

A new source of oxygenated organic aerosol and oligomers

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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Abstract

A large oxygenated organic uptake to aerosols was observed when exposing ambient urban air to inorganic acidic and non-acidic sulfate seed aerosol. For non-acidic seed aerosol the uptake was attributed to the direct condensation of primary vehicle exhaust gases, and was correlated to the initial seed sulfate mass. The uptake of primary oxygenated organic gases to aerosols in this study represents a significant amount of organic aerosol (OA) when compared to that reported for primary organic aerosol (POA), but is considerably more oxygenated (O : C \sim 0.3) than traditional POA. Consequently, a fraction of measured ambient oxygenated OA, which correlate with secondary sulfate, may in fact be of a primary, rather than secondary source. These results represent a new source of oxygenated OA on neutral aerosol and imply that the uptake of primary organic gases will occur in the ambient atmosphere, under dilute conditions, and in the presence of pre-existing SO₄ aerosols. Under acidic seed aerosol conditions, oligomer formation was observed with the uptake of organics being enhanced by a factor of three or more compared to neutral aerosols, and in less than 2 min. This resulted in a trajectory in Van Krevelen space towards higher O : C (slope \sim -1.5), despite a lack of continual gas-phase oxidation in this closed system. The results demonstrate that high molecular weight species will form on acidic aerosols at the ambient level and mixture of organic gases, but are otherwise unaffected by subsequent aerosol neutralization, and that aerosol acidity will affect the organic O : C via aerosol-phase reactions. These new processes under both neutral and acidic conditions can contribute to ambient OA mass and the evolution of ambient aerosol O : C ratios and may be important for properly representing organic aerosol O : C ratios in air quality and climate models.

1 Introduction

Despite the recognized importance of organic aerosol (OA), its varied sources remain only partially understood. Broadly OA can be divided into primary organic aerosol

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A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(POA) or secondary organic aerosol (SOA). The relative importance of SOA and POA to total OA has been the focus of numerous studies. Typically, SOA dominates the OM mass (Zhang et al., 2007; Jimenez et al., 2009), yet its formation mechanisms remains uncertain, with traditional oxidation mechanisms (via OH, O₃ and NO₃) unable to account for SOA observations (Volkamer et al., 2006; Zhang et al., 2011) and oligomer formation via aerosol-phase chemistry potentially increasing in importance (Nguyen et al., 2011; Hall and Johnston, 2011).

Precursor VOC oxidation leads to products with a higher oxygen content and lower saturation vapor pressures, thus enabling the products to partition to aerosols. Hence, the degree of oxygenation in OA, represented by the O : C ratio, has been used to infer source types (POA vs. SOA) (Liggio et al., 2010; Sun et al., 2011), and is related to aerosol properties such as volatility and hygroscopicity (Jimenez et al., 2009; Murphy et al., 2011; Huffman et al., 2009). High O : C ratios in OA have been linked to SOA and oxidative aging (Jimenez et al., 2009); conversely, low O : C indicate POA (Aiken et al., 2008; Chirico et al., 2010). In addition, the relationship between the H:C and O : C ratios has been used to describe organic functional group evolution and aging from field and laboratory experiments (Tkacik et al., 2012; Lambe et al., 2012; Heald et al., 2010; Ng et al., 2011a). Those results show that a continual evolution of OA to higher O : C ratios will occur under oxidative conditions leading to more highly oxidized functional groups in the OA. Understanding the processes which alter organic aerosol mass and O : C is thus critical to modeling aerosol properties and ultimately their effect on climate.

Recent laboratory studies have shown that the direct condensational uptake of vehicle exhaust gases to neutral sulfate aerosols (Li et al., 2011b) can increase OA mass in those experiments. If the uptake involves primary oxygenated species as hypothesized, then it may lead to changes in the degree of aerosol oxygenation if significant OA mass is added under ambient dilute exhaust conditions. Such a process occurring on short time and spatial scales could lead to oxygenated OA mass which will be

A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

indistinguishable from SOA, implying that POA may be more oxygenated than previously considered.

Furthermore, aerosol-phase chemistry leading to high MW species and oligomers has been shown to be a potentially important pathway to OA (Hall et al., 2011), yet the role of aerosol acidity in oligomer formation remains uncertain. While some studies have noted enhanced oligomer mass under acidic aerosol conditions (Denkenberger et al., 2007; Gao et al., 2004), others have observed an insignificant effect (Zhang et al., 2012). Additionally, many smog chamber experiments are performed utilizing single gaseous organic species at high concentrations, and/or very high initial seed mass loading. These conditions may not be entirely representative of the ambient atmosphere, and hence the importance of the above processes under dilute ambient conditions, where a multitude of species exist simultaneously remains somewhat unclear, as does its effect on the oxygen content of the resultant aerosols.

In the present study, the partitioning and reactive uptake of the ambient mixture and concentration of gases to aerosols is investigated by exposing urban ambient air to sulfate aerosols. The results demonstrate that the condensation of existing ambient primary species will lead to significant oxygenated OA prior to gas-phase oxidation. In contrast, the uptake of ambient gaseous organics to acidic aerosol and subsequent aerosol-phase chemistry will result in high MW species and/or oligomers which also significantly enhance aerosol oxygenation. The implications of this new route to oxygenated OA to the overall aerosol mass and oxygenation levels are discussed.

2 Methods

Experiments were performed in a 2 m³ Teflon chamber in the dark by exposing aerosol filtered, urban ambient air to sulfuric acid aerosols and ammonia. Details of the experimental procedure have been given elsewhere (Liggio et al., 2011) and initial experimental conditions are given in Table 1. Experiments were conducted by filling the chamber with particle filtered ambient air over several hours, followed by the formation

A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



predominantly gasoline light duty vehicle traffic. The calibrated concentrations of selected species during these experiments were representative of urban and biogenic emissions and are given in Table 1. Ammonia was measured with a modified chemiluminescence instrument (Thermo Scientific, 42C). The modified chemiluminescence instrument (Thermo Scientific, 42C) measured NH_3 every 10 s with a detection limit of approximately 500 pptv. During several experiments additional NH_3 (10–70 ppb) was added to the chamber after several hours and in a short pulse (< 5 s; Table 1) to study the organic uptake reversibility with respect to aerosol neutralization.

3 Results and discussion

Results for ambient (E1–E14) and control (B1–B3) experiments are given in Table 2. Exposure to organic free air and NH_3 resulted in immediate aerosol neutralization and no measurable organic uptake ($0.03 \pm 0.03 \mu\text{g m}^{-3}$). In contrast, experiments with ambient air (E1–E14) resulted in 0.1 – $2.5 \mu\text{g m}^{-3}$ of organic mass taken up on the seed aerosols (5 – $22 \mu\text{g m}^{-3} \text{SO}_4^{2-}$ seed) in the first 2 min and much faster than could be measured with the AMS. These ambient exposure experiments can be separated into two groups; those which begin with sufficient $\text{NH}_3(\text{g})$ in the chamber initially to fully neutralize the aerosols as indicated by the molar neutralization potential (i.e., $[\text{NH}_3/\text{SO}_4]_i > 2$; E4–E14), and those in which the aerosols should remain acidic ($[\text{NH}_3/\text{SO}_4]_i < 2$; E1–E3). A time series of the measured aerosol organic mass (normalized by sulphate to remove the effect of aerosol wall losses) for experiments within these groups is given in Fig. 1a and b. These two scenarios are discussed further below.

3.1 Oxygenated organic uptake on non-acidic seed

There is an initial aerosol organic mass increase (Org/SO_4) for these experiments (and all other experiments) in the first 2 min, which occurred faster than the AMS measurement time resolution (2 min), which for non-acidic aerosols is essentially complete

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(Fig. 1a). This initial organic mass added is plotted as a function of the initial SO_4^{2-} seed mass in Fig. 2a. According to Fig. 2a, the mass of organics taken up on non-acidic seed aerosol is proportional to the mass of sulphate seed aerosols. Data points in Fig. 2a are shaded by the neutralization potential ($[\text{NH}_3/\text{SO}_4]_i$), which indicates that those experiments with excess NH_3 fall closest to the best fit line. Since the integrated surface area in these experiments also increases with increasing SO_4 seed mass, it is difficult to deduce if the initial uptake of gases is volume or surface area dependent. However, a mass dependence in Fig. 2a is consistent with the results of Li et al. (2011). In that study, organic gases from a single gasoline engine were exposed to mono-dispersed, non-acidic $(\text{NH}_4)_2\text{SO}_4$ seed aerosols, and the fast organic uptake found to be due to the dissolution of gaseous species (i.e., seed aerosol mass dependent). The organic to sulfate ratio in those studies was shown to be related to the organic vapor pressures, and was approximately 5 %, (Fig. 2a) which is in good agreement with the current study (~ 7 %).

The AMS organic mass spectrum from Li et al. (2011) and the average organic spectrum for the experiments with highest $[\text{NH}_3/\text{SO}_4]_i$ (Table 1) in the present study are shown in Fig. 2b. The two spectra (each normalized to the total signal) are remarkably similar, with a high degree of correlation ($R^2 = 0.96$, Slope = 0.9). This is not only true for the fragments which contribute to the majority of the mass (i.e., m/z 27, 41, 43, 43, 55, 67, 69) but also many of the less prevalent fragments. Removing the contribution of the dominant fragments in the spectra (i.e., m/z 27, 41, 44, 55) does not significantly degrade the overall correlation ($R^2 = 0.90$). The spectra for the condensed organics on neutral aerosols in this study were also compared with those of other sources (Fig. 3). The results of Fig. 3 indicate that the added organics in this study are vastly different than those from primary organic aerosol (POA) generated from a gasoline vehicle (Mohr et al., 2009) ($R^2 = 0.45$, Slope = 0.65) despite the fact that gasoline exhaust vapours were likely the largest contributors to the initial uptake. The spectra from this study are also significantly different than the spectra derived from positive matrix factorization (PMF) used to de-convolve ambient aerosol sources

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

and/or processes (Ng et al., 2011b) (Fig. 3); particularly those of HOA (a surrogate for POA) ($R^2 = 0.57$, Slope = 0.66), semi-volatile SOA (SV-OOA; $R^2 = 0.66$, Slope = 0.57) or more aged, low-volatility SOA (LV-OOA; $R^2 = 0.47$, Slope = 0.84).

The results of Figs. 2 and 3 most importantly demonstrate that the majority of organics taken up from ambient air likely arose from the condensation of gasoline vehicle emissions (under neutral conditions), and that the concentrations of these vapors were not significantly different than the diluted engine exhaust studies of Li et al. (2011). These results are consistent with gasoline engine exhaust being the dominant source of VOCs/SVOCs during the present study, as shown by the relatively high benzene and toluene concentrations in the ambient air (Table 1) and the close proximity to a major roadway (< 100 m). Furthermore, the ratio of toluene to benzene in the chamber during these experiments was approximately 3.0 (mean), which represents a moderately fresh vehicle emission, as compared to the values (~ 3.7 to 5.2) reported for fresh urban plumes, and in contrast to that of photo-chemically aged air masses (< ~ 1) (De Gouw et al., 2005; Cubison et al., 2006; Warneke et al., 2007; Vlasenko et al., 2009). Given the multitude of gas phase organic species present in the ambient air, including those of biogenic origin (Table 1), it is possible that other species may partly contribute to organic uptake here (Liggio et al., 2008) thus explaining some of the small differences in the spectra (this study vs. Li et al., 2011). The gas-phase HR-ToF-PTR-MS spectra obtained during experiments with the most acidic seed aerosols (and thus highest added organic mass) are also consistent with an exhaust source rich in unsaturated hydrocarbons as demonstrated previously (Liggio et al., 2011). However, a VOC decrease from the gas-phase for neutral aerosol experiments could not be observed due to the inherently less organic mass taken up and thus precision limitations of the HR-ToF-PTR-MS.

3.1.1 Potential uncertainties

Given the volatility of ambient OA, the possibility of organic aerosol evaporation during the filtration process followed by re-partitioning to seed aerosol (as a source of

A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(Xu and Zhang, 2012; Yu et al., 2012). No amines were observed in the gas-phase as measured by the PTR-ToF-MS and high O:C indicative of small di-acids was not observed in the initial aerosol. Secondly, the large final sulphate mass ($5\text{--}22\ \mu\text{g m}^{-3}\ \text{SO}_4^{2-}$) implies that H_2SO_4 vapour concentrations were sufficiently high that molecular collisions with organics were less likely than those of H_2SO_4 and H_2O . The high degree of correlation between organic aerosol spectra of this study and that of Li et al., 2011 (Fig. 2b), despite the use of atomization as a seed aerosol source (i.e., without nucleation) also suggests a minor role for organics in the nucleation process. Finally, organic incorporation during nucleation implies that the initial organic aerosol spectra should be similar for all experiments, as the seed aerosols are generated identically in all cases. However, acidic aerosol experiments have initial spectra that are significantly dissimilar to others (Fig. 5a).

3.1.2 Organic aerosol O : C on neutral seed

The condensation of gasoline exhaust vapours to a polar inorganic seed aerosol suggests that the condensing organics were likely oxygenated to some degree. The O : C ratios for ambient aerosols at the time of experiments and those of the added organics (on the seed aerosols) is given in Table 2. The O : C ratios in the ambient aerosols ranged from 0.35–0.55 (Mean = 0.42), similar to that of a semi-volatile oxygenated secondary organic aerosol (SV-OOA; Ng et al., 2001b). Conversely, the O : C ratios for the organics taken up onto the seed aerosols were substantially lower (0.21–0.32; Mean = 0.29), in agreement with that of Li et al. (2011), but much higher than that reported for gasoline derived POA (~ 0.04) (Mohr et al., 2009), hydrocarbon-like organic aerosols (HOA); a factor thought to represent ambient POA (Ng et al., 2011b), and much lower than that of more aged SOA (less volatile; LV-OOA) (Ng et al., 2011b). These observations together point to a new mechanism for forming oxygenated OA which is neither as oxygenated as reported surrogates of SOA (OOA; Ng et al., 2011b) nor as hydrocarbon-like as reported primary sources (Mohr et al., 2009; Ng et al., 2011b) despite a predominantly gasoline exhaust source. The condensation of primary

A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



oxygenated exhaust gases to the seed aerosols, as also shown in Li et al. (2011), is likely responsible for much of oxygen content in the aerosols of this study under neutral conditions. This is in agreement with recent studies which have demonstrated that carbonyls may account for up to 37 % of the total primary organic mass (> 80 % in the gas-phase) emitted from light duty gasoline vehicles compared to less than 4 % for diesel (Jakober et al., 2008). Fast and reversible olefin hydration reactions are known to occur under acidic conditions (Liggio et al., 2008; Liu et al., 2010). This may also explain some of the added oxygen within the neutral seed aerosols, since these aerosols were initially acidic for a very short time, and because a significant uptake from the gas-phase was demonstrated to be of olefin functionality under acidic conditions (Liggio et al., 2011). However, as demonstrated below, olefin hydration and/or condensation of oxygenated exhaust gases are insufficient to explain the high degree of oxygenation in aerosols which remain acidic.

3.2 Reactive organic uptake on acidic seed

Experiments with insufficient NH_3 for full neutralization of seed aerosols (i.e., acidic, E1–E3) show that acquired organic masses on the seed aerosols are notably above the best fit line of Fig. 2a. This suggests heterogeneous and/or aerosol phase chemistry is occurring, increasing the organic mass by a factor of three above the best fit line, and above that which would immediately partition from the gas-phase to a non-acidic seed aerosol. The existence of Aerosol-phase chemistry resulting in oligomers is further demonstrated by the slow increases in organic mass on the aerosols over time during the acidic experiments (Fig. 1b) compared to neutral aerosols which reach a steady state immediately (Fig. 1a). Concurrent with aerosol reactive uptake is the formation of high mass fragments in the organic mass spectra of the aerosols (Fig. 5a) which extend beyond 450 amu. Given the large ionization energies utilized in the HR-ToF-AMS (~ 70 eV), these higher m/z fragments are likely to arise from even larger parent compounds in the aerosol, which are highly unlikely to arise from the gas-phase. A shift to larger m/z over time (i.e., chemical reaction) in this closed system is demonstrated in

A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Fig. 5a which shows that the relative importance of fragments greater than ~ 150 amu increases over several hours (2 min–5 h). Figure 5b compares the background raw signal in the absence of particles during this experiment with the spectra at 106 min, which clearly illustrates that fragments as large as ~ 600 amu are orders of magnitude above the noise level (note Log scale). While high mass fragments are clearly linked to high MW species, the destructive nature of the AMS ionization precludes the use of these fragments as a quantitative measure of the oligomer fraction. However, a qualitative measure of the oligomers was obtained as the sum of all AMS fragments greater than 300 amu. The sum of $m/z > 300$ (normalized by SO_4) is shown in Fig. 1b and demonstrates that there is an obvious difference between the time evolution of high mass fragments and the total organic aerosol mass, with the m/z 300/ SO_4 increase being slower without ever reaching a steady state. Also, the rate of increase of m/z 300/ SO_4 is correlated with the final aerosol acidity as determined by the NH_4/SO_4 ratio of Table 2 ($E1 < E2 < E3$). Taken together, these observations are consistent with an acid-catalyzed oligomerization mechanism.

3.2.1 Organic uptake reversibility

The organic uptake reversibility on acidic aerosol with respect to NH_3 exposure, and effect on oligomer formation and aerosol O : C ratios was studied by introducing a subsequent pulse of excess NH_3 (Fig. 1b, Table 1) after significant organic uptake had occurred which drives the aerosols to neutrality instantly. This results in a corresponding decrease (20–40 %) in the organic mass (Fig. 1b), demonstrating a degree of reversibility. In neutralizing the aerosol with NH_3 , a new gas-particle equilibrium with water vapour must be established; in this case resulting in a decrease in the aerosol water content. A loss of aerosol water and corresponding decrease in organic mass is consistent with the known overall reversibility of alkene and carbonyl hydration reactions (Liggio et al., 2008; Liu et al., 2010; Wade, 2003) as depicted generally in Eqs. (1) and (2).



Equations (1) and (2) are also the first steps to other reactions leading to oligomeric compounds such as aldol, acetal, and cationic polymerization products (Noziere et al., 2003; Liggio et al., 2007) which are not reversible. This explains why the oligomerization products, as represented by $m/z > 300/\text{SO}_4$ in Fig. 1b do not decrease upon addition of NH_3 and subsequent aerosol neutralization. Addition of excess ammonia during neutral aerosol experiments did not result in any significant loss of organics.

3.2.2 Organic aerosol O : C on acidic seed

The addition of NH_3 resulting in the partial reversibility of organic uptake can also give an indication of the degree of oxygenation of the high MW products and their starting materials. The fraction of total organic fragments attributed to high MW fragments (using $(m/z > 300/\text{Total Org})$ as a surrogate) and the associated organic O : C ratios for two experiments with an additional NH_3 pulse is given in Fig. 6a. Figure 6a demonstrates that the relative importance of high MW products increases as a result of aerosol neutralization (green shaded region) at the expense of reversible products. This is consistent with the $(m/z > 300)/\text{SO}_4$ of Fig. 1b, where high MW products are irreversible, thus accounting for a greater fraction of the organic aerosol after the loss of reversible products. More importantly, the corresponding O : C ratios increased after the NH_3 addition (Fig. 6a). This implies that the irreversible oligomers were more oxygenated than the reversible uptake species, and that the oligomers arose from more oxygenated building blocks, facilitated by the increased aerosol acidity. If it is assumed that what remains after neutralization is primarily high MW products, then they likely will possess an O : C

A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ratio greater than ~ 0.3 . In comparison, increases in the O : C ratios over time were not observed for experiments with neutral aerosols, suggesting that acidity played a key role in the increases of the O : C ratios.

The evolution of the organic O : C ratios during these experiments can also be represented in a Van Krevelen diagram (Fig. 6b), as has been shown for ambient and laboratory SOA datasets (Tkacik et al., 2012; Lambe et al., 2012; Heald et al., 2010; Ng et al., 2011a). The slope of the lines in Fig. 6b represent the net functional group changes in the idealized case (red dashed lines), ambient observations (blue and green), and the current study (black). For acidic cases during this study the data fall along a slope of approximately -1.5 . This is significantly less than has been observed for ambient or laboratory SOA (-0.5 to -1), where gas-phase/heterogeneous oxidation, multiple source inputs and/or dilution determine the slope. In the present study, the combination of primary oxygenated and hydrocarbon condensation (i.e., Li et al., 2011) and oligomer formation results in a net conversion from hydrocarbon-like to approaching carbonyl functionality (slope = -2). A steep slope indicative of carbonyl addition has been observed previously in oxidative systems (Ng et al., 2011a). In contrast, the slope in this study is facilitated by the aerosol-phase chemistry, enhanced by particle acidity. These results further imply that hydration reactions while possibly important in the first few minutes, is not responsible for the changes in the O : C ratios or the majority of the organic mass. Hydration reactions should result in a positive (i.e., upwards; $+2$) slope (Fig. 6b), however there was insufficient time resolution in these measurements to observe this behaviour. A trajectory in the Van Krevelen space towards higher O : C ratios is in agreement with the increased relative importance of high MW species (which have a higher O : C ratio) over time as demonstrated in Fig. 6a. These are formed on a slower time scale than the condensation of primary gases and/or fast hydration reactions. The slope is consistent with hemi-acetal and/or aldol reaction mechanisms, forming oligomeric species containing carbonyl functional groups (Nguyen et al., 2010; Li et al., 2011). Increases in O : C over time, possibly due to oxidative chemistry in the

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



dark (i.e., O_3 and NO_3) are not likely, since an increase in organic mass and O : C was only observed for acidic aerosol experiments.

4 Implications and conclusions

The present results have several implications for ambient organic OA mass and composition in the presence of neutral and acidic aerosol. Foremost, they imply that the condensation of gasoline exhaust vapours onto pre-existing neutral seed mass as demonstrated previously (Li et al., 2011), will occur under ambient conditions (with fully diluted exhaust). Extrapolating the relationship in Fig. 2a (Organic : $\text{SO}_4 \sim 7\%$) to a regional scale, downwind of urban sources ($\sim 2 \mu\text{g m}^{-3}$ neutral SO_4 ; Zhang et al., 2007) suggests that $\sim 0.14 \mu\text{g m}^{-3}$ of organics can be added to the OA burden via this mechanism. This amount of organic mass is small with respect to typical SOA levels in these regions; $\sim 1.5\text{--}5.4 \mu\text{g m}^{-3}$ OOA (Zhang et al., 2007). However, if this uptake is considered to be primary, then it represents a significant amount of POA compared to the average POA (represented by HOA) measured in these areas ($\sim 0.6 \mu\text{g m}^{-3}$; Zhang et al., 2007). Furthermore, this process represents a source of oxygenated OA that can be categorized as POA (i.e., condensation of primary gases).

Typically, OA and/or oxygenated PMF factors (i.e., LV, SV-OOA) correlate well with secondary sulfate (Huang et al., 2011; Hersey et al., 2011), from which a secondary source is inferred. However in this study the organic uptake is demonstrated to be both proportional to the SO_4 mass and with relatively high O : C ratios, which implies that a fraction of the measured oxygenated OA, which correlates with secondary sulphate and assigned as SOA, may in fact be primary in nature. Indeed, in using the PMF technique to determine contributing factors to a dataset collected in mid continental North American regional ambient air, Slowik et al. (2011) derived an AMS PMF factor which correlated with SO_4 but which they could not attribute to specific processes. This unknown factor does have a spectrum with some qualitatively similar major fragments to those presented here. However, the current finding suggests that, due to the correlation

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with sulphate, it is unlikely that spectra from this process can be resolved from SOA factors derived from PMF analysis of aerosol mass spectral data.

Organic mass uptake in the present study, utilizing the ambient mixture and concentration of gases is also greatly enhanced under acidic conditions, due to aerosol-phase reactions forming products which are more oxygenated than condensed species on neutral aerosols. Consequently, ambient aerosols which are initially acidic, can add significant amounts of organic mass, and with a high degree of oxygenation via reactive uptake in a very short time, despite being neutralized shortly thereafter (i.e., irreversible). Since significant mass is taken up in less than 2 min under these acidic conditions, this process will be highly relevant for freshly nucleated aerosols, during cloud processing of sulfate, or anywhere that acidic sulphate or other acidic substances are available for even a short time. These results strongly suggest that similar oxygenated organic mass and high molecular weight products formed in this manner are ubiquitous in areas of moderate to high levels of SO₂ and/or other acid-forming precursors and enhanced further at low NH₃. The results also imply that on-going aerosol chemistry facilitated by acidity can affect to the O : C ratio evolution in ambient OA as depicted in Van Krevelen diagrams, without the need for oxidation to occur. These new processes under neutral and acidic conditions, and their effect on ambient O : C ratios, have not been previously considered, but will be important in properly representing organic aerosol O : C ratios in air quality and climate models.

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A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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A new source of oxygenated organic aerosol and oligomers

J. Liggio and S.-M. Li

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Tkacik, D. S., Presto, A. A., Donahue, N. M., and Robinson, A. L.: Secondary Organic Aerosol Formation from Intermediate-Volatility Organic Compounds: Cyclic, Linear, and Branched Alkanes, *Environ. Sci. Technol.*, 46, 8773–8781, doi:10.1021/es301112c, 2012.

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Table 1. Initial experimental and ambient parameters.

Exp. ^a	SO ₄ ²⁻ (μg m ⁻³) ^b	NH ₃ (g) (ppbv) ^c	(NH ₃ /SO ₄) _i ^d	Mode Diam. (nm)	Tol/Benz (ppb) ^e	Terp/Isop (ppb) ^e	Additional [NH ₃] Pulse ^f
B1	11.0	16.7	6.0	113	BDL	BDL	–
B2	28.4	28.6	4.0	168	BDL	BDL	–
B3	6.8	153	89.2	117	BDL	BDL	–
E1	5.8	1.1	0.75	238	0.27/0.18	0.12/0.57	–
E2	15.3	2.3	0.6	108	1.0/0.43	0.25/0.80	–
E3	16.5	3.8	0.9	112	0.83/0.37	0.23/0.82	10.1
E4	22.0	26.0	4.7	200	2.8/0.83	0.45/1.3	69.8
E5	5.8	2.7	1.9	82	0.76/0.32	0.20/0.48	50.2
E6	6.8	10.5	6.1	187	0.81/0.44	0.21/1.0	–
E7	2.7	9.0	13.2	117	1.4/0.6	0.41/0.79	–
E8	8.9	11.6	5.2	155	2.2/0.63	0.27/0.78	–
E9	9.1	9.6	4.2	151	0.72/0.27	0.25/1.3	–
E10	5.8	8.8	6.1	125	0.57/0.31	0.26/0.55	–
E11	9.9	22.5	9.0	190	0.54/0.28	0.27/0.48	–
E12	17.0	43.3	10.1	115	2.0/0.34	0.37/0.52	–
E13	11.4	24.0	8.4	123	NA	NA	–
E14	20.0	10.0	2.0	252	NA	NA	71.0

^a B1–B3 refers to background experiments with zero air but with added ammonia.

^b Initial CE corrected sulfate loading at t ~ 3 min.

^c Initial concentration prior to addition of H₂SO₄.

^d Initial molar ratio; a value of 2.0 indicates that particles should be neutral at the end of experiment. Estimated uncertainty in NH₄/SO₄ is approximately 25 %.

^e Ambient concentrations in chamber 5 min prior to H₂SO₄ addition. Tol = toluene (mean: 1.1 ppb), Benz = benzene (mean: 0.4 ppb), terp = terpenes (mean: 0.27 ppb), Isop = Isoprene (mean: 0.79 ppb), BDL = Below Detection limit.

^f Increase in NH₃ concentration during an additional pulse of NH₃ for selected experiments.

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new source of oxygenated organic aerosol and oligomers

J. Ligio and S.-M. Li

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 2. Results of organic uptake experiments and concurrent ambient data.

Exp.	Org. ($\mu\text{g m}^{-3}$) ^a	(NH_4/SO_4) _f ^b	Ambient Org ($\mu\text{g m}^{-3}$) ^c	Org/ SO_4 ^b	O : C (ambient) ^c	O : C (exp) ^b
B1	0.03 ± 0.02	2	–	–	–	–
B2	0.03 ± 0.02	2	–	–	–	–
B3	0.03 ± 0.02	2	–	–	–	–
E1	0.95	0.3	0.38	0.75	0.55	0.29
E2	2.5	0.5	0.6	0.55	0.50	0.28
E3	2.1	0.6 ^d	1.04	0.25	0.47	0.27
E4	1.51	1.5 ^d	1.3	0.07	0.42	0.17
E5	0.65	1.75 ^d	0.53	0.17	0.36	0.25
E6	0.4	1.8	1.6	0.04	0.51	0.26
E7	0.1	1.9	0.62	0.1	0.35	0.28
E8	0.5	1.7	1.7	0.1	0.38	0.30
E9	0.77	1.8	0.66	0.09	0.40	0.27
E10	0.2	2	0.76	0.14	0.36	0.32
E11	0.51	1.9	0.62	0.04	0.37	0.21
E12	0.11	2	0.7	0.03	0.36	0.30
E13	0.32	2	–	0.04	–	0.31
E14	1.95	1.5 ^g	0.8	0.15	0.44	0.24

^a Initial organics (~ 2 min).

^b At end of experiment. Estimated uncertainty in NH_4/SO_4 is approximately 25 %.

^c Non-filtered ambient air value averaged for 10 min prior to experiment.

^d Prior to additional pulse of NH_3 .

A new source of oxygenated organic aerosol and oligomers

J. Ligio and S.-M. Li

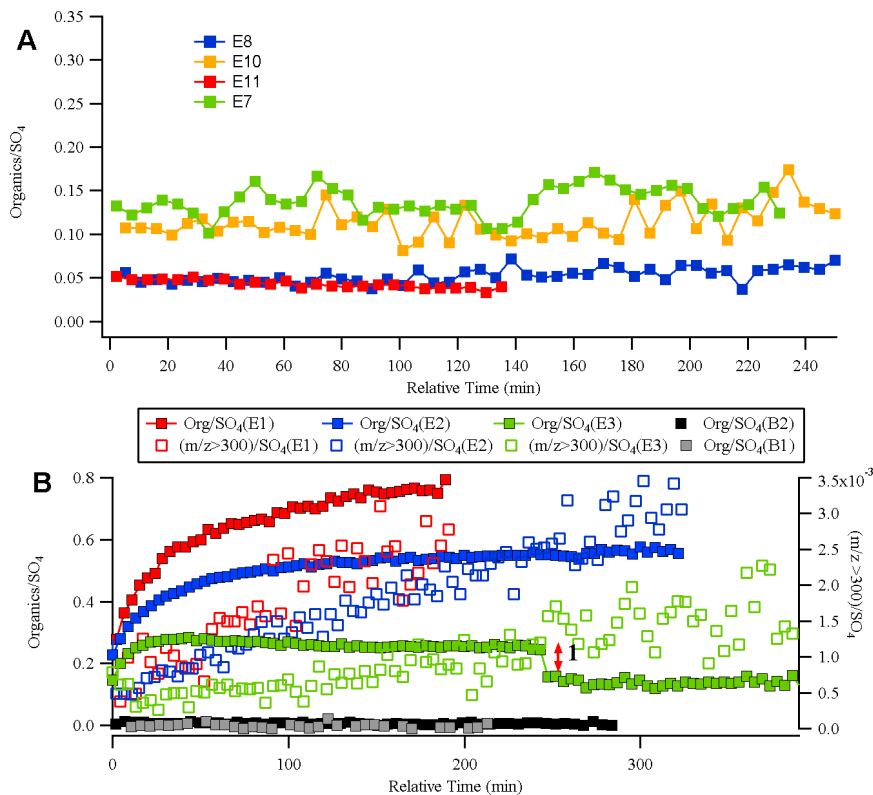


Fig. 1. (A) Organic/sulfate for non-acidic seed experiments as a function of time relative to aerosol SO₄ addition. SO₄ normalization removes aerosol wall loss effects. (B) Organic/sulfate and (m/z > 300)/SO₄ for acidic seed experiments as a function of time relative to aerosol SO₄ addition. Red arrow represents an additional NH₃ pulse.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new source of oxygenated organic aerosol and oligomers

J. Ligio and S.-M. Li

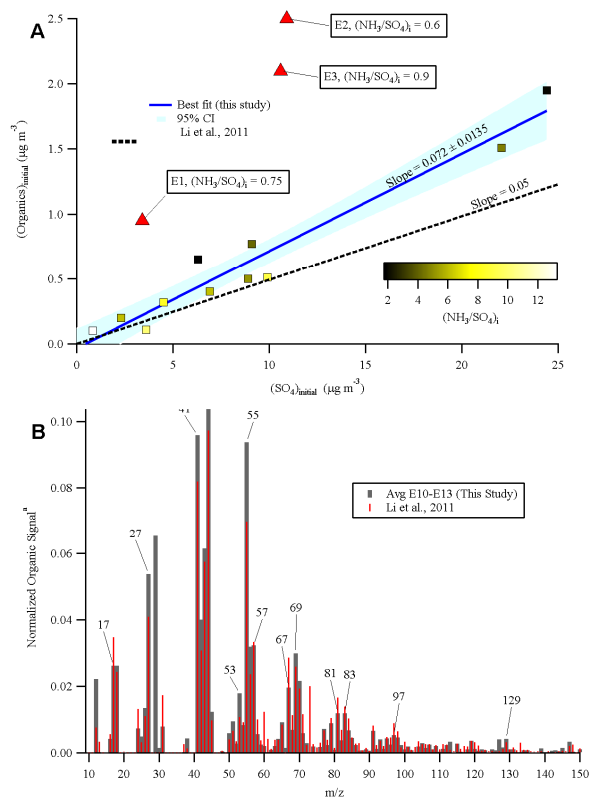


Fig. 2. (A) Initial organics as a function of initial SO_4 seed mass ($t \sim 2$ min) for this study and that of Li et al. (2011). Triangles represent acidic experiments. Data points shaded by neutralization potential ($(\text{NH}_3/\text{SO}_4)_i$). Best fit line through shaded points only. (B) Average organic mass spectra for neutral aerosol experiments and that of Li et al. (2011).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

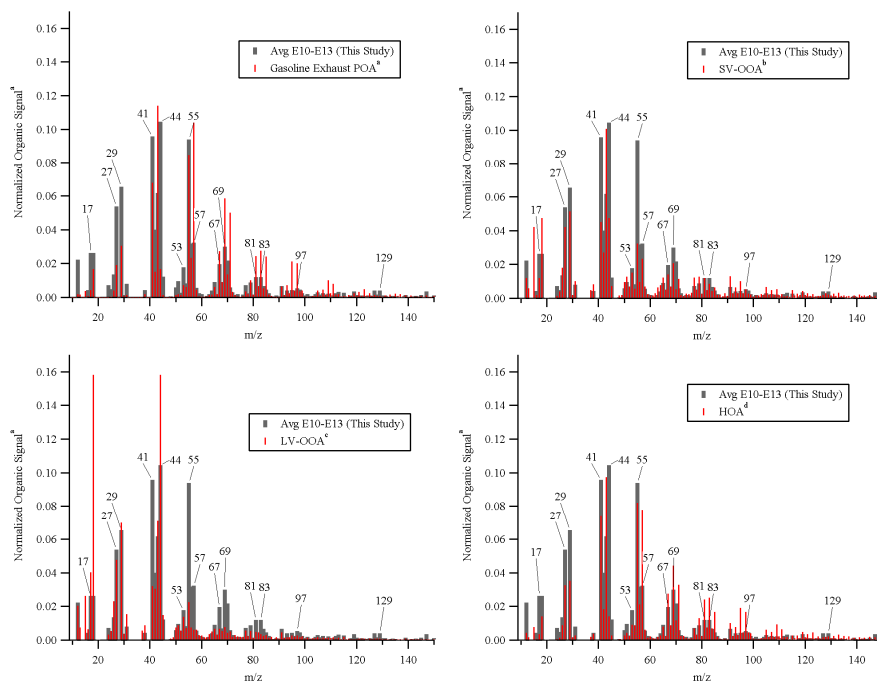


Fig. 3. Comparison of average organic aerosol mass spectrum from initial uptake to SO_4 (this study) with reported gasoline exhaust POA and various average PMF derived spectra from worldwide datasets (Ng et al., 2011b). **(a)** Mohr et al. (2009). **(b)** SV-OOA = Semi-volatile oxygenated organic aerosol. **(c)** LV-OOA = Less-volatile oxygenated organic aerosol. **(d)** HOA = Hydrocarbon-like organic aerosol (surrogate for POA). Reference spectra obtained via AMS Spectral Database; Ulbrich, I. M., Lechner, M., and Jimenez, J. L.; <http://cires.colorado.edu/jimenez-group/AMSSd/> (Ulbrich et al., 2009).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

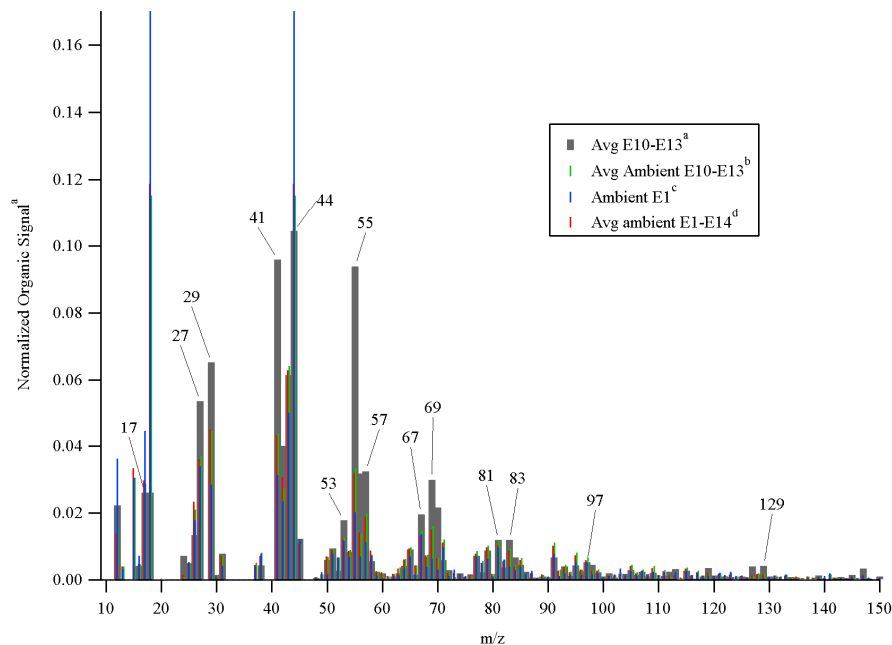


Fig. 4. Comparison of average organic aerosol mass spectrum (non-acidic; this study) with various ambient spectra 10 min prior to exposure in these experiments. **(a)** Average (E10–E13) 3 min after uptake. **(b)** Average ambient spectra (E10–E13) 10 min prior to exposure. **(c)** Ambient spectra for E1 10 min prior to exposure. **(d)** Average ambient spectra for all experiments 10 min prior to exposure.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

A new source of oxygenated organic aerosol and oligomers

J. Liggió and S.-M. Li

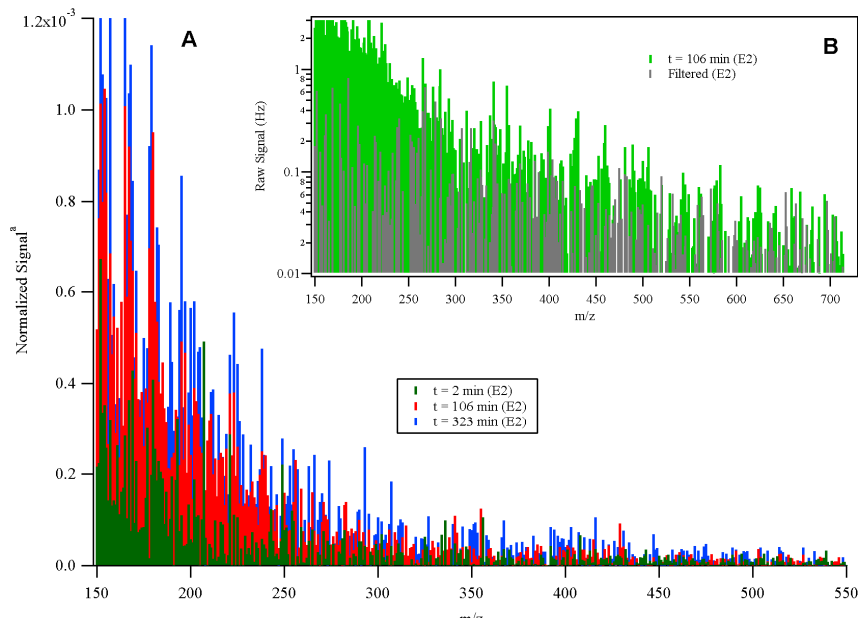


Fig. 5. Organic spectrum (> 150 amu) as a function of relative time for E2. **(A)** Normalized to total organic signal. **(B)** Raw signal ($m/z > 150$ amu) in the absence of aerosols (i.e., noise level) during E2 compared to the spectra at 106 min.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

A new source of oxygenated organic aerosol and oligomers

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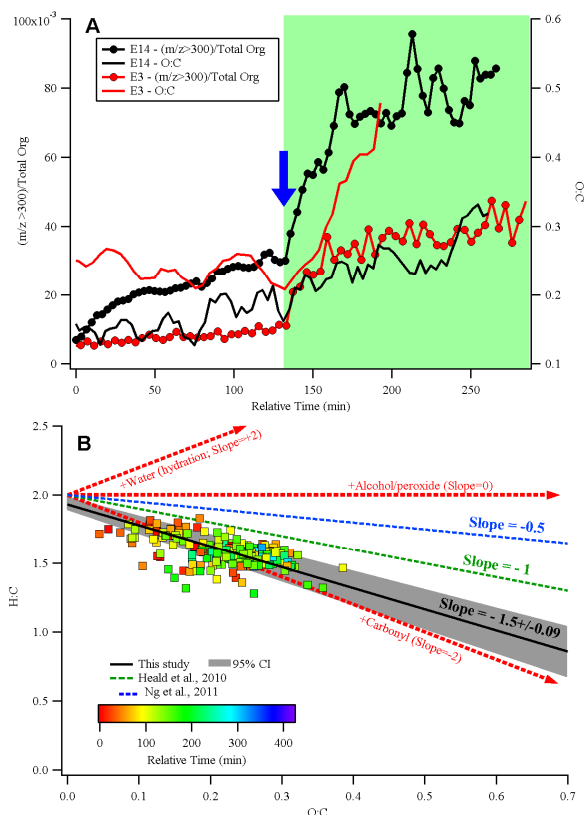


Fig. 6. (A) Relative importance of > 300 amu fragments to the total organics and associated organic O:C ratios before and after the addition of an NH_3 pulse (green shaded area). (B) VanKrevelen diagram for experiments which remain acidic (E1–E5, E14), with the slopes from previous studies.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion