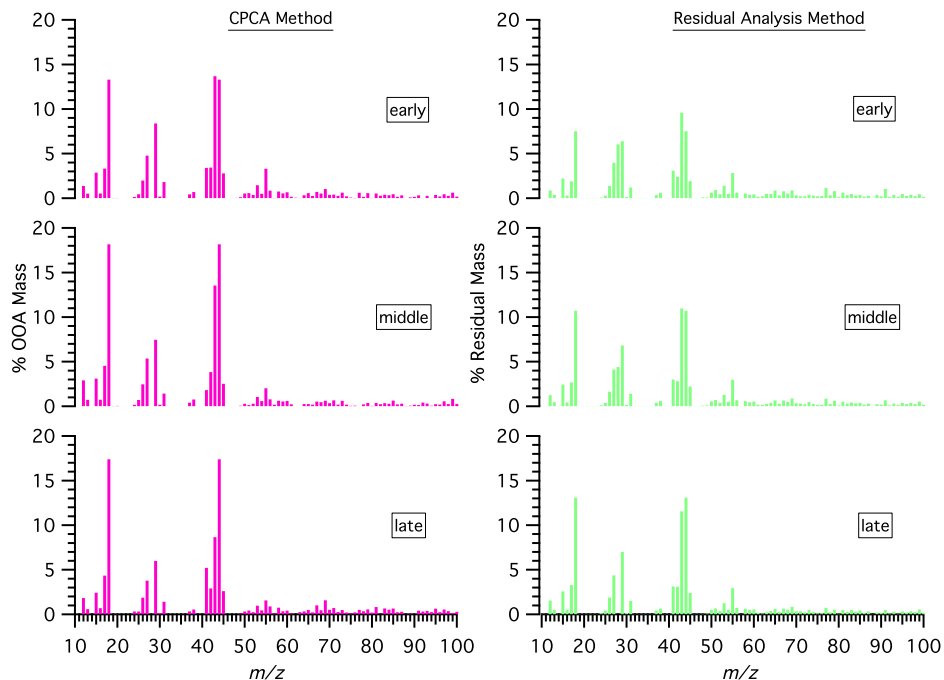
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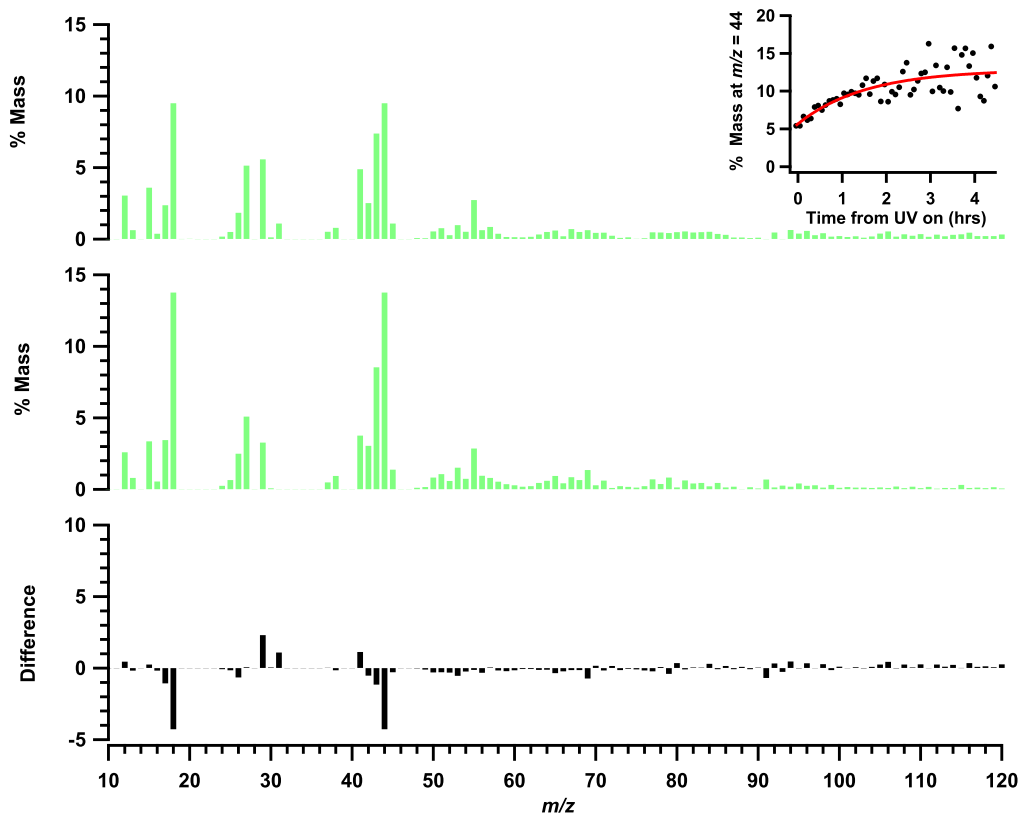


**Fig. 6.** Results of piecewise analyses performed by breaking the dataset shown in Fig. 2 into three 105-min segments. Shown are the oxidized components of the mass spectrum as calculated by the CPCA (left, pink) and residual (right, green) methods for the early, middle and late periods of the experiment.



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**Fig. 7.** Comparison between laboratory and ambient spectra. The top panel shows the final organic MS for the 31 March experiment (low mass) with an inset that shows the fraction of the total organic mass appearing at  $m/z=44$  as a function of time throughout the experiment. Red line is an exponential fit. The middle panel shows ambient oxidized aerosol from Alfarrá et al. (2004). The bottom panel shows the difference between the two.

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