Temperature Effects on Secondary Organic Aerosol (SOA) from the Dark Ozonolysis and Photo-Oxidation of Isoprene

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ABSTRACT: Isoprene is globally the most ubiquitous nonmethane hydrocarbon. The biogenic emission is found in abundance and has a propensity for SOA formation in diverse climates. It is important to characterize isoprene SOA formation with varying reaction temperature. In this work, the effect of temperature on SOA formation, physical properties, and chemical nature is probed. Three experimental systems are probed for temperature effects on SOA formation from isoprene, NO + H₂O₂ photo-oxidation, H₂O₂ only photo-oxidation, and dark ozonolysis. These experiments show that isoprene readily forms SOA in unseeded chamber experiments, even during dark ozonolysis, and also reveal that temperature affects SOA yield, volatility, and density formed from isoprene. As temperature increases SOA yield is shown to generally decrease, particle density is shown to be stable (or increase slightly), and formed SOA is shown to be less volatile. Chemical characterization is shown to have a complex trend with both temperature and oxidant, but extensive chemical speciation are provided.

1. INTRODUCTION

Isoprene is the most abundant nonmethane hydrocarbon observed in the atmosphere.¹ Isoprene is found in the ambient in diverse meteorological, gas-phase oxidant concentration, and geographical environments, from boreal forests² to marine environments³ and oil tanker emissions.⁴ It is therefore important to study secondary organic aerosol (SOA) formation from isoprene under varying oxidizing conditions, humidity, and temperatures to provide reaction conditions analogous to ambient conditions globally. Many have studied the effect of various oxidizing environments including, O₃, NO, nitrate radical, and hydroxyl radical.⁵⁻⁹ Most of these studies have focused on isoprene SOA formation from NO photo-oxidation. Though study of NO photo-oxidation provides a good analog for the formation of SOA from isoprene in the daytime urban environment, where NO is abundant, it does not provide a complete picture of SOA formation from isoprene. It is further of interest to study hydroxyl and ozone independently of NO for mechanistic insight into SOA formation; for when NO is present both O₃ and hydroxyl radical will be present. A study spanning common atmospheric oxidant sources also gives insight into effects in rural environments where NO concentrations would be low and hydroxyl radical or O₃ would be the more prevalent atmospheric oxidants. The effect of humidity on SOA formation from isoprene has also been probed by others, but it is not studied here.¹⁰

Currently, little or no literature exists on the temperature effects of isoprene SOA formation. Here, a temperature and humidity controlled environmental chamber is used to study the effect of reaction temperature on the chemical and physical properties of SOA formed from isoprene photo-oxidation and dark ozonolysis. Increasing the ambient temperature of SOA formation forms less volatile products; the aerosol contain more oligomer-like products of higher density and lower volatility. Further, chemical speciation changes of SOA under different temperature and oxidation conditions are reported.

2. MATERIALS AND METHODS

2.1. Environmental Chamber. All experiments presented here were run in the UC Riverside/CE-CERT dual 90 m³ environmental chambers.¹¹ Briefly, the reactors are constructed of Teflon film and suspended and kept under constant positive differential pressure (>0.01 in. H₂O). The insulated enclosure is temperature controlled (within ±1 °C) and is continuously flushed with clean, dry (T₂<0 °C) air generated by an Aadco 737 purification system. For photo-oxidation experiments, 276 115W Sylvania 350BL black lights are used. Due to the change in NO₂ photolysis rate at different temperatures
Table 1. Experimental Conditions and Results

<table>
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<tr>
<th>run</th>
<th>temperature (K)</th>
<th>ΔHC (μg m⁻³)</th>
<th>[NO]₀ (ppb)</th>
<th>[H₂O₂]₀ (ppm)</th>
<th>O₃₀ (ppb)</th>
<th>final SOAₚ (μg m⁻³)</th>
<th>SOA yield</th>
<th>reaction notes</th>
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<td>278</td>
<td>278</td>
<td>0</td>
<td>0</td>
<td>125</td>
<td>25</td>
<td>0.09</td>
<td>dark ozonolysis</td>
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<td>EPA1739A</td>
<td>278</td>
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<td>0</td>
<td>0</td>
<td>135</td>
<td>27</td>
<td>0.09</td>
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<td>669</td>
<td>0</td>
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<td>500</td>
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<td>446</td>
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<td>0</td>
<td>42</td>
<td>0.12</td>
<td>photo-oxidation</td>
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</table>

*Initial H₂O₂ concentration is not measured but estimated by isoprene decay. Assumed average measured density of 1.34 g cm⁻³. Data previously published in ref 9. Light intensity was higher in these experiments with an estimated NO₂ photolysis rate of 0.51 min⁻¹.*

(described by Qi et al.12), the number of black lights used are adjusted for hot and cold photo-oxidation experiments. Unless otherwise noted, photolysis rate was controlled at 0.29 min⁻¹ by changing the number of bulbs. All isoprene (Sigma-Aldrich, 99.5%), H₂O₂ (50 wt % in H₂O, stabilized, Sigma-Aldrich), and perfluorohexane dilution tracer (Sigma-Aldrich, 99%) injections are performed via a a heated glass manifold system pure N₂. Precise concentrations of NO (ultra high purity, Matheson) were generated from clean air by a Horiba OZG-UV-01 Ozone Generator Unit and injected into the chambers by a controlled flow rate.

2.2. Gas and Particle Analysis. Hydrocarbon precursors and products were measured with an Agilent 6890 GC-FID. NO, CO, and O₃ concentrations were monitored using a Thermo Environmental Instruments Inc. model 42C trace level NO-NO₂-NOy analyzer, Thermo Environmental Instruments Inc. model 48C trace level CO analyzer and Dasibi O₃ analyzer, respectively. Before the start of each experiment, all gas-phase instruments are checked with a calibration standard.

Particle size distribution between 27 and 686 nm was monitored by a custom built Scanning Mobility Particle Sizer (SMPS) similar to that described by Cocker et al.13 Particle volatility was monitored with a house-built volatility tandem differential mobility analyzer (VTDMA). The first DMA column size-selects (Dₙₙ) the aerosol based off of the peak diameter seen by the SMPS and sends it through a Dekati thermodenuder (TD) at 100 °C. The particle size after the TD (Dₙₙ) is then measured by the second DMA. Volume fraction remaining (VFR) is then calculated as VFR = (Dₙₙ/Dₙₙ)³.

Particle effective density was measured with a Kanomax Aerosol Particle Mass Analyzer (APM)14 and in series with an SMPS. The APM is located upstream of the SMPS, providing improved time resolution and sensitivity (S/N), with a detailed description of the system its data algorithms described elsewhere.15 Briefly, the aerosol is size selected by the APM based on its mass and the resulting mobility diameter of the aerosol is then measured by the SMPS.

An Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS)16 were operated in high resolution, or “W”, mode throughout all experiments. Elemental analysis (EA) of the resulting data was used to determine the bulk chemical ratios (H/C, O/C, and N/C) of nonrefractory organic aerosols.17

A particle-into-liquid-sampler (PILS)18,19 was interfaced with an Agilent 6210 time-of-flight mass spectrometer (TOFMS), hereafter referred to as the PILS-ToF. The instrument was equipped with a multimode ionization source for both electrospray and atmospheric pressure chemical ionization (ESI/APCI), providing accurate online mass analysis of water-soluble organic compounds.9 HPLC pumps were used in addition to a common peristaltic pump to couple the PILS (Brechtel Manufacturing Inc.) to the TOFMS. This coupling was critical in order to overcome the backpressure of the TOFMS inlet and to supply steady flow of water (18.2MΩ, Milli-Q, Millipore) to the boiler. The PILS-ToF system is described in detail elsewhere. For all TOFMS data reported in this work, the electrospray ionization source (ESI) was operated in the negative ion mode with a vaporizer temperature of 200 °C, nebulizer pressure of 40 psig, corona current of 2 μA, and fragmentor voltage of 100 V.

Occasionally during the sample analysis, higher mass errors (up to 100 ppm) were observed, resulting in a consistent shift of mass throughout the range of the instrument. Since the extent of the shift can be inferred from repeatedly observed ions (e.g., methyl vinyl ketone), formulas were carefully assigned based on tendency of shift and repeat experiments.

3. RESULTS AND DISCUSSIONS

3.1. SOA Formation. Wall-loss corrected aerosol mass concentration was measured for 16 isoprene experiments. All experiments reported here have the same initial isoprene concentration, 697 μg m⁻³ (250 ppb). SOA yield (Y) is calculated as the mass of aerosol formed (wall-loss-corrected) (M₀) divided by mass of hydrocarbon reacted (ΔHC)

\[ Y = \frac{M₀}{\Delta HC} \quad (1) \]

Table 1 presents environmental chamber conditions for the experiments presented here. In the yield data reported from SMPS measurements in Table 1 and Figure 1, size distributions
of all experiments were reviewed with no significant or patterned variations in size distribution with temperature observed.

Figure 1. Experimental SOA yield as a function of environmental chamber reaction temperature for (a) NO and H2O2 photo-oxidation experiments and (b) dark ozonolysis experiments.

In Figure 1 the effect of environmental chamber reaction temperature on SOA yield is shown for both photo-oxidation and dark ozonolysis experiments. SOA yield decreases in Figure 1 by more than 2-fold between a reaction temperature of 278 and 300 K for NO + H2O2 photo-oxidation, H2O2 only photo-oxidation, and dark ozonolysis. This result supports a volatility driven process indicating the isoprene SOA at 278 K is made up, primarily, of semivolatile species.

For the NO photo-oxidation reactions with isoprene, SOA yield is seen to decrease by more than half as the reaction temperature is raised from 278 to 300 K. This decrease in yield is thought to be due to vaporization of semivolatile components during this increase in reaction temperature. As reaction temperature is further increased from 300 to 313 K SOA yield for the NO photo-oxidation system is seen to increase slightly, arguably within measurement error. This increase in yield could either be random measurement error or further reaction of isoprene to form less volatile components, potentially long chained and low volatility oligomers.

As temperature is increased in the photo-oxidation reaction of isoprene with H2O2 and during the dark ozonolysis of isoprene, SOA yield is seen to continually decrease as temperature is raised from 278 to 300 K and finally to 313 K. The final yields observed in both isoprene H2O2 photo-oxidation and dark ozonolysis at 313 K are very low. This large and continuous reduction of yield as temperature increases indicates that SOA formed through isoprene with H2O2 photo-oxidation or the reaction with O3 in the dark has very few nonvolatile constituents. It should be noted that at 300 K two isoprene dark ozonolysis experiments give different values for yield, this discrepancy can be attributed to low SOA mass formation for these experiments. This discrepancy within the SOA yield measurements for isoprene dark ozonolysis leads to potentially two interpretations of the trend in SOA yield decrease with increasing temperature, either linear or nonlinear (continually decreasing or asymptotic decrease).

For SOA formation from isoprene in the presence of NO and H2O2 at high temperature Criegee intermediates will be stabilized, allowing further oxidation in the presence of OH. Further, as Lambe et al. point out, OH concentration serves both SOA yield and the rate of formation of SOA. It is assumed that OH is in abundance for NO and H2O2 experiments, but no measurements of hydroxyl concentration for the experiments reported here are available.

In addressing SOA yield in experiments conducted in an atmospheric chamber, wall loss must be accounted for.

Table 2. Summary of SOA Chemical and Physical Characterization Data

<table>
<thead>
<tr>
<th>run</th>
<th>density (g cm⁻³)</th>
<th>VFR</th>
<th>AMS H:C</th>
<th>AMS O:C</th>
<th>AMS N:C</th>
<th>PILS-ToF H:C</th>
<th>PILS-ToF O:C</th>
<th>PILS-ToF N:C</th>
<th>PILS-ToF percent ions matched</th>
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<tr>
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<td>0.06</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.76</td>
<td>0.00</td>
<td>75</td>
<td>a,b</td>
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*a*No APM-SMPS data available. *b*No VTDMA data available. *c*No AMS data available. *d*No PILS-ToF data available.
Matsunaga and Ziemann as well as Zhang et al. conclude that vapor wall loss in SOA production in a Teflon film chamber is significant; leading to underestimation of SOA yield. In the CE-CERT chamber, used in experiments reported here, wall loss has been considered through many experiments, beginning with Carter et al. Further, the large size, 90 m$^3$, of the CE-CERT chamber was intended to minimize or virtually eliminate chamber wall losses. With the preface on wall losses above it should be noted that wall losses for SOA formation from isoprene have not been investigated in the CE-CERT chamber, but wall loss for other SOA systems, such as α-pinene and m-xylene, have been investigated. In these investigations the CE-CERT chamber wall losses have been characterized with no indication of significant vapor wall loss has been observed, beyond that of Carter et al. These observations of no significant wall loss hold even during temperature cycling of the chamber (hot to cold and cold to hot) when SOA formation from α-pinene is studied.

3.2. SOA Physical Characterization. Particle density and particle volatile fraction remaining were measured for a representative subset of the isoprene SOA experiments by APM-SMPS and VTDMA respectively. The physical and chemical SOA characterization data is summarized in Table 2. It should be noted that particle density and VFR are reported as a mean of measurements after particle nucleation, with error bars indicating the observed deviation from this mean.

SOA density, as measured by the APM-SMPS, is provided in Figure 2 for all three isoprene oxidant systems. The error bars in Figure 2 represent the maximum observed range of density observed in the SOA after nucleation, as measured by APM-SMPS. Density measurements for SOA formed from the reactions of isoprene range from 1.31 to 1.49 g/cm$^3$ and are generally consistent with previous measurements of Kuwata et al. and Engelhart et al. In comparing the broad observations from Kuwata et al. and the data presented in Figure 2, the SOA density data presented here is consistent with dicarboxylic acids. The assertion that the SOA from isoprene is made up of dicarboxylic acids is further supported in the SOA chemical characterization data presented in section 3.3 and in Table S1.

Within the observed measurement error, SOA density from isoprene photo-oxidation experiments with H$_2$O$_2$ alone does not vary with reaction temperature. The approximate mean density at all observed temperatures for isoprene reacting with H$_2$O$_2$ is 1.45 g/cm$^3$. This is comparable to isoprene photo-oxidation experiments conducted by Kuwata et al. where the reaction was conducted with H$_2$O$_2$, but in the absence of NO.

SOA density for isoprene dark ozonolysis also does not vary with reaction temperature. Nevertheless, the average density for SOA produced in isoprene dark ozonolysis of 1.38 g/cm$^3$ is lower than the average observed for isoprene H$_2$O$_2$ only photo-oxidation, but still within the range reported by others previously.

During isoprene photo-oxidation experiments done in the presence of NO, SOA density is observed to decrease slightly with increasing reaction temperature. This decrease is observed outside the margins of experimental error. This observation of decreasing density with increased temperature for the isoprene photo-oxidation experiments in the presence of NO indicates that the semivolatile species observed at lower reaction temperature are of higher density. The densities at 278 K for the NO photo-oxidation are, within error, the same as those from H$_2$O$_2$ only photo-oxidation and dark ozonolysis. Furthermore, densities at higher temperatures for the NO photo-oxidation experiments have the lowest observed densities. These lower observed densities could be a product of evaporated dicarboxylic acids leaving organic nitrate oligomer cores as indicated by volatility data and chemical characterization data reported here and previously.

Figure 3 plots SOA volatile fraction remaining (VFR) for all three isoprene oxidation systems. Less semivolatile products are formed at higher temperatures; VFR increases with temperature for all three oxidation systems. In Figure 3, isoprene NO + H$_2$O$_2$ photo-oxidation VFR is the same value at 300 and 313 K, indicating little change in particle volatility at higher temperature. Both isoprene NO + H$_2$O$_2$ and H$_2$O$_2$ only photo-oxidation show nonlinear VFR trends, they plateau at 300 K. However, dark ozonolysis VFR does not plateau at the two higher temperatures but behaves linearly continuing to increase throughout the temperature range tested. In all three scenarios VFR is increasing with temperature, indicating a nonvolatile SOA core. Overall, the high particle volatilities at low temperature indicate that the SOA is made up of semivolatile species. The trend of the SOA VFR results agrees with the SOA yield and density. It is hypothesized that upon heating the SOA reaction, less semivolatile species are present in the particle phase and reactions are occurring faster leading to an aerosol made of more oligomer products of much lower volatility. This hypothesis will be further supported by PILS-ToF chemical characterization.

3.3. SOA Chemical Characterization. Two mass spectral particle characterization data sets are compared from the AMS and the PILS-ToF. The HR-AMS gives quantitative chemical
description through the elemental ratios, O:C, H:C, and N:C. The PILS-ToF provides qualitative chemical speciation of the particle phase compounds and elemental ratios are then interpolated from molecular formula. AMS and PILS-ToF calculated average particle elemental ratios H:C, O:C, and N:C ratios are presented in Table 2. The overall chemical characterization of O:C, H:C, and N:C ratios of particle composition of the two methods agree. PILS-ToF reports slightly higher O:C ratios for all of the isoprene SOA experiments. Another discrepancy between AMS and PILS-ToF is isoprene NO + H2O2 where an average of data for photo-oxidation experiments (EPA1559A, EPA1353A, and EPA1288A) shows that regardless of reaction temperature, the PILS-ToF observed H:C ratio is approximately 0.5 less than that observed by AMS. Table 2 shows that AMS elemental ratios are insensitive (within the error of the data) to changes in reaction temperature.

Figure 4 shows the PILS-ToF mass spectra for isoprene NO + H2O2 photo-oxidation experiments at two reaction temperatures, 300 and 278 K. For NO + H2O2 isoprene photo-oxidation performed at 300 K (Figure 4a), the PILS-ToF mass spectra have a clear repeating ion peak pattern indicative of oligomerization. It should be noted that the data reported in Figure 4a has been presented and discussed elsewhere and used here as a base of comparison.

In contrast, PILS-ToF mass spectra of an isoprene NO + H2O2 photo-oxidation experiment EPA1559A performed at 278 K does not have an evident repeating pattern of mass spectral peaks indicative of oligomerization (Figure 4b). Yet oligomers could be present. Detailed PILS-ToF molecular formula matching provided in Figure 7 and Table S1 show that there are oligomers observed in Figure 4b, but clearly not as many. Instead the PILS-ToF mass spectra in Figure 4b is shifted to a lower molecular weight with a broad diverse “hump” of peaks observed between m/z 200 and m/z 600. It is thought that these smaller molecular weight species correlate to semivolatiles. SOA formation at 278 K may be dominated by the condensation of semivolatiles with reaction rates of oligomerization slowed by kinetic effects of decreased temperature and decreased concentrations of oligomer precursors.

In Figure 5a, isoprene H2O2 photo-oxidation experiment EPA1566A performed at 313 K, mass spectral peak intensity lies below m/z 400, with most mass spectral peak intensity falling below m/z 200. In Figure 5b, photo-oxidation experiment EPA1467A performed at 300 K in the absence of initial NO, larger m/z are observed with the mass spectral intensity existing in another broad “hump” of mass spectral peaks between m/z 100 and m/z 400. The PILS-ToF mass spectra of the H2O2 photo-oxidation experiment EPA1556A performed at 278 K is shown in Figure 5c. Figure 5c shows a further mass spectral intensity increase at higher molecular weights, greater than m/z 200, in comparison to Figure 5a and b. Furthermore, the mass spectral “hump” observed in Figure 5b has decreased between m/z 200–300 with discrete high intensity and higher m/z peaks in its place at above m/z 300. In contrast to the PILS-ToF mass spectral results for the NO + H2O2 photo-oxidation, PILS-ToF mass spectral peak intensity for the H2O2 only system increases at all m/z with increasing temperature, including high m/z; a result indicative of a volatility driven process. PILS-ToF results in Figure 5a low molecular weight and high volatility SOA.

Figure 6 shows PILS-ToF mass spectral results for isoprene dark ozonolysis experiments at three temperatures, 313, 300, and 278 K. In Figure 6a, isoprene dark ozonolysis experiment EPA1563A performed at 313 K, nearly all mass spectral intensity is observed below 400 m/z. Although in Figure 6b, the PILS-ToF mass spectra for isoprene dark ozonolysis experiment EPA1563A performed at 300 K, mass spectral intensity is below m/z 400 with two sets of peaks at higher m/z ranges observed between m/z 400–500 and m/z 600–700. For Figure 6c, the PILS-ToF mass spectra for isoprene dark ozonolysis experiment EPA1563A performed at 278 K, overall mass spectral intensity increase below m/z 400 while the mass spectral peaks observed in Figure 6b above m/z 400 are present but far less intense. Like the case of H2O2 photo-oxidation, the change in PILS-ToF mass spectra with temperature observed in Figure 6 for isoprene dark ozonolysis supports an SOA
formation process driven by chemical species volatility and not by reactions forming high molecular weight chemical species.

Figure 7 shows Van Krevelen diagrams of molecular matches for PILS-ToF mass spectral ions observed to have intensity greater than 1000 ion counts in Figure 4, the PILS-ToF mass spectra for isoprene NO + H2O2 photo-oxidation experiments. The observed intensity in Figure 7 is provided by a gray scale, where a black open circle represents a molecular match at 5000 ion counts and above and no circle (white) represents zero ion counts. Details of the mass spectral peaks observed in Figure 7 are provided in Table S1. For isoprene NO + H2O2 photo-oxidation experiments EPA1353A and EPA1559A performed at 300 and 278 K, respectively, show the same general focal point at O:C = 1 and H:C = 1.5 (Figure 7a and b). However, Figure 7a and b differ in the quadrant below O:C = 1 and H:C = 1.5; many more points are observed in this quadrant in Figure 7b. It is hypothesized that these points with lower O:C and H:C in Figure 7b are less oxidized hydrocarbons species of higher volatility.

Van Krevelen diagrams of molecular matches to PILS-ToF mass spectral ions observed at intensities above 1000 ion counts observed in Figure 5, for isoprene H2O2 photo-oxidation experiments done in the absence of initial NO, are provided in Figure 8. The detailed molecular matches in Figure 8 are presented in Table S1. In Figure 8a-c, for H2O2 photo-oxidation experiments EPA1566A, EPA1467A, and EPA1556 performed at environmental chamber temperatures of 313, 300, and 278 K respectively, some trends can be observed. First, though the eye is drawn to the focal point in all three Van Krevelen diagrams at O:C = 1.0 and H:C = 2.0 matched to the molecule C5H10O5, most of the molecules and mass spectral intensity lies in the quadrant below O:C = 1.0 and H:C = 2.0. The molecular abundance and intensities grow in the lower left quadrant of Figure 8a-c as temperature decreases. Indicating, as was hypothesized for NO + H2O2 photo-oxidation, that semivolatile species occur at lower O:C
greater than 1000 ion counts in Figure 4, the PILS-ToF mass spectra for isoprene dark ozonolysis experiments. The observed intensity in Figure 9 is provided by a gray scale as in Figures 7 and 8. The details of the mass spectral peaks observed in Figure 9 are provided in Table S1. In comparing Figure 9a–c, for isoprene dark ozonolysis experiments EPA1563A, EPA1445A, and EPA1483A performed at 313, 300, and 278 K, respectively, a focal point can be found, as observed in Figure 8, at O:C = 1 and H:C = 2. The molecular abundance and intensities grow in the lower left quadrant of Figure 9a–c, below O:C = 1 and H:C = 2, as temperature decreases. This result indicates, as was the hypothesis for the photo-oxidation systems, that semivolatile species occur at lower O:C and H:C.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05524.

Table S1, a detailed table of PILS-ToF observed ions and corresponding ion formula matches (PDF)

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Notes

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REFERENCES


