# High-Resolution Electrospray Ionization Mass Spectrometry Analysis of Water-Soluble Organic Aerosols Collected with a Particle into Liquid Sampler[†]

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**This work demonstrates the utility of a particle-into-liquid sampler (PILS), a technique traditionally used for identification of inorganic ions present in ambient or laboratory aerosols, for the analysis of water-soluble organic aerosol (OA) using high-resolution electrospray ionization mass spectrometry (HR-ESI-MS). Secondary organic aerosol (SOA) was produced from 0.5 ppm mixing ratios of limonene and ozone in a 5 m³ Teflon chamber. SOA was collected simultaneously using a traditional filter sampler and a PILS. The filter samples were later extracted with either water or acetonitrile, while the aqueous PILS samples were analyzed directly. In terms of peak abundances, types of detectable compounds, average O/C ratios, and organic mass to organic carbon ratios, the resulting high-resolution mass spectra were essentially identical for the PILS and filter based samples. SOA compounds extracted from both filter/acetonitrile extraction and PILS/water extraction accounted for >95% of the total ion current in the ESI mass spectra. This similarity was attributed to high solubility of limonene SOA in water. In contrast, significant differences in detected ions and peak abundances were observed for pine needle biomass burning organic aerosol (BBOA) collected with PILS and filter sampling. The water-soluble fraction of BBOA is considerably smaller than for SOA, and a number of unique peaks were detectable only by the filter/acetonitrile method. The combination of PILS collection with HR-ESI-MS analysis offers a new approach for molecular analysis of the water-soluble organic fraction in biogenic SOA, aged photochemical smog, and BBOA.**

Secondary organic aerosol (SOA) produced via oxidation of biogenic volatile organic compounds (VOC) represents a large fraction of the global aerosol budget and is a major source of water-soluble organic carbon (WSOC) in the atmosphere.[1] Biomass-burning organic aerosol (BBOA), although less water-soluble, also makes a significant contribution to WSOC.[1,2] On the whole, organic aerosol (OA) compounds associated with particulate matter have been found to be 10−70% water-soluble.[3−5] An estimated 47 TgC/year of WSOC is being washed out of the atmosphere through wet deposition alone.[6] Characterization of the water-soluble components of OA at the molecular level should improve our understanding of this important component of the global carbon cycle.

The complex matrix of compounds in OA samples requires sophisticated analytical methods for the detailed characterization of their composition.[7−19] High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) is a powerful tool for molecular level characterization of complex mixtures, especially OA samples.[7−15] ESI is a "soft ionization" technique that provides

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molecular formulas for hundreds of OA constituents when coupled with a high-resolution mass analyzer. One caveat to conventional ESI analyses, including those relying on chromatographic separation, is that samples must be dissolved in a solvent. Therefore, most ESI-MS studies of OA samples have relied on filter collection or particle impaction, followed by a separate solvent extraction step with various solvents: pure organic,[8,10-13] organic/aqueous mixture,[7,14] and pure aqueous.[9] Polar organic solvents are generally preferred for the ESI process. However, for the purpose of real-time or offline WSOC analysis, collection of OA directly into an aqueous solution is preferred.

A particle-into-liquid-sampler (PILS) was developed in 2001 exactly for this purpose: the collection and real-time analysis of water-soluble compounds in aerosols.[20] The PILS approach relies on rapid growth of particles to the size of microdroplets in the presence of supersaturated water vapor, followed by impaction onto a surface covered with a flow of water that washes out the impacted particles. A syringe pump directs the "wash", either into small glass vials for offline analysis, or into an instrument for real-time measurements and thus eliminates many of the common artifacts attributed to particle collection on filters.[20] Some of the advantages of the PILS collection method compared to the filter-based method include improvement in time resolution through automation of sampling, reduction in contamination associated with the filter extraction process, and selectivity for water-soluble compounds.

Traditionally, PILS has been coupled with ion chromatography, allowing for quantitative measurements of common atmospheric water-soluble inorganic ions and several small carboxylic acids in ambient and lab generated aerosols.[21-45] More recent applications include PILS coupled to an online total organic carbon analyzer for measurements of the total WSOC content;[5,46-52] PILS coupled to a liquid waveguide capillary cell and absorption spectrometer for detection of water-soluble iron in atmospheric aerosols;[53] and PILS coupled to offline ESI-MS, gas chromatography/mass spectrometry (GC/MS), or liquid chromatography/mass spectrometry (LC/MS) measurements.[54,55]

PILS coupled to online LC/MS was successfully deployed for collection and analysis of organic acids in ambient atmospheric

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aerosol.[56] No field instruments involving PILS coupled to ESI-MS have been reported yet. While such an online PILS/ESI-MS approach would have been ideal, the size and weight of modern high-resolution ESI-MS instruments have so far precluded their use in field sampling. However, PILS collection into vials followed by offline ESI-MS analysis can be just as useful provided that molecules in the sample do not undergo extensive hydrolysis between collection and analysis. As both collection and offline analysis can be automated, the labor requirements of the offline PILS/ESI-MS method are not significantly higher compared to the real-time analysis.

The objective of this work is to examine the utility of PILS for detailed molecular characterization of water-soluble organics in aerosols in conjunction with the HR-ESI-MS approach. In the present study, laboratory generated SOA, from the ozone initiated oxidation of d-limonene, and BBOA, collected from burning pine needles and sticks, are used as model systems. During each SOA or BBOA experiment, particles are simultaneously collected using two methods: (1) filter collection with extraction into either acetonitrile or water and (2) PILS collection with direct extraction into water. The resulting extracts are subsequently analyzed using HR-ESI-MS. Chemical characterization (molecular formulas, O/C, H/C, organic mass/organic carbon (OM/OC), and double bond equivalency) of the detected compounds are used to determine the types of water-soluble compounds present in organic aerosol. The comparison of mass spectra shows that PILS/HR-ESI-MS is a suitable method for the molecular analysis of water-soluble compounds in both biogenic SOA and BBOA.

## EXPERIMENTAL SECTION

Limonene SOA was generated by the reaction of d-limonene (Acros Organics, 98% purity) vapor and ozone in a 5 m³ inflatable Teflon chamber.[57] The reaction was carried out at room temperature, in the dark, and with dry purified air. Ozone was added to the chamber by passing ultrahigh purity oxygen (99.994%) through a Teflon tube with inserted Hg pen-ray UV lamp (Jelight Company, Inc.), until the desired ozone mixing ratio was reached (0.5 ppm). The ozone mixing ratio was monitored throughout the experiment with a commercial ozone monitor (Ebara Jitsugyo EG-2001). After the ozone mixing ratio stabilized for ∼30 min, 16 $\mu$L of d-limonene was injected through a gastight septum and carried in the chamber through $^1/_4$ in. tubing with a 10 standard liters per minute (SLM) flow of dry purified air. The amount of injected limonene was chosen to make the initial mixing ratio of limonene and ozone equal to each other. No OH scavenger was added. The chamber was mixed with a fan for the first 5 min after the injection. The fan was subsequently turned off to reduce loss of particles to the chamber walls.

The particle concentration in the chamber was monitored with a scanning mobility particle sizer (SMPS), which consisted of a differential mobility analyzer (DMA) platform (TSI model 3080), DMA column (TSI model 3081), and condensation particle counter (TSI model 3775). Particles appeared ∼5 min after the limonene

injection. The mixture was allowed to react in the chamber for 1 h before particle collection began.

The initial reactant concentrations of both limonene and ozone were 0.5 ppm, resulting in particle mass concentrations of approximately 2000 $\mu$g/m³ (assuming an effective density of 1.2 g/cm³). The collection time lasted 40 min. Particles were collected simultaneously with a PILS instrument[42] (Brechtel Manufacturing, Inc.) and with a Teflon-coated filter (Millipore, 0.2 $\mu$m pore) at 15 SLM flow rate for both collection methods. To compensate for the 30 SLM withdrawn from the chamber by the collection, an equivalent amount of dry purified makeup air was added to the chamber. The PILS uses a steam saturator to grow entering particles into larger droplets which are impacted onto a vertical surface with a constant flow of water. This flow was set at 100 $\mu$L/min and four 1 mL samples were collected during the 40 min particle collection time. Only one filter sample was collected during the particle collection time, via the filter technique.

BBOA samples were collected from the burning/smoldering of approximately 10 g of dried pine needles and sticks, which were placed in a small charcoal grill, ignited, and covered with the grill lid. Smoke was collected about 10 cm above a vent in the cover with a copper collection tube. Particles produced from the biomass burning were first passed through a diffusion dryer filled with DriRite desiccant to reduce the amount of water vapor and then collected simultaneously using a PILS and a filter sampler. The filter and PILS collection flows were 15 SLM each. The collection time for BBOA particles was 5 min for both the filter samples and PILS samples. Even though the smoke was barely visible the particle concentration was high enough to significantly contaminate the PILS impaction plate with insoluble deposits after collecting several samples, and the filter contained visible amounts of BBOA. The PILS vials and collected filters from all experiments were promptly placed on dry ice and kept frozen until later HR-ESI-MS analysis.

Immediately prior to the ESI-MS analysis the PILS vials from both SOA and BBOA were thawed and 0.5 mL of each sample was mixed with 0.5 mL of acetonitrile, in order to decrease the surface tension and facilitate a more stable electrospray.[58] The limonene SOA filters were cut in half and each half was sonicated in 2 mL of acetonitrile for 30 min. A 0.5 mL aliquot of the resulting organic extract was diluted with 0.5 mL of Milli-Q $H_2O$, prior to ESI-MS analysis. The BBOA filters were cut in half with one-half sonicated in 0.5 mL of acetonitrile and the other half sonicated in 0.5 mL of Milli-Q $H_2O$, each for 30 min. These extracts were then diluted with 0.5 mL of the opposite solvent to achieve the desired 1:1 volume ratio of acetonitrile and Milli-Q $H_2O$. This ensured equal dilutions and equal solvent compositions for the electrosprayed solutions between all filter and PILS samples analyzed in this study. Therefore, differences in the mass spectra could be attributed to the collection/solvent extraction efficiency and not solvent or analyte concentration effects on the ESI mass spectra. In the following discussion, organic aerosol will be distinguished as either SOA or BBOA, and samples will be referred to as "PILS samples", "filter/ACN samples", and "filter/$H_2O$ samples" depending on the collection/extraction method (where ACN = acetonitrile).

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All samples were analyzed using a Finnigan LTQ (linear ion trap)-Orbitrap hybrid mass spectrometer (Thermo Electron Corporation, Inc.) with a modified ESI source (Prosolia, Inc.). Samples were injected through a pulled fused silica capillary tip (50 $\mu$m i.d.) at a flow rate of 0.5–1.0 $\mu$L/min. The instrument was operated in positive and negative ionization modes with resolving power of $m/\Delta m \sim 60\,000$ at $m/z$ 400. Calibration was frequently verified using a standard solution of caffeine, MRFA, and Ultramark 1621 (calibration mix MSCAL 5, Sigma-Aldrich, Inc.).

Batch processing tools for the analysis of high-resolution mass spectra have been described previously.[11] Briefly, tables of detected peaks from all mass spectra were aligned to a common $m/z$ axis and solvent peaks were subtracted. For all mass spectra, the observed peaks were assigned molecular formulas based on their accurate masses. Only C, H, O, and Na atoms were allowed in formulas of ions for SOA samples; N atoms were included in assignments for BBOA. These molecular formulas were adjusted to represent the neutral compounds before ionization (mass of Na was subtracted from $C_xH_yO_zN_nNa^+$ or mass of H subtracted from $C_xH_yO_zN_nH^+$ for positive ion mode or mass of H added to $C_xH_{y-1}O_zN_{n-}$ for negative ion mode).

For each individual compound $C_cO_oH_hN_n$, containing $c$ carbon atoms, $h$ hydrogen atoms, $o$ oxygen atoms, and $n$ nitrogen atoms, a double bond equivalent (DBE)[59,60] value was calculated by the following equation,

$$\text{DBE} = 1 - \frac{h}{2} + \frac{n}{2} + c \qquad (1)$$

For OA compounds, the DBE value is equal to the total number of double bonds and rings in the molecule. Average DBE values, O/C ratios, and H/C ratios for all observable compounds in a given mass spectrum were calculated as follows:

$$\langle \text{DBE} \rangle = \frac{\sum_i x_i \text{DBE}}{\sum_i x_i} \qquad (2)$$

$$\langle \text{O/C} \rangle = \frac{\sum_i x_i o_i}{\sum_i x_i c_i} \qquad (3)$$

$$\langle \text{H/C} \rangle = \frac{\sum_i x_i h_i}{\sum_i x_i c_i} \qquad (4)$$

where $x_i$ corresponds to the observed ion peak abundance. Finally, the corresponding organic mass (OM) to organic carbon (OC) ratio was calculated from

$$\frac{\text{OM}}{\text{OC}} = 1 + \frac{16}{12}\langle \text{O/C} \rangle + \frac{1}{12}\langle \text{H/C} \rangle + \frac{14}{12}\langle \text{N/C} \rangle \qquad (5)$$

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The assumptions used to generate the above formulas have been discussed previously.[11] Briefly, eqs 2–5 assume that all observed compounds can be detected with equal sensitivities. This approximation rarely applies in practice, therefore the quantities calculated from eqs 2–5 should be treated as approximate.

## RESULTS

**Limonene SOA: Aqueous vs Organic Extraction.** We recorded SOA mass spectra in both positive and negative ion modes. The comparison between the PILS and filter based spectra results in the same conclusions regardless of the ion mode; therefore, only positive ion mode data will be presented in this paper. The corresponding negative ion mode data can be found in the Supporting Information, Figures S1 and S2.

The limonene SOA mass spectra recorded here, Figure 1a, are similar in appearance to the spectra of limonene SOA that we previously reported for higher (10 ppm) mixing ratios of limonene and ozone.[8] The spectrum can be clearly divided into regions corresponding to monomeric (100–300 g/mol), dimeric (300–500 g/mol), trimeric (500–700 g/mol), and tetrameric (700–900 g/mol) products, where the numbers in parentheses are the neutral compounds' molecular weights. The compounds detected in mass spectra obtained from PILS and filter/ACN samples are nearly identical; furthermore, all major peaks were observed in both PILS and filter/ACN mass spectra (Figure 1a). To emphasize the extent of similarity, Figure 1b shows peaks that were detected in mass spectra solely from either the PILS or filter/ACN extraction methods (Figure S1 of the Supporting Information contains the corresponding figure from negative mode ESI data). Most peaks that are unique to PILS or filter/ACN samples are less than 1% in relative abundance. In fact, the calculated percentage of total ion signal is dominated (96%) by compounds detected from both extraction methods, while compounds unique to only one extraction method, either filter/ACN or PILS, represent only 4% of the total ion signal. However, these compounds are not distributed equally across the entire mass spectrum, there is a somewhat greater density of peaks above 500 g/mol in the filter/ACN samples, as can be seen in Figure 1b.

Additional analysis of the limonene SOA chemical composition is provided in Table 1. The average atomic ratios, O/C and H/C, are essentially identical in PILS and filter/ACN samples. DBE values appear to be more sensitive to the extraction method; the filter sample resulted in slightly but a reproducibly larger average DBE value than the PILS sample. The DBE values in limonene SOA compounds varies approximately linearly with molecular weight ($\sim$1 DBE unit per 100 g/mol).[11] Therefore, the oligomeric species present in SOA have larger DBE values than the monomers. An increase in the average DBE value can be attributed to an increase in the relative amount of oligomeric material. Additionally, the filter/ACN samples contain a somewhat higher percentage of the total ion signal above 500 g/mol than the PILS samples, 8% versus 6%, respectively. These two observations suggest that the filter/ACN samples contained slightly more extractable oligomeric material than the PILS samples, possibly due to better solubility of oligomers in acetonitrile relative to water.

In addition to observing closely overlapping subsets of compounds, there is a remarkable correlation between relative peak abundances in the two extraction methods. To facilitate the
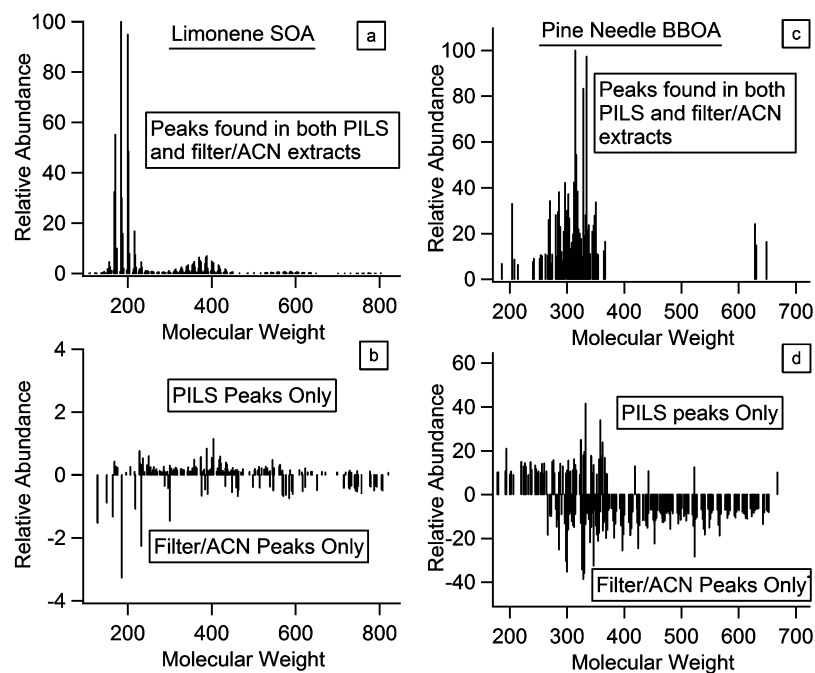
**Figure 1.** Positive ion mode ESI mass spectra of SOA (left panels) and pine needle BBOA (right panels). Panels a and c display peaks due to SOA/BBOA compounds detected from both PILS and filter/ACN extraction. Panels b and d display compounds detected only from the PILS extraction (positive peak abundances) and compounds detected only from the filter/ACN extraction (negative peak abundances). The peak abundances are normalized by setting the abundance of the largest peak in each spectrum to 100.

**Table 1. Intensity Weighted Average Values of O/C, H/C, DBE, and OM/OC for SOA and BBOA Compounds Collected from PILS and Filter/ACN SOA Extracts[a]**

|  |  | $\langle O/C \rangle$ | $\langle H/C \rangle$ | $\langle DBE \rangle$ | OM/OC |
|---|---|---|---|---|---|
| SOA | PILS | 0.39 | 1.59 | 3.69 | 1.64 |
|  | filter/ACN | 0.38 | 1.57 | 4.10 | 1.65 |
| BBOA | PILS | 0.29 | 1.51 | 5.39 | 1.51 |
|  | filter/ACN | 0.19 | 1.62 | 5.18 | 1.38 |

[a] The table is calculated from the list of assigned molecules observed in positive ion mode mass spectra.

comparison between various mass spectra, peaks detected in all mass spectra were sorted onto a single mass axis by the formulas of the neutral SOA compounds. The relative abundance of each compound was compared for both extraction methods. Figure 2a demonstrates remarkable correlation between the filter/ACN and PILS peak abundances; most observed peaks fall close to the reference 1:1 line corresponding to equal abundances in mass spectra generated from both collection techniques (Figure S2 of the Supporting Information contains the corresponding figure from negative mode ESI data). The correlation coefficients for the abundance vs abundance linear fits are close to 1. Clearly, most SOA compounds are collected/extracted with near equal efficiencies by both methods.

**Pine Needle BBOA: Aqueous vs Organic Extraction.** Sample BBOA mass spectra are shown in Figure 1c. Additional mass spectra obtained from sampling BBOA using PILS, filter/ACN, and filter/H$_2$O methods are displayed in Figure S3 of the Supporting Information. A number of peaks that have been previously reported from BBOA ESI mass spectra are present, including levoglucosan, $m/z$ = 185.042 (C$_6$H$_{10}$O$_5$Na$^+$), and compounds at $m/z$ 293.209 (C$_{16}$H$_{30}$O$_3$Na$^+$), 315.193 (C$_{18}$H$_{28}$O$_3$Na$^+$), 325.177 (C$_{19}$H$_{26}$O$_3$Na$^+$), 335.125 (C$_{19}$H$_{20}$O$_4$Na$^+$), 335.219 (C$_{18}$H$_{32}$O$_4$Na$^+$, octadecenedioic
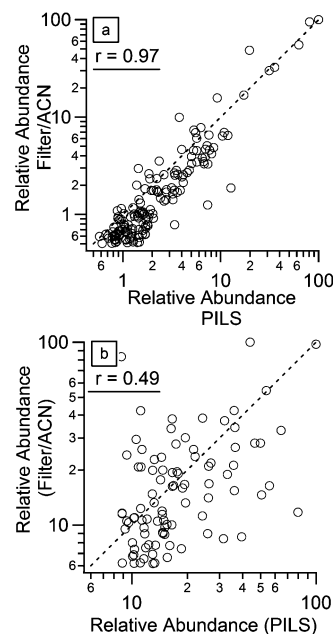


**Figure 2.** Log−log relative abundance plots generated from the mass spectra in Figure 1. Abundances in the positive ion mode PILS and filter/ACN ESI mass spectra are plotted against each other for (a) limonene SOA and (b) pine needle BBOA. As a reference, the dashed lines represent a 1:1 ratio. The $r$ values are the correlation coefficients.

acid), and 375.214 (C$_{20}$H$_{32}$O$_5$Na$^+$).[12,13] Unlike limonene SOA mass spectra, the PILS and filter/ACN mass spectra are quite different, and many major peaks are observed selectively in only PILS or filter/ACN mass spectra. These differences are apparent in Figure 1d, which shows peaks that were detected in mass spectra solely from either the PILS or filter/ACN methods. Many compounds unique to filter/ACN samples have molecular weights

**Table 2. Number of Peaks Observed in PILS and Filter Extracted BBOA[a]**

| method | total no. of peaks detected | no. of peaks common to all three methods | no. of peaks unique to this method |
|---|---|---|---|
| PILS | 162 | 68 (42%) | 65 (40%) |
| filter/ACN | 338 | 68 (20%) | 234 (70%) |
| filter/H$_2$O | 91 | 68 (75%) | 6 (7%) |

[a] In each mass spectrum, common compounds represent the peaks observed by all three collection methods and unique compounds represent the peaks observed by this collection method only (percentage of total peak number is in parentheses). The numbers do not add to 100% due to compounds that were detected by two out of three collection methods.

**Table 3. Percentage of Total Ion Signal Calculated from Detected Compounds with O/C Ratios of 0.0−0.3, 0.3−0.4, 0.4−0.5, 0.5−0.6, and 0.6−0.9 from Both SOA and BBOA Compounds Collected Using PILS and Filter/ACN Extracts[a]**

| compound O/C ratio | avg OM/OC | SOA | | BBOA | |
|---|---|---|---|---|---|
| | | PILS | filter/ACN | PILS | filter/ACN |
| 0.0−0.3 | 1.39 | 10.0 | 12.2 | 75.9 | 96.3 |
| 0.3−0.4 | 1.56 | 35.3 | 35.5 | 12.1 | 2.1 |
| 0.4−0.5 | 1.69 | 40.6 | 37.9 | 1.4 | 0.1 |
| 0.5−0.6 | 1.82 | 11.7 | 12.3 | 1.0 | 0.1 |
| 0.6−0.9 | 2.08 | 2.0 | 2.0 | 10.0 | 1.0 |

[a] The table is calculated from the list of assigned molecules observed in positive ion mode mass spectra.

between 400 and 700 g/mol, indicating that acetonitrile extracts high molecular weight BBOA compounds more efficiently than water does. Unlike the SOA case, the fractional abundance of common peaks is considerably smaller than 100%. In fact, the majority of the total ion current for filter/ACN (61%) comes from peaks that are unique to this collection/extraction method.

Comparison of the PILS, filter/ACN, and filter/H$_2$O methods can help attribute the source of the differences discussed above to the collection method (PILS vs filter) or extraction solvent (water vs acetonitrile). Table 2 lists the total number (not total abundance) of assignable peaks (excluding $^{13}$C isotopes) found from each sample: PILS, filter/ACN, and filter/H$_2$O, number of peaks common to all three samples, as well as compounds found in only one of the methods. A total of 68 common compounds were detected in BBOA from the three collection methods, representing a large portion of the total number of compounds found in the filter/H$_2$O mass spectrum (75%). In contrast, this fraction is much smaller for filter/ACN (20%) samples further confirming that more compounds are extracted by ACN than H$_2$O. Clearly, many BBOA compounds are extracted into organic solvent but not into aqueous solvent.

While the overlapping subset of compounds is not as extensive as in the SOA case, there is correlation between the relative peak abundances for BBOA compounds observed in all three spectra. Similar to the limonene SOA mass spectra, peaks detected in all mass spectra were sorted onto a single mass axis by the compounds' molecular weights. The relative abundance of each compound was compared for all extraction methods. Figure 2b shows the results for PILS vs filter/ACN comparison and Figure S4a in the Supporting Information compares relative abundances for filter/H$_2$O and filter/ACN. In all cases, the abundance correlation between the filter and PILS data sets is less defined ($r < 0.78$) than for the SOA samples ($r > 0.97$). In Figure S4b in the Supporting Information, which compares relative abundances for PILS and filter/H$_2$O, the majority of compounds falls below the reference 1:1 line, suggesting that PILS is the more efficient collection method for WSOC compared to the filter/H$_2$O extraction method.

## DISCUSSION

Limonene SOA samples collected using an aqueous PILS extraction and more traditional filter collection followed by extraction into acetonitrile resulted in nearly identical ESI mass spectra. It was found that compounds extracted via both methods/

solvents accounted for >95% of the total ion signal at very large aerosol loadings in excess of 1 mg m$^{-3}$ and corresponding extract mass concentrations approaching gram/liter levels. This similarity implies high solubility of limonene SOA in both water and acetonitrile, likely due to the polyfunctional nature of its components. Indeed, the OM/OC ratio of 1.65 obtained here for limonene SOA as measured via HR ESI-MS falls in the range of OM/OC values that are considered water-soluble, 1.5−3.8.[61] Additionally, less than 5% of the ionization current in limonene SOA is detected as compounds with an OM/OC ratio less than 1.5 (considered to be nonsoluble on average).

Pine needle BBOA samples collected using the same techniques resulted in substantially different mass spectra. Mass spectra generated from PILS, filter/ACN, and filter/H$_2$O samples showed only marginal correlation. Specifically, we found that compounds extracted via all three methods/solvents only accounted for about a third of the total ion signal detected from acetonitrile extracts. These observations are consistent with high water solubility of limonene SOA (estimated WSOC fraction ~100%) and only partial water solubility of BBOA (estimated WSOC fraction ~40%). This conclusion is consistent with the type of compounds observed in the BBOA sample. Table 1 lists the OM/OC ratio obtained for pine needle BBOA extracted from PILS and filter/ACN. The BBOA compounds extracted with filter/ACN method have an average OM/OC ratio of 1.38, lower than the suggested value for water-soluble compounds.[61] This also indicates that the filter/ACN method is extracting more compounds with poor water solubility. In comparison, BBOA compounds extracted with PILS method have an average OM/OC ratio of 1.51, suggesting barely soluble compounds.

The average O/C ratio is sometimes used as an alternative to OM/OC for predicting the solubility in water. Previous research suggests that compounds with O/C ratios greater than 0.4 can generally be considered water-soluble.[62,63] Taking advantage of the high mass resolution, assigned compounds in SOA and BBOA can be grouped according to their individual O/C ratios, as illustrated in Table 3. The average OM/OC ratio increases with each successive O/C bin as expected from eq 5. For the SOA case, the majority of compounds have O/C ratios between 0.3 and 0.6, while the majority of BBOA compounds have O/C ratios

(61) Turpin, B. J.; Lim, H. J. *Aerosol Sci. Technol.* **2001**, *35*, 602–610.
(62) Saxena, P.; Hildemann, L. M. *J. Atmos. Chem.* **1996**, *24*, 57–109.
(63) Pang, Y.; Turpin, B. J.; Gundel, L. A. *Aerosol Sci. Technol.* **2006**, *40*, 128–133.

between 0.0 and 0.3. Comparing PILS and filter/ACN extracted BBOA compounds indicates that acetonitrile extracts a higher percentage of low O/C material (0.0−0.3) while PILS extracts a higher percentage of higher O/C material (0.3−0.6). These observations are again consistent with the high water solubility of limonene SOA and low solubility of BBOA compounds and support the known correlation between elemental ratios and solubility in water.[61,63] Tables S1 and S2 of the Supporting Information list the average elemental ratios, number of peaks, and percentage of peaks found in each O/C bin for SOA in both ionization modes and BBOA in positive ionization mode, respectively.

Given the high solubility of limonene SOA in both water and ACN, any difference between the PILS and filter/ACN mass spectra should be attributed to artifacts generated from either filter or PILS collection methods. Analysis of blank samples from both methods effectively removes ESI-MS impurity compounds that are unique to each collection method. Artifacts that would contribute to an increase (or decrease) of certain SOA constituents, for example, evaporation of SOA compounds from the filter, physisorption of VOCs onto the filter, reaction of SOA compounds with residual ozone, hydrolysis of compounds in PILS vials, etc., cannot be corrected for with blank samples. However, because of the similarity of mass spectra generated from both extraction methods, these effects appear to be insignificant for limonene SOA.

The differences in collection methods appear to be more significant for BBOA. If all WSOC in BBOA was accessible to the solvent in PILS vials or in filter extracts we would have obtained similar results for the PILS and filter/H$_2$O samples. The large difference between these two methods suggests that some water-soluble BBOA compounds are buried inside the particles and cannot be extracted easily from the filtered samples. It is notable that the PILS method resulted in mass spectra containing more compounds and higher abundances than the filter/H$_2$O method, suggesting that the PILS method is more efficient for extracting WSOC from BBOA. PILS creates an internally mixed water/BBOA particle mixture favoring extraction of WSOC from particles,[52] whereas particles on the filter may be sintered and resist penetration of water even under sonication conditions.

The discussion above has dealt with qualitative observation of various compounds by the PILS/ESI-MS and filter/ESI-MS methods. We also need to briefly comment on the possibility of quantitative measurements of specific OA compounds with these methods. The main limitation on quantitative measurements with either PILS or filter extraction coupled to an offline ESI mass spectrometer is nonlinear ESI dependence on the solution concentration and on the "matrix" of ions competing for charge.[58] Therefore, absolute concentrations of the unknown OA constituents cannot be recovered from PILS coupled with ESI-MS, without additional analytical techniques. We therefore expect that the PILS/ESI-MS method will be primarily used for identification of water-soluble organic compounds in aerosols.

## CONCLUSIONS

We have demonstrated that PILS can be used in combination with HR-ESI-MS methods to allow the simultaneous detection of hundreds of water-soluble organic species in a single measurement and characterization of the distribution of their molecular formulas. This method works best for organic aerosol samples dominated by WSOC (OM/OC > 1.5) such as laboratory generated biogenic SOA examined in this work. No significant differences in the ESI-MS peak abundances of limonene SOA samples collected with PILS or more traditional filter extraction methods were observed. For aerosols dominated by water-insoluble organic species such as BBOA, PILS can still be used for the analysis of the molecular composition of the WSOC fraction, although one has to consider the issues associated with incomplete extraction of WSOC from particles and the difficulties associated with quantitative measurements of specific compounds. Despite these limitations, PILS/HR-ESI-MS is a valuable method for the molecular analysis of WSOC in organic aerosols and for the determination of the average properties of WSOC such as effective OM/OC values.

## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.