

**Oxidation of chamber
organic aerosol**

P. S. Chhabra et al.

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Elemental composition and oxidation of chamber organic aerosol

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Abstract

Recently, graphical representations of aerosol mass spectrometer (AMS) spectra and elemental composition have been developed to explain the oxidative and aging processes of secondary organic aerosol (SOA). It has been shown previously that oxygenated organic aerosol (OOA) components from ambient and laboratory data fall within a triangular region in the f_{44} vs. f_{43} space, where f_{44} and f_{43} are the ratios of the organic signal at m/z 44 and 43 to the total organic signal, respectively; we refer to this model as the “triangle plot.” Alternatively, the Van Krevelen diagram has been used to describe the evolution of functional groups in SOA. In this study we investigate the variability of SOA formed in chamber experiments from twelve different precursors in both “triangle plot” and Van Krevelen domains. Spectral and elemental data from the high-resolution Aerodyne aerosol mass spectrometer are compared to offline species identification analysis and FTIR filter analysis to better understand the changes in functional and elemental composition inherent in SOA formation and aging. We find that SOA formed under high- and low- NO_x conditions occupy similar areas in the “triangle plot” and Van Krevelen diagram and that SOA generated from already oxidized precursors starts higher on the “triangle plot.” As SOA ages, it migrates toward the top of the triangle, suggesting higher organic acid content and decreased mass spectral variability. The most oxidized SOA come from the photooxidation of methoxyphenol precursors which yielded SOA O/C ratios near unity. α -pinene ozonolysis and naphthalene photooxidation SOA systems have had the highest degree of mass closure in previous chemical characterization studies and also show the best agreement between AMS elemental composition measurements and elemental composition of identified species. In general, compared to their respective unsaturated SOA precursors, the elemental composition of chamber SOA follows a slope shallower than -1 on the Van Krevelen diagram. From the spectra of SOA studied here, we are able to reproduce the triangular region originally constructed with ambient OOA components with chamber aerosol showing that SOA becomes more chemically similar as it ages. Ambient data

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in the middle of the triangle represent the ensemble average of many different SOA precursors, ages, and oxidative processes.

1 Introduction

Organic compounds comprise a significant fraction of ambient submicron aerosol mass (Zhang et al., 2007; Jimenez et al., 2009) with numerous sources and atmospheric processes contributing to their chemical complexity (Hallquist et al., 2009). Secondary organic aerosol (SOA) forms from the gas-phase oxidation of a number of anthropogenic and biogenic volatile organic compounds (VOCs) (Kroll and Seinfeld, 2008; Robinson et al., 2007; Lim et al., 2010; Donahue et al., 2009; Goldstein and Galbally, 2007; De Gouw and Jimenez, 2009). Although typically only a portion of the multitude of compounds present in SOA can be identified on a molecular level, on-line instruments like the Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000) can provide bulk, chemical characterization in real-time.

Recently, two important methods using AMS data to characterize the chemical nature of OA have been proposed. Heald et al. (2010) applied the Van Krevelen diagram to the bulk elemental composition of ambient and laboratory OA formed under a wide range of reaction conditions. Previous investigations have used the Van Krevelen diagram to map individual masses identified by high resolution electrospray ionization mass spectrometry (ESI-MS), but not for OA as a whole (Reinhardt et al., 2007; Walser et al., 2008; Bateman et al., 2009). Originally developed to describe the elemental composition of coal, the Van Krevelen diagram has axes of hydrogen to carbon (H/C) molar ratios and oxygen to carbon (O/C) molar ratios. Changes in functionality of OA are traced in this space along a line of a particular slope. For instance, when an aliphatic functionality is replaced by a carbonyl functionality, the resulting line on a Van Krevelen has a slope of -2 . Substituting aliphatic to alcohol or peroxide functionality produces a line with a slope of zero. Addition of carboxylic acids or hydroxycarbonyls gives a -1 slope. Hydration or condensation reactions follow a line with a slope of

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+2. Heald et al. (2010) found that bulk OA elemental ratios from both laboratory and ambient atmospheres occupy a tight range on the Van Krevelen diagram with a slope of -1 , implying that OA aging involves, on average, the addition of carboxylic acids or equal amounts of alcohol and carbonyl functionalities.

Ng et al. (2010) used positive matrix factorization techniques (Zhang et al., 2005; Lanz et al., 2007; Ulbrich et al., 2009) and compiled the factor analysis for 43 Northern Hemisphere AMS datasets of OA. They found that at most sites AMS spectra can be separated into oxygenated OA (OOA) and hydrocarbon-like OA (HOA) components (Zhang et al., 2007). For many datasets, OOA was further subcategorized into low-volatility OOA (LV-OOA) and semi-volatile OOA (SV-OOA) (Jimenez et al., 2009). LV-OOA has been described as aged OOA, with spectra dominated by mass fragment CO_2^+ at m/z 44, and SV-OOA, described as “fresh” OOA with an intense signal at $\text{C}_2\text{H}_3\text{O}^+$ at m/z 43 as well. Mass fragment CO_2^+ has been considered a marker ion for organic acids in OA, as it is known to form from the thermal decarboxylation of many different oxo-, di-, and polycarboxylic acids (Alfarra, 2004; Aiken et al., 2007; Takegawa et al., 2007; Duplissy et al., 2011). Fragment ion $\text{C}_2\text{H}_3\text{O}^+$, conversely, has been hypothesized to form from non-acid oxygen-containing organic compounds. Since m/z 43 and 44 are the dominant ions in SV- and LV-OOA spectra and represent different functionalities, Ng et al. (2010) plotted f_{44} vs. f_{43} for all OOA spectra from different sites, where f_{44} and f_{43} are the ratios of m/z 44 and m/z 43 to the total OA signal in the spectrum, respectively. Ng et al. (2010) found that the OOA components clustered into a triangular region with wide variability across f_{43} at low values of f_{44} that narrows as f_{44} increases. As a consequence, LV-OOA data tend to group in the top half of the “triangle plot” and SV-OOA in the lower half. Ng et al. (2010) concluded that OOA components become more similar in terms of oxidation state with increasing photochemical age, regardless of source. The most oxidized spectra tend to resemble that of fulvic acid.

Chamber experiments have long been the gold standard to determine SOA formation mechanisms and to constrain the chemistry and yields of SOA. The studies of both Chhabra et al. (2010) and Ng et al. (2010) found, however, that SOA from chamber

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studies typically does not reach the degree of oxygenation of ambient LV-OOA. For example, Heald et al. (2010) presented data from Shilling et al. (2009), in which the most oxidized SOA from α -pinene ozonolysis has an O/C of approximately 0.4, whereas SOA from the MILAGRO (Mexico City) campaign (Aiken et al., 2009) surpasses 0.6.

Ng et al. (2010) noted that most laboratory chamber data fall into the lower half of the “triangle plot”, showing that laboratory OA is closer to SV-OOA than LV-OOA. Like SV-OOA, chamber SOA has high variability in f_{43} , likely a result of the variety of precursors, oxidants, and other experimental variables. In chamber investigations in which SOA is generated at total organic loadings higher than those of ambient OA, more volatile, less oxygenated species partition into the particle phase than would at lower aerosol loadings. Additionally, chamber experiments are typically carried out for less than ~ 24 h, shorter than the atmospheric lifetime (~ 1 week) of ambient aerosol, and therefore not accessing further oxidation that might be occurring over this extended time scale. A comprehensive study by Chhabra et al. (2010) compared the elemental composition of five different chamber systems and found that single-ring aromatic- and naphthalene-derived SOA can reach O/C ratios upward of 0.7, approaching those of ambient measurements, and thus emphasizing the importance of OH exposure and precursor identity on SOA oxidation state.

In this study, we build on the previous investigation of Chhabra et al. (2010) by exploring the variability of chamber SOA in both Van Krevelen and “triangle plot” spaces. In addition to the systems studied in Chhabra et al. (2010) (glyoxal uptake, α -pinene ozonolysis, isoprene photooxidation, single-ring aromatic photooxidation, and naphthalene photooxidation), we present high-resolution time-of-flight AMS (HR-ToF-AMS) spectra and elemental composition of chamber SOA from α -pinene photooxidation, methoxyphenol photooxidation, and unsaturated aldehyde photooxidation. Structures for each of the twelve precursors are shown in Fig. 1. We compare the elemental composition as measured by the AMS to molecular species identified by off-line methods for each SOA system as well as FTIR measurements of α -pinene photooxidation and guaiacol photooxidation SOA. The goal of this work is to assess the extent to which

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SOA molecular and functional group composition analyses support the overall analysis of SOA formation and aging as represented in the Van Krevelen and “triangle plot” spaces.

2 Experimental section

2.1 Chamber operation

Chamber operation and experimental methods for glyoxal uptake, α -pinene ozonolysis, single-ringed aromatic, isoprene, and naphthalene photooxidation experiments are described in Chhabra et al. (2010). Experimental methods for α -pinene, methoxyphenol, and aldehyde photooxidation were nearly identical and are described in detail in Chan et al. (2010). In experiments in which methyl nitrite (CH_3ONO) was used as the OH precursor, CH_3ONO was vaporized into an evacuated 500 mL glass bulb and introduced into the chamber with an air stream of 5 L min^{-1} . The mixing ratio of CH_3ONO injected was estimated to be 200–400 ppb, based on the vapor pressure in the glass bulb measured using a capacitance manometer (MKS). Experimental conditions for each system are summarized in Table 1. All experiments were performed in the Caltech dual 28 m^3 Teflon laboratory chambers (Cocker et al., 2001; Keywood et al., 2004) over the period 2007–2010. A Differential Mobility Analyzer (DMA, TSI model 3081) coupled with a condensation nucleus counter (TSI model 3760) measured aerosol size distribution and number concentration. Temperature, relative humidity (RH), ozone (O_3), NO, and NO_x were continuously monitored. For seeded experiments, ammonium sulfate seed particles were generated by atomization of a dilute aqueous ammonium sulfate solution using a constant rate atomizer.

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2.2 High-resolution time-of-flight aerosol mass spectrometer

HR-ToF-AMS (Canagaratna et al., 2007; DeCarlo et al., 2006) spectra were analyzed as described in Chhabra et al. (2010). Briefly, in the mode of operation, the AMS was switched once every minute between the high-resolution “W-mode” and the lower resolution, higher sensitivity “V-mode”. The “V-mode” data were analyzed using a fragmentation table to separate sulfate, ammonium, and organic spectra and to time-trace specific mass-to-charge ratios (Allan et al., 2004). “W-mode” data were analyzed using a separate high-resolution spectra toolbox known as PIKA to determine the chemical formulas contributing to distinct mass-to-charge (m/z) ratios (DeCarlo et al., 2006). “V-mode” data were used in “triangle plots” and “W-mode” data were used in Van Krevelen diagrams.

Default values were used for the CO_2^+ signal originating from chamber air as FTIR measurements showed the concentration of CO_2 in the chamber air is nominally the same as that in the atmosphere. Ratios of the particle-phase signals of CO^+ to CO_2^+ were determined to be close to 1 (Supplement) for most experiments so this value was used for all experiments except those of glyoxal uptake for which a value of 5 was used. The signals from H_2O^+ , OH^+ , and O^+ in the particulate organic mass may suffer interference from gas-phase H_2O , and their organic contributions were estimated as suggested in Aiken et al. (2008). Particulate nitrogen signals were observed in high- NO_x photooxidation experiments, originating mostly from NO^+ and NO_2^+ ions. Although gas-phase nitric acid is produced from the $\text{OH} + \text{NO}_2$ reaction, at low chamber humidities nitric acid is not expected to partition appreciably into the particle phase. Thus, the signals of NO^+ and NO_2^+ ions were included as part of the organic mass in high- NO_x photooxidation experiments.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Samples for FTIR analysis were collected on Teflon filters (Pall Inc., Ann Arbor, MI, 37 mm diameter, 1.0 μm pore size, teflo membrane), following the collection, storage,

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analysis, and peak-fitting techniques described by Russell et al. (2009). Specifically, a Bruker Tensor 27 FTIR Spectrometer with a DTGS detector (Bruker, Waltham, MA) was used to scan filters before and after sample collection; samples were frozen during transport and storage to reduce evaporative loss of organics and reaction. An automated algorithm was used for subtracting Teflon (using the pre-scanned spectra) and ammonium, baselining, peak-fitting, and error estimation (Russell et al., 2009). Mass concentrations of alkane, carboxylic acid, hydroxyl, amine, non-acid carbonyl, organonitrate, alkene, and aromatic functional groups were quantified using previously reported algorithms and standards (Russell et al., 2009; Day et al., 2010).

FTIR O/C and H/C ratios were determined from measured organic bond absorbances by calculating the estimated moles of oxygen, carbon, and hydrogen associated with each measured bond and its associated functional group (Russell et al., 2009; Russell, 2003). Since alkene groups were below detection, an upper bound was considered to be their detection limit and a lower bound was considered zero. The degree of saturation for other functional groups was weighted by the saturation in the reactants (α -pinene and guaiacol). Hydrogen associated with amine groups was omitted since it is assumed that any ammonium is part of the inorganic seed rather than SOA. To account for oxygen and carbon associated methoxy, hydroperoxy, and nitro groups that are obscured by the use of Teflon substrates, the upper bound O/C ratio for guaiacol was incremented by 3O:7C, equivalent to one methoxy group and one hydroperoxy or nitro group (typical groups found in low- and high-NO_x) to guaiacol's seven carbon structure. No ether groups are expected for α -pinene products.

3 Results

Elemental composition and high resolution-spectra of SOA derived from α -pinene ozonolysis, glyoxal uptake into seed aerosol, and single-ring aromatic, isoprene, and naphthalene photooxidation have been described in detail in Chhabra et al. (2010). Tabulated elemental ratios and high-resolution spectra for α -pinene, methoxyphenol,

and unsaturated aldehyde photooxidation SOA are provided in the Supplement. High-resolution spectra for SOA formed under similar conditions for each parent organic were identical; thus, one experiment for each system is presented. Uncertainty in AMS elemental analysis and offline speciation is discussed in detail in Chhabra et al. (2010).

3.1 α -pinene SOA

Figure 2 illustrates the “triangle plot” (Panel A) and Van Krevelen diagram (Panels B and C) for SOA derived from α -pinene ozonolysis and photooxidation. The time progression of each system is illustrated in Panel A with open and closed circles representing the beginning and end of each experiment, respectively. Consistent with previous studies (Chhabra et al., 2010; Shilling et al., 2009), as the SOA mass formed by α -pinene ozonolysis increases, the O/C ratio and f_{44} decrease, behavior that is a result of increased partitioning of less oxidized semivolatile compounds into a growing OA medium. Oxygen-to-carbon ratios for α -pinene photooxidation SOA are approximately the same as those of ozonolysis SOA, however H/C ratios are slightly higher at 1.6. Similar to α -pinene ozonolysis SOA, the O/C ratios of photooxidation SOA under both NO_x conditions decrease as OA mass increases, behavior manifested in the Van Krevelen diagram but more readily apparent in the “triangle plot” with decreases in f_{44} and increases in f_{43} . In contrast to ozonolysis SOA, however, photooxidation processes eventually overtake semivolatile partitioning and the oxidation state of photooxidation SOA increases, represented by increases in f_{44} (Ng et al., 2010). Towards the end of α -pinene photooxidation experiments, data in Panel A tend to migrate toward the top of the “triangle plot”.

The elemental composition of identified compounds in α -pinene SOA are also shown on the Van Krevelen diagrams in Fig. 2 (Panels B and C). Chhabra et al. (2010) found close agreement between the bulk elemental ratios measured by the AMS and those of compounds detected by offline GC-MS by Yu et al. (1999), who were able to identify >90% of the α -pinene ozonolysis SOA mass. The species identified by Yu et al. (1999) are represented in Panel B by gray squares and show close agreement to AMS data.

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Peroxy-pinic acid, represented by the blue square, is a product of α -pinene ozonolysis proposed by Docherty et al. (2005) and is an approximate O/C upper bound. Similar elemental compositions to those measured by the AMS have also been measured by other methods (Tolocka et al., 2006; Reinhardt et al., 2007). Many of the same products identified in α -pinene ozonolysis SOA have been identified in photooxidation SOA (Panel C) by Jaoui and Kamens (2001) (black circles), who determined that particle-phase products accounted for approximately 20% of the reacted carbon; therefore there is close agreement between AMS elemental composition and that of identified products. Tri-carboxylic acid species (pink circle) observed in ambient aerosol filter samples have been proposed as photooxidation products of α -pinene (Szmigielski et al., 2007), though it is unlikely the α -pinene photooxidation experiments achieved OH exposures high enough to form these highly oxygenated species in substantial concentrations.

The crosses in Panel C of Fig. 2 represent the estimated ranges of H/C and O/C ratios of α -pinene SOA as measured by FTIR filter analysis. The lower bound elemental measurements for both SOA systems agree well with measured AMS O/C and H/C ratios and those of identified products suggesting that undetectable alkene signal is significant to the H/C calculation. Functional group analysis shows substantial mass contributions of alkane and acid groups, consistent with the structures illustrated in Panel C.

3.2 Isoprene SOA

The triangle and Van Krevelen plots for isoprene-photooxidation SOA appear in Fig. 3. The Van Krevelen diagram (Panel B) illustrates that the SOA elemental composition does not change appreciably over the course of the oxidation or at different NO_x concentrations (Chhabra et al., 2010). However, f_{44} increases as f_{43} decreases over the course of the experiment for both NO_x conditions (Panel A), suggesting that organic acid content increases with continued oxidation. High- NO_x spectra also display higher f_{44} values than low- NO_x spectra, consistent with filter measurements identifying

methylglyceric acid oligomers as the dominant species in high-NO_x SOA and non-acid methyltetrols as the dominant species in low-NO_x SOA. Panel A shows that data for both systems migrate to the top of the triangle with continued photooxidation.

The main species and classes of compounds identified in isoprene SOA under both high-NO_x and low-NO_x conditions are shown in Fig. 3, Panel B (Surratt et al., 2010; Gomez-Gonzalez et al., 2008; Szmigielski et al., 2007; Surratt et al., 2007, 2006; Claeys et al., 2004; Wang et al., 2005). Surratt et al. (2006) found that under low-NO_x conditions, ~25–30% of the SOA mass in seeded experiments is organic peroxides, and under high-NO_x conditions, oligomers comprise ~22–34% of the SOA mass. Oligomerization of both methyltetrols and methylglyceric acid (or peroxides and nitrates thereof) results in the loss of water, especially under low RH conditions and therefore leads to lower H/C and O/C ratios. Products resulting from the linear oligomerization of 2-methyltetrol, 2-methylglyceric acid, and 2-methylglyceric acid nitrate are shown in Fig. 3, Panel B with the oligomerization limits denoted with circles. The locations of the circles highlight the importance of oligomerization in the isoprene system by suggesting that the elemental composition measured by the AMS represents that of highly oligomerized compounds rather than individual monomers or dimers; even better agreement between oligomers and AMS data is possible if one considers crosslinked oligomerization and other dehydration reactions. This observation is consistent with Dommen et al. (2006) who, based on volatility tandem differential mobility analyzer (VTDMA) measurements, found that under lower humidities isoprene SOA volatility is suppressed, suggesting the effect of oligomerization.

3.3 Single-ring aromatic SOA

Figure 4 presents both diagrams for toluene and *m*-xylene photooxidation SOA. Like isoprene and α -pinene photooxidation SOA, toluene and *m*-xylene SOA spectra sit on the right side of the triangle and migrate upwards, likely representing an increase in organic acid content and a decrease in non-acid oxygenates, possibly unsaturated carbonyls. This is consistent with studies showing small organic acids as a major

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aromatic SOA product (Fisseha et al., 2004). Increasing SOA oxygenation is also apparent in the Van Krevelen diagram as the AMS data show decreasing H/C ratios and increasing O/C ratios with continued oxidation. In addition, both plots show that *m*-xylene SOA is less oxidized than toluene SOA due to the presence of the second methyl group in *m*-xylene.

Structures of identified SOA products from toluene photooxidation are indicated in the Van Krevelen diagram Fig. 4, (Panel B). Despite numerous studies investigating the aerosol composition of aromatic SOA, substantial mass closure has been difficult to achieve. For instance Forstner et al. (1997) studied the molecular composition of SOA formed from the photooxidation of several aromatic compounds and could quantify only 15–30% of the aerosol mass. In subsequent studies, typically 1% of toluene SOA could be identified (Hamilton et al., 2005; Sato et al., 2007). A study by Fisseha et al. (2004) determined 20–45% of SOA from trimethylbenzene photooxidation were small organic acids. The uncertainty in the composition of aromatic SOA is illustrated by the wide spread of SOA products around the AMS data and the absence of a clear representative compound or process explaining the measured elemental composition. AMS measurements indicate SOA that is less oxidized than the indicated compounds would suggest. The presence of unsaturated carbonyls or aromatic-ring retaining species in the particle phase along with oligomerization may serve to limit O/C ratios.

3.4 Naphthalene SOA

Figure 5 presents the Van Krevelen and “triangle plots” for naphthalene photooxidation SOA. In contrast to the preceding SOA systems, naphthalene AMS data lie to the left of the “triangle plot” and migrate straight upwards (Panel A), consistent with elemental AMS measurements on the Van Krevelen diagram which show increasing O/C ratios (Panel B). The aromaticity of naphthalene allows for multiple oxidation pathways, including bicyclic peroxy radical and ring-opening routes that lead to substantial organic acid yields. Kautzman et al. (2009) determined that about 16% of SOA formed

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under high-NO_x conditions and 33% of SOA formed under low-NO_x conditions are organic acids. Higher organic acid concentrations under low-NO_x conditions are also consistent with AMS data which exhibit higher f_{44} values and O/C ratios than those of high-NO_x data, likely a result of higher OH exposures (Chhabra et al., 2010).

Structures of SOA products identified by Kautzman et al. (2009) in naphthalene SOA and their elemental compositions are presented in Fig. 5, Panel B. Kautzman et al. (2009) were able to chemically characterize 53–68% of the SOA mass and Chhabra et al. (2010) found close agreement between the elemental ratios of compounds identified and bulk ratios determined by AMS analysis. Oxygen-to-carbon ratios of identified species also span a range similar to that of AMS measurements of low-NO_x SOA, evidence of continuous aging.

3.5 Phenol and methoxyphenol SOA

Phenol and methoxyphenol compounds have been investigated as they are semivolatile species formed from the pyrolysis of lignin, the dominant process in biomass burning. Hawthorne et al. (1992) found that phenols and methoxyphenols accounted for forming 21% and 45% of aerosol mass from wood smoke, respectively. Like naphthalene SOA, phenol and methoxyphenol SOA lie to the left of the “triangle” with the highest f_{44} values of any precursor studied (Fig. 6a). Similarly, O/C ratios of methoxyphenols range from 0.8 to 1.0; syringol SOA achieves the highest O/C ratios measured for any chamber aerosol precursor system. The O/C values measured here are in close agreement with those of compounds formed in aqueous reactions of phenolic compounds (Sun et al., 2010). Addition of methoxy groups to the phenol ring increases the H/C but tends to lead to decreases of the f_{44} of the resulting SOA. The presence of methoxy groups, while increasing the bulk oxygenation of SOA, may be retained in the SOA and inhibit acid formation.

Structures of identified SOA products from guaiacol photooxidation are indicated in the Van Krevelen diagram (Fig. 6, Panel B). AMS measured elemental compositions of SOA formed under high- and low-NO_x regimes agree well with those of compounds

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formed under low-NO_x conditions but have higher H/C ratios than those of compounds formed under high-NO_x. It is possible that the UPLC-MS technique is biased to detect the high-NO_x compounds shown, compounds with lower H/C ratios.

The crosses in Panel B of Fig. 6 represent the estimated ranges of H/C and O/C ratios of guaiacol SOA as measured by FTIR filter analysis. The best agreement between FTIR and AMS data occurs at the upper bound O/C calculation which could imply that the nitro, hydroperoxy, or methoxy groups that the FTIR analysis is not able to measure account for at least some of the oxygen present in the SOA.

3.6 Unsaturated aldehyde SOA

Aldehydes are widely formed in the atmospheric oxidation of SOA precursors; methacrolein is a gas-phase product of the high-NO_x photooxidation of isoprene. Recent studies have shown that aldehydes are important intermediates to SOA formation and sensitive to NO and NO₂ concentrations (Chan et al., 2010; Surratt et al., 2010). The “triangle plot” and Van Krevelen Diagram for SOA formed from the high-NO_x photooxidation of methacrolein, acrolein, and crotonaldehyde are given in Fig. 7. As shown in Fig. 1, crotonaldehyde and methacrolein are structural isomers of each other while acrolein lacks the additional methyl group. SOA from all three precursors cluster high in the “triangle plot” with acrolein having the highest f_{44} values. Such high oxidation states are likely due to carboxylic acids and esters contributing a larger fraction of the OA mass. This is consistent with acrolein SOA exhibiting the highest O/C ratios (~ 0.8) of the three systems. SOA from methacrolein photooxidation has higher f_{43} values than that of crotonaldehyde SOA, implying that the position of the methyl group on the oligomeric chain affects fragmentation in the AMS, but does not change the elemental composition of the SOA substantially.

Oligomers identified in crotonaldehyde and acrolein SOA are depicted in Fig. 7, Panel B. The monomers and oligomers formed from methacrolein photooxidation are the same as those of high-NO_x isoprene SOA (Surratt et al., 2010). Like isoprene SOA, the addition of each monomer to the oligomeric chain results in the loss of a

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water molecule. The elemental composition of the limit of a linear oligomer is represented by a circle and approaches the AMS measurement suggesting that the AMS measurement is that of a highly esterified compound rather than individual monomers. The lower O/C ratios measured by the AMS is likely due to the inability of the AMS to efficiently detect oxygen in an organic nitrate group (Farmer et al., 2010; Rollins et al., 2010).

3.7 SOA from reactive uptake of glyoxal

The reactive uptake of glyoxal onto ammonium sulfate aerosol and the elemental composition of its OA have been described in previous investigations (Galloway et al., 2009; Chhabra et al., 2010). Glyoxal OA exhibits high O/C ratios due to its high oxygen content and its ability to hydrate and polymerize in the aerosol phase (Fig. 8, Panel B). Despite a high measured O/C ratio, glyoxal OA sits on the bottom left of the “triangle plot”, a result of insignificant signals at m/z 43 and 44. Most of the oxygen signal in glyoxal OA spectra resides in m/z 29 (CHO^+), 30 (CH_2O^+), 31 (CH_3O^+), and 47 (CH_3O_2^+) (Chhabra et al., 2010).

Structures proposed to form in the aqueous particle phase are shown in Panel B. Hydrated glyoxal has the highest O/C and H/C values; with consecutive additions of glyoxal, water is removed and the oligomer follows a dehydration route with a limit at the same elemental composition of glyoxal itself. Also shown on the Van Krevelen plot is 1H-imidazole-2-carboxaldehydhe, a compound formed from the reaction of glyoxal with ammonium (Chhabra et al., 2010). The AMS elemental composition measurement lies roughly in the middle of the wide range spanned by the proposed species. Further work is needed in characterizing glyoxal OA, its interaction with inorganic species, and the extent of its oligomerization in SOA.

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4 Discussion and conclusions

We investigate two different analysis methods (“triangle plot” and Van Krevelen diagram) for representing the general processes of formation and aging of SOA. Figure 9 summarizes SOA data in a “triangle plot” and Van Krevelen diagram for the variety of laboratory systems studied. Despite the variety of experimental conditions, differences in oxidative conditions have relatively little effect on the spectral identity and elemental composition of SOA as measured by the AMS compared to the identity of the SOA precursor. Most SOA formed under high- and low-NO_x conditions occupy similar areas in the “triangle plot” and Van Krevelen diagram. Typically, chemical characterizations of SOA find significant concentrations of peroxides under low-NO_x conditions and organic nitrates under high-NO_x conditions. However, it is likely that these differences in functionality do not lead to substantial differences in f_{43} and f_{44} and the elemental composition as the underlying chemical structure of SOA remains relatively unchanged. All individual photooxidation systems, apart from the aldehydes that are not large enough to support continued oxidation, also show that AMS spectra head toward the top of the “triangle plot” as they age, consistent with an increase in O/C ratios in the Van Krevelen diagram. Evidence from other AMS studies suggest that this movement toward the top of the “triangle plot” is representative of an increase in organic acids (Alfarra, 2004; Aiken et al., 2007; Takegawa et al., 2007; Duplissy et al., 2011).

We find close agreement between the f_{43} and f_{44} values presented in Ng et al. (2010) and those presented here for the traditional set of SOA systems: single-ringed aromatic, α -pinene, and isoprene SOA. These SOA systems cluster in the lower half of the “triangle plot” indicating relatively low oxygen content and a high degree of mass spectral variation, similar to SV-OOA components. The additional SOA precursors studied here exhibit more mass spectral variation and show that highly oxidized OA with similar O/C ratios to LV-OOA can be formed in a laboratory chamber. The most oxidized SOA formed in the systems studied here results from the photooxidation of already oxidized VOCs, methoxyphenols and unsaturated aldehydes, suggesting that OH exposure is

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the limiting variable in SOA oxidation. Starting with an oxidized SOA precursor gives SOA a “head start” to the oxidative aging process, a phenomenon apparent when comparing the methacrolein and isoprene high-NO_x systems. Methacrolein, a gas-phase product and major SOA intermediate of isoprene photooxidation under high-NO_x conditions, yields SOA with f_{43} and f_{44} values just beyond those of the isoprene SOA range. It is likely that methacrolein SOA formed under high-NO_x does not occupy the same space of high-NO_x isoprene SOA because high-NO_x isoprene SOA could also contain products of low-NO_x photooxidation, thereby lowering it in the “triangle plot.” In the extreme case, methoxyphenols are subject to multiple oxidation steps on an already oxidized compound, leading to O/C ratios that approach unity. Although containing aromatic functionality, both methoxyphenols and naphthalene generate SOA spectra that group on the left side of the “triangle plot” while *m*-xylene and toluene generate SOA spectra that group on the right side. Similarly, Ng et al. (2010) found that benzene SOA spectra sit on the left side of the “triangle plot” and 1, 3, 5-trimethylbenzene SOA spectra sit on the right. It is likely that functionality on the aromatic ring of the SOA precursor affects the fragmentation of the resultant SOA. Specifically, electron donating groups like –CH₃ on the aromatic ring yield SOA spectra with high f_{43} values while electron withdrawing groups like –OH and –OCH₃ or the lack of functionality on the aromatic ring yield SOA spectra with low f_{43} values.

The Van Krevelen diagrams of the elemental composition of individual SOA systems reveal that elemental ratios measured by the AMS agree most closely with SOA systems for which the greatest degree of mass closure has been achieved. Yu et al. (1999) were able to speciate >90% of the α -pinene ozonolysis aerosol composition by mass, and Kautzman et al. (2009) were able to speciate 53–68% of the SOA formed from naphthalene photooxidation, the two systems with the closest agreement between measured elemental ratios and identified compounds. The diagrams also illustrate that highly oligomerized compounds may dominate, in particular, SOA systems such as isoprene and unsaturated aldehyde photooxidation. Conversely, in systems for which mass closure has been difficult, such as single-ringed aromatics, AMS and filter data

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do not agree. This may be due to poorly characterized processes occurring in the particle phase such as oligomerization or dehydration or measurement artifacts (Chhabra et al., 2010).

From a variety of ambient and laboratory measurements, Heald et al. (2010) found that atmospheric OA occupy a narrow range in the Van Krevelen diagram following a line with slope of -1 implying the addition of carboxylic acids or equal amounts of hydroxy and carbonyl functional groups on average to a saturated carbon chain. From Fig. 9, Panel B, for the set of compounds studied here the slope is shallower than -1 if one considers a y -intercept within the range of SOA precursors. In the systems studied here, most SOA precursors do not resemble a saturated chain, and many have cyclic chains, alkene, or aromatic groups. This allows for oxidation of the precursor without substantial loss of hydrogen, leading to a slope shallower than -1 , even with the addition of carbonyl and acid groups. Aging pathways on the Van Krevelen diagram are likely to be different for different precursor species like isoprene and α -pinene and for different precursor classes like biogenic and anthropogenic VOCs. Recently Ng et al. (2011) developed a parameterization to transform ambient OOA components in the “triangle plot” directly onto the Van Krevelen space. The transformed ambient “VK-triangle” (shown in Fig. 9, Panel B) is consistent with the chamber data and also yields a slope shallower than -1 .

Figure 9, Panel A shows that precursor structure and functionality determine the SOA “starting point” on the “triangle plot” and that the path taken is largely dependent on identity of the SOA precursor. Ng et al. (2010) showed that as SOA photochemically ages, and becomes more oxidized, spectral uniqueness is lost and SOA on the “triangle plot” becomes chemically similar. Panel A supports this model with SOA converging at the pinnacle of the triangle which corresponds to an oxidation state ($OS_C \approx 2 \times O/C - H/C$) (Kroll et al., 2011) of around 1 (Ng et al., 2011; Kroll et al., 2011). Panel A also shows that with a finite set of SOA precursors, one can essentially recreate the “triangle plot” as originally created by Ng et al. (2010). The SOA spectra represented on the boundaries of the triangle do not mean that they are

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not representative of ambient spectral components. Rather this SOA represents AMS spectral extremes. Thus, ambient spectra and components falling within the triangle represent the ensemble average of many different SOA precursors and oxidative processes that mix spatially and temporally, and as SOA becomes more oxidized, it loses its source history. Indeed more chamber experiments would help to more fully characterize the “triangle plot” space. High-resolution analysis with species identification can more accurately assign functional groups to individual ions in the AMS spectra. Molecular level chemical characterization of SOA will also be useful in comparison to AMS elemental measurements, especially in systems for which mass closure has been difficult.

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys-discuss.net/11/10305/2011/acpd-11-10305-2011-supplement.pdf>.

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Table 1. Experimental conditions and results.

Expt.#	VOC System	Experiment Type	RH (%)	[NO] ₀ (ppb)	[NO ₂] ₀ (ppb)	VOC Reacted (ppb)	Seed Vol. (μm ³ cm ⁻³)	ΔM ₀ (Max) ^d (μg m ⁻³)
1	glyoxal uptake	humid	60	<det ^a	<det ^a	182 ^b	87	68.3
2	α-pinene + O ₃	ozonolysis	5.4	<det ^a	<det ^a	50 ^c	12.5	56.8
3	α-pinene + OH	low NO _x	4.2	<det ^a	<det ^a	46	13.7	63.9
4	α-pinene + OH	high NO _x	4.9	447	400	47	15.4	53.7
5	isoprene + OH	low NO _x	5.2	<det ^a	<det ^a	49	16.2	3.7
6	isoprene + OH	high NO _x	< 10	536	400	267	11.7	4.3
7	toluene + OH	low NO _x	< 10	<det ^a	<det ^a	112	10.9	141.5
8	toluene + OH	high NO _x	< 10	583	423	136	9.3	50.3
9	<i>m</i> -xylene + OH	low NO _x	< 10	<det ^a	<det ^a	114	9.8	190.4
10	<i>m</i> -xylene + OH	high NO _x	< 10	501	538	200	9.3	52.0
11	naphthalene + OH	low NO _x	8.3	<det ^a	<det ^a	20 ^c	10.5	53.1
12	naphthalene + OH	high NO _x	6.3	431	370	25 ^c	12.8	39.0
13	phenol + OH	low NO _x , nucleation	4.9	<det ^a	<det ^a	21	0.1	30.5
14	phenol + OH	high NO _x , nucleation	3.7	332	545	19	0.0	24.8
15	guaiacol + OH	low NO _x	5.7	<det ^a	<det ^a	6	16.3	11.9
16	guaiacol + OH	high NO _x	4.8	267	427	7	12.6	12.8
17	syringol + OH	low NO _x	3.7	<det ^a	<det ^a	108	10.8	228
18	syringol + OH	high NO _x , nucleation	3.7	238	508	50	0.0	34.8
19	acrolein + OH	high NO _x	7.2	215	389	412	13.2	21.3
20	methacrolein + OH	high NO _x	9.3	725	368	186	11.4	10.1
21	crotonaldehyde + OH	high NO _x	9.0	215	370	252	12.1	14.0

^a Below the detection limit of the measurement.

^b Equilibrium concentration.

^c Approximate initial concentration.

^d Mass loadings are calculated by multiplying the change in DMA volume by an estimated density. Estimated densities of glyoxal, α-pinene, isoprene (and unsaturated aldehydes), single-ringed aromatics, naphthalene, and methoxyphenol SOA were taken from Galloway et al. (2009); Bahreini et al. (2005); Kroll et al. (2006); Ng et al. (2007); Chan et al. (2009) respectively.

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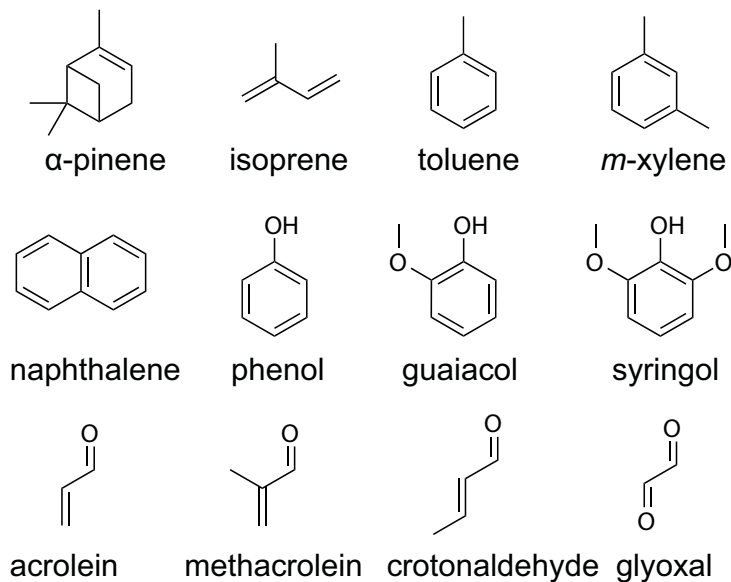


Fig. 1. Structures of the SOA precursors presented in this study.

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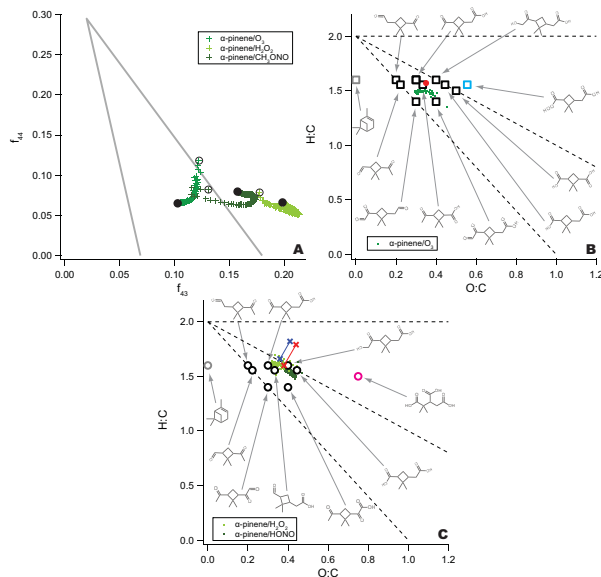


Fig. 2. (A) Triangle plot for α -pinene SOA formed from ozonolysis and high- and low-NO_x photooxidation. Here and in subsequent figures, the outline of the triangle (Ng et al., 2010) is shown in gray. Open and closed black circles represent the beginning and end of the experiments, respectively. (B) Van Krevelen diagram for SOA formed from α -pinene ozonolysis. α -pinene and SOA products identified by Yu et al. (1999) represented by gray and black boxes respectively. The molar weighted average of the elemental ratios of identified SOA products is represented by the red circle (Chhabra et al., 2010). The blue square denotes peroxy-pinic acid, a product of α -pinene ozonolysis proposed by Docherty et al. (2005). Here and in subsequent figures, lines with slopes of 0, -1 and -2 are represented by dashed lines. (C) Van Krevelen diagram for SOA formed from the high- and low-NO_x photooxidation of α -pinene. α -pinene is represented by a gray square, and SOA products identified by Jaoui and Kamens (2001) and Szmigielski et al. (2007) are represented by black and pink circles, respectively. Ranges of elemental ratios as measured by FTIR data are represented by red (low-NO_x) and blue (high-NO_x) crosses.

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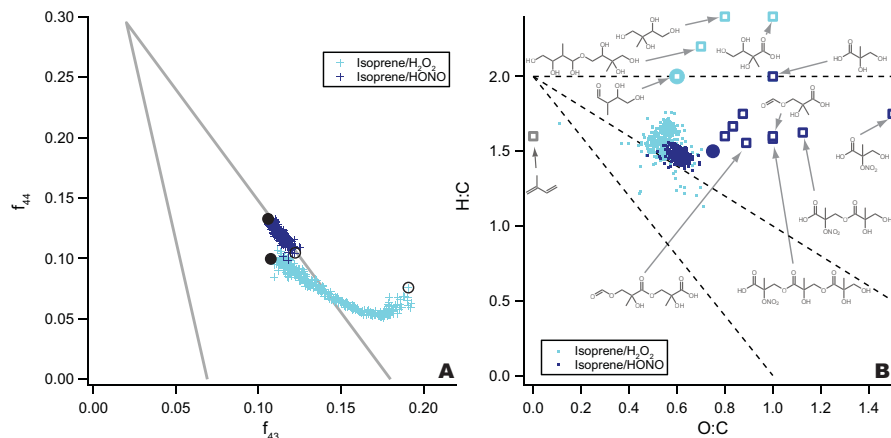


Fig. 3. (A) Triangle plot for SOA formed from photooxidation of isoprene under low- and high- NO_x conditions. Open and closed black circles represent the beginning and end of the experiments, respectively. (B) Van Krevelen diagram for SOA formed from photooxidation of isoprene under low- and high- NO_x conditions. Identified SOA products of each NO_x condition are presented in blue boxes of the corresponding color (Surratt et al., 2006; Claeys et al., 2004; Wang et al., 2005; Surratt et al., 2007; Gomez-Gonzalez et al., 2008). Surratt et al. (2006) found that under low- NO_x conditions, ~25–30% of the SOA mass in seeded experiments is organic peroxides, and under high- NO_x conditions, oligomers comprise ~22–34% of the SOA mass. Oligomeric limits for each NO_x condition are represented by circles.

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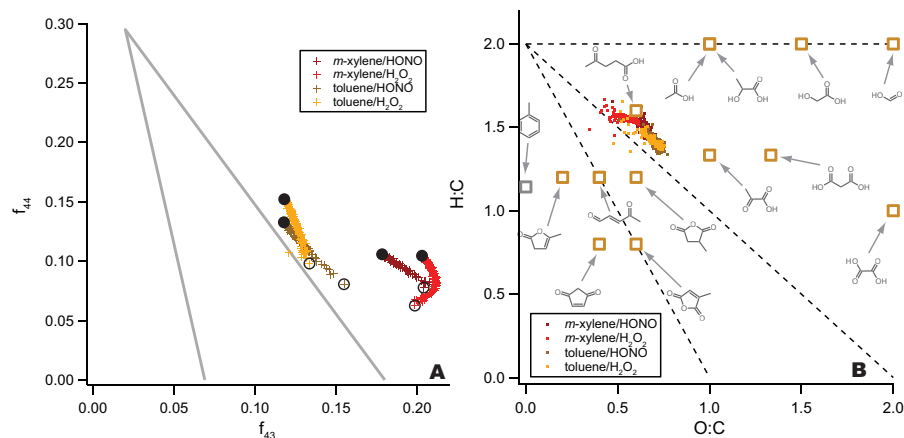


Fig. 4. (A) Triangle plot for SOA formed from photooxidation of toluene and *m*-xylene under low- and high-NO_x conditions. Open and closed black circles represent the beginning and end of the experiments, respectively. (B) Van Krevelen diagram for SOA formed from photooxidation of toluene and *m*-xylene under low- and high-NO_x conditions. Identified toluene-SOA products are presented in tan boxes (Sato et al., 2007; Hamilton et al., 2005; Bloss et al., 2005; Fisseha et al., 2004; Jang and Kamens, 2001). Substantial mass closure has been difficult to achieve in molecular characterization studies.

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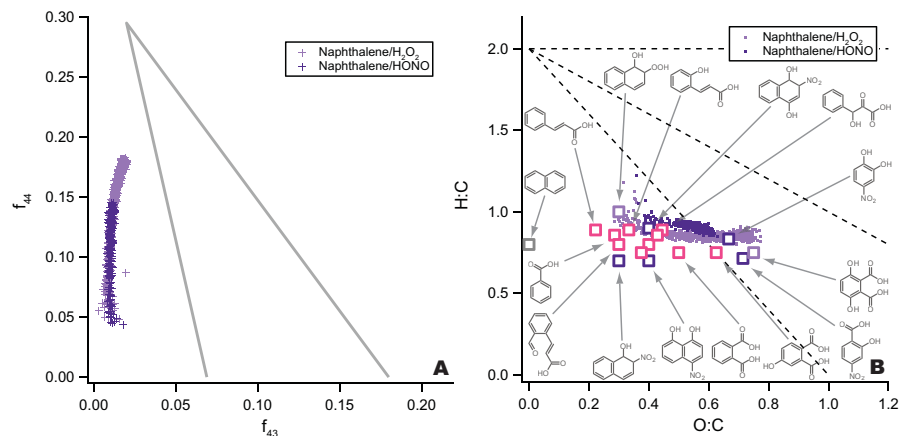


Fig. 5. (A) Triangle plot for SOA formed from photooxidation of naphthalene under low- and high- NO_x conditions. Experiment progression is from bottom to top. (B) Van Krevelen diagram for SOA formed from photooxidation of naphthalene under low- and high- NO_x conditions. Identified SOA products of high-, low-, and both NO_x conditions are presented in dark purple, light purple, and pink boxes, respectively (Kautzman et al., 2009). Kautzman et al. (2009) were able to chemically characterize 53–68% of the SOA mass.

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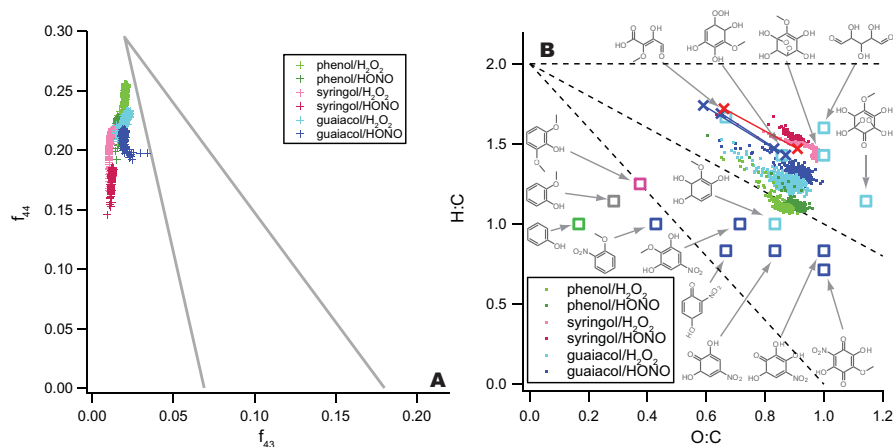


Fig. 6. (A) Triangle plot for SOA formed from photooxidation of phenol, guaiacol, and syringol under low- and high- NO_x conditions. Experiment progression is from bottom to top. (B) Van Krevelen diagram for SOA formed from photooxidation of phenol, guaiacol, and syringol under low- and high- NO_x conditions. Identified guaiacol-SOA products of high- and low- NO_x conditions are presented dark and light blue boxes respectively. Ranges of elemental ratios as measured by FTIR data are represented by red (low- NO_x) and blue (high- NO_x) crosses. Quantification of molecular species in methoxyphenol SOA systems has not yet been accomplished.

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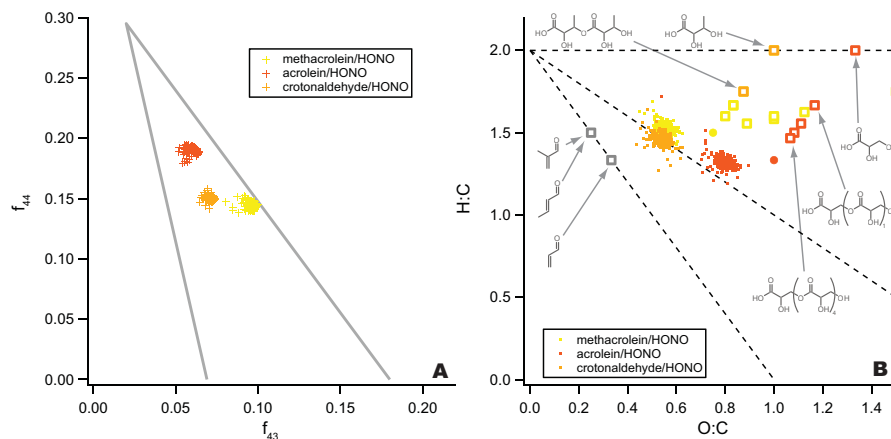


Fig. 7. (A) Triangle plot for SOA formed from photooxidation of methacrolein, acrolein, and crotonaldehyde. (B) Van Krevelen diagram for SOA formed from photooxidation of methacrolein, acrolein, and crotonaldehyde. Identified SOA products of each system are presented in boxes of the corresponding color (Chan et al., 2010). Oligomeric limits for each system condition are represented by circles.

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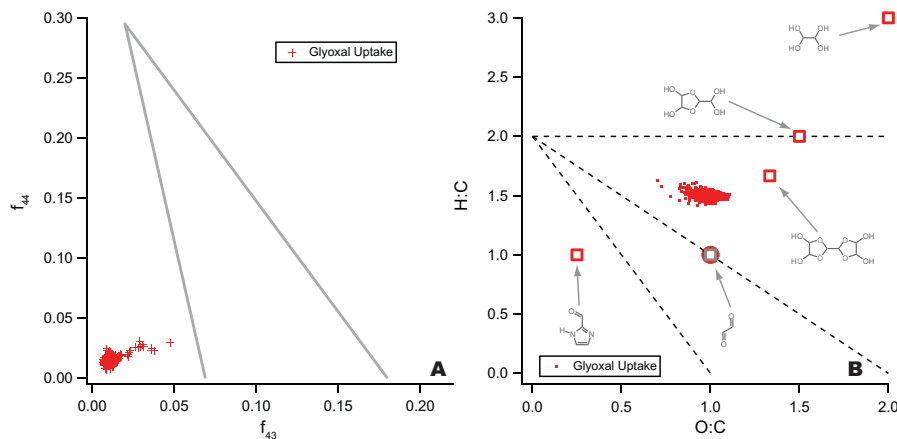


Fig. 8. (A) Triangle plot for SOA formed from reactive uptake of glyoxal onto wet ammonium sulfate aerosol. (B) Van Krevelen diagram for SOA formed from the uptake of glyoxal onto wet ammonium sulfate aerosol. Proposed SOA products are presented in boxes (Galloway et al., 2009; Kua et al., 2008; Loeffler et al., 2006). Oligomeric limits for glyoxal oligomerization condition is represented by a circle.

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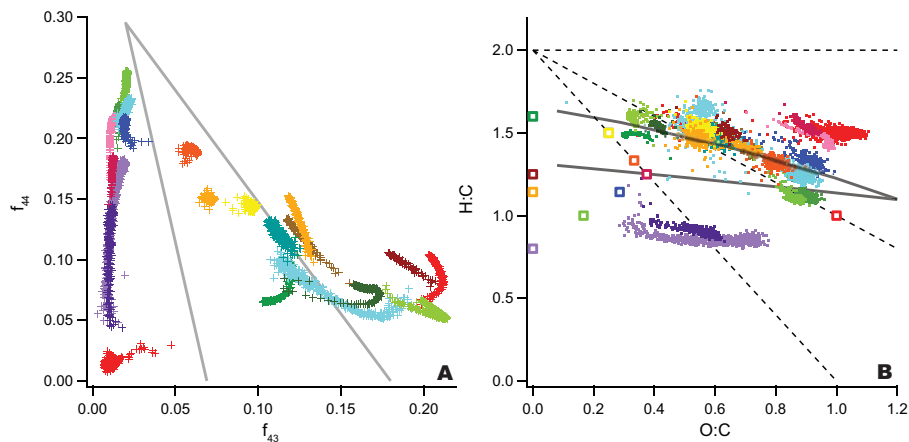


Fig. 9. (A) Triangle plot for all SOA systems (B) Van Krevelen diagram for all SOA systems. SOA precursors are represented by corresponding colored boxes. The “VK-triangle” parameterization developed by Ng et al. (2011) is represented by solid gray curves.

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