# Supporting Information Section for "Photochemical processing of secondary organic aerosols dissolved in cloud droplets"

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**Figure S1**. Representative ESI (+) mass spectra of SOA collected via PILS extraction for the four initial concentrations studied: (a) 0.05 ppm; (b) 0.10 ppm; (c) 0.5 ppm; (d) 1.0 ppm of limonene and $O_3$. Trimer and tetramer species were not visible in the 0.05 ppm spectrum, and tetramer species were not visible in the 0.1 ppm spectrum because these peaks fell below the signal-to-noise threshold used in the analysis.
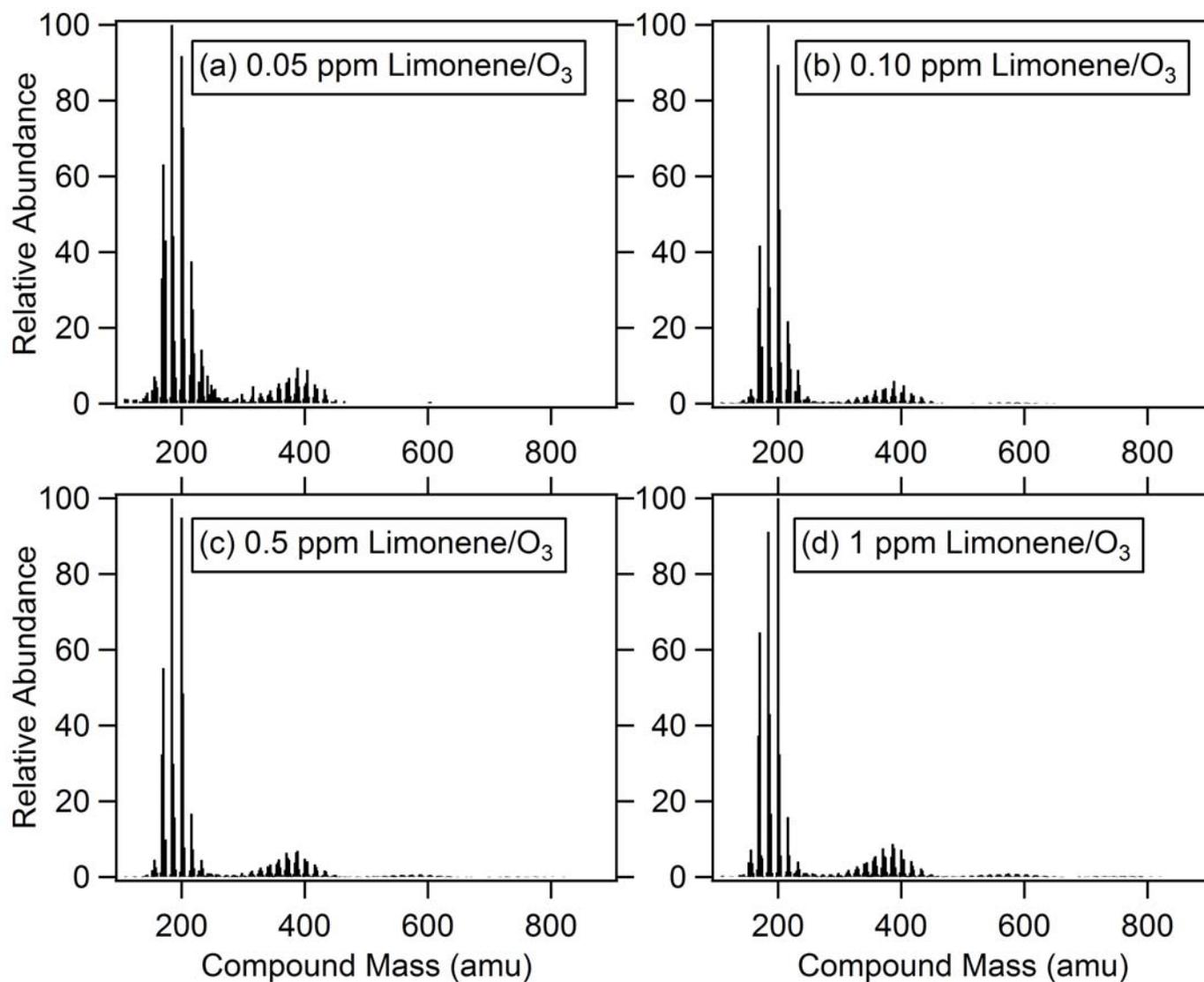
**Figure S2**. Representative ESI (-) mass spectra of SOA collected via PILS extraction for the four initial concentrations studied: (a) 0.05 ppm; (b) 0.10 ppm; (c) 0.5 ppm; (d) 1.0 ppm of limonene and $O_3$. Tetramer species were not visible in the 0.05 and 0.10 ppm spectra because these peaks fell below the signal-to-noise threshold used in the analysis.
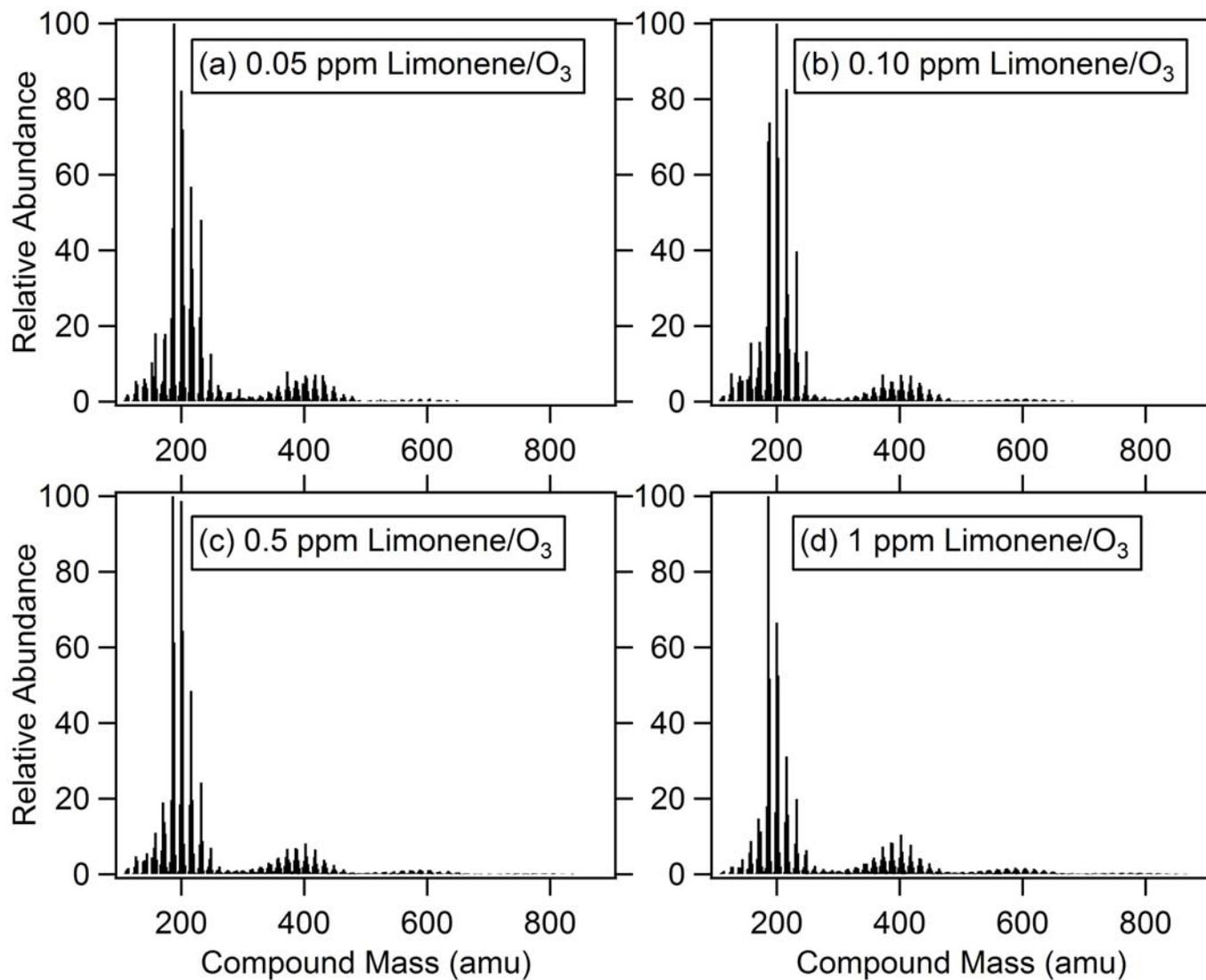
**Figure S3.** Representative ESI(+) mass spectra of 1 ppm limonene/$O_3$ SOA collected via PILS: (a) before photolysis; (b) after 2 hours of photolysis; (c) after 24 hours of photolysis. All peaks are normalized to the most abundant peak in each mass spectrum. The observed m/z values have been converted to molecular weights of the neutral compounds.
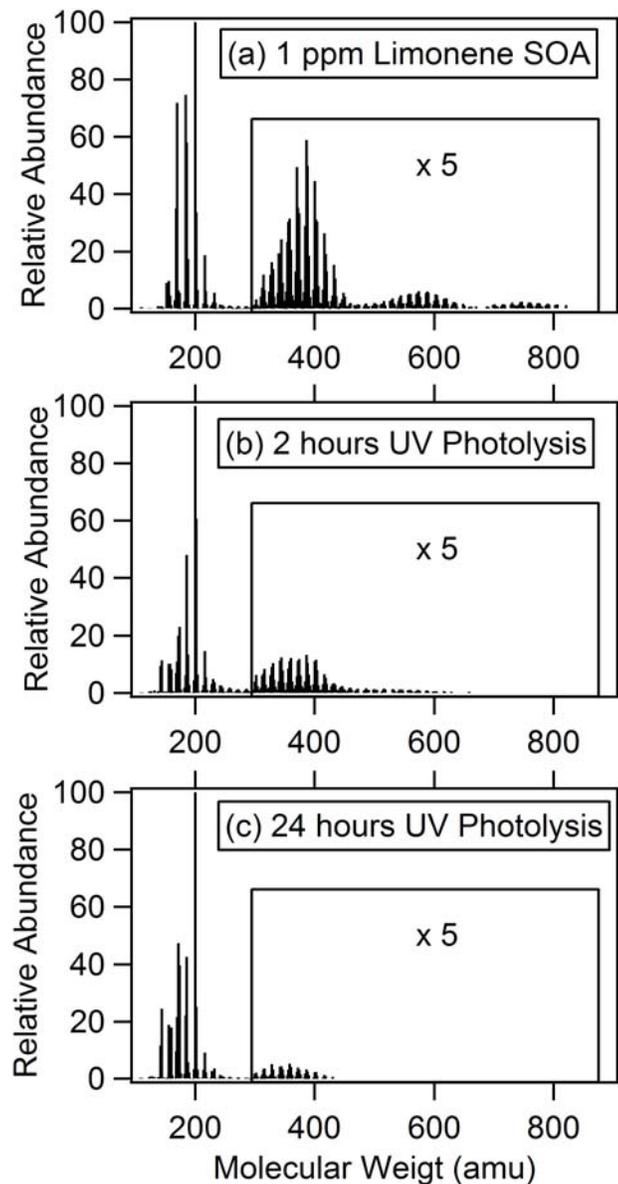
**Table S1.** Intensity weighted average values of O/C, H/C, DBE and OM:OC limonene SOA extracts for each initial concentration of limonene and $O_3$. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively.

| | | | | |
|---|---|---|---|---|
| SOA Precursor Concentration (ppm) | 0.05 | 0.10 | 0.50 | 1.00 |
| Percent of Peaks Assigned | 30 | 48 | 62 | 58 |
| ⟨O/C⟩ Before UV | 0.53 | 0.52 | 0.49 | 0.50 |
| ⟨O/C⟩ 2 hr UV | 0.54 | 0.53 | 0.54 | 0.55 |
| ⟨O/C⟩ 24 hr UV | - | - | 0.57 | 0.57 |
| ⟨H/C⟩ Before UV | 1.55 | 1.54 | 1.55 | 1.55 |
| ⟨H/C⟩ 2 hr UV | 1.56 | 1.55 | 1.55 | 1.54 |
| ⟨H/C⟩ 24 hr UV | - | - | 1.53 | 1.53 |
| ⟨DBE⟩ Before UV | 3.54 | 3.56 | 3.85 | 4.10 |
| ⟨DBE⟩ 2 hr UV | 3.34 | 3.22 | 3.37 | 3.73 |
| ⟨DBE⟩ 24 hr UV | - | - | 3.23 | 3.27 |
| ⟨OM:OC⟩ Before UV | 1.83 | 1.80 | 1.78 | 1.79 |
| ⟨OM:OC⟩ 2 hr UV | 1.83 | 1.83 | 1.84 | 1.85 |
| ⟨OM:OC⟩ 24 hr UV | - | - | 1.88 | 1.88 |
| SOA Precursor Concentration (ppm) | 0.05 | 0.10 | 0.50 | 1.00 |
| Percent of Peaks Assigned | 19 | 22 | 22 | 21 |
| ⟨O/C⟩ Before UV | 0.42 | 0.41 | 0.39 | 0.39 |
| ⟨O/C⟩ 2 hr UV | 0.40 | 0.42 | 0.43 | 0.44 |
| ⟨O/C⟩ 24 hr UV | - | - | 0.43 | 0.45 |
| ⟨H/C⟩ Before UV | 1.58 | 1.60 | 1.59 | 1.59 |
| ⟨H/C⟩ 2 hr UV | 1.57 | 1.60 | 1.61 | 1.59 |
| ⟨H/C⟩ 24 hr UV | - | - | 1.55 | 1.54 |
| ⟨DBE⟩ Before UV | 3.45 | 3.31 | 3.69 | 3.80 |
| ⟨DBE⟩ 2 hr UV | 3.60 | 3.04 | 3.11 | 3.35 |
| ⟨DBE⟩ 24 hr UV | - | - | 3.26 | 3.15 |
| ⟨OM:OC⟩ Before UV | 1.67 | 1.66 | 1.64 | 1.64 |
| ⟨OM:OC⟩ 2 hr UV | 1.66 | 1.68 | 1.70 | 1.71 |
| ⟨OM:OC⟩ 24 hr UV | - | - | 1.69 | 1.73 |

The top section is labeled "Negative ESI Mode" and the bottom section is labeled "Positive ESI Mode".

**Table S2.** Effect of limonene/$O_3$ mixing ratios on estimated percent fractions of carbonyls and carboxyls in the limonene SOA extract. The ion current was subdivided by compounds known to contain carbonyl, carboxyl, both carbonyl and carboxyl, or neither group. Only compounds with MW < 500 g/mol were included in the analysis. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively.

| | | Carbonyl | Carboxyl | Both | Other | Total ion Signal |
|---|---|---|---|---|---|---|
| **Negative ESI Mode** | 0.05 ppm | 4.31 | 13.41 | 65.44 | 16.84 | 11653 |
| | 0.1 ppm | 4.24 | 11.22 | 69.97 | 14.56 | 19407 |
| | 0.5 ppm | 5.97 | 9.29 | 72.83 | 11.91 | 28154 |
| | 1 ppm | 6.19 | 8.24 | 74.01 | 11.57 | 28928 |
| | | Carbonyl | Carboxyl | Both | Other | Total Ion Signal |
| **Positive ESI Mode** | 0.05 ppm | 8.43 | 21.01 | 51.73 | 18.83 | 6125 |
| | 0.1 ppm | 5.86 | 22.06 | 64.56 | 7.51 | 18623 |
| | 0.5 ppm | 7.35 | 16.67 | 66.55 | 9.44 | 29316 |
| | 1 ppm | 8.09 | 13.88 | 69.31 | 8.73 | 32910 |

**Table S3.** Effect of photolysis on estimated fraction of carbonyls and carboxyls in the limonene SOA extract for each of the concentrations studied. Percent ion current was calculated from limonene SOA before photolysis, after 2 hours of photolysis, and after 24 hours of photolysis (only in the case of 0.5 ppm samples). The ion current was subdivided by compounds found to contain carbonyl, carboxyl, both carbonyl and carboxyl, or neither group. Only compounds with MW < 500 amu were included in the analysis. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively. The loss of carbonyls to photolysis is less apparent at lower limonene/$O_3$ concentrations (their relative amounts actually increase in the 0.05 ppm data set)

| | **1 ppm** | Carbonyl | Carboxyl | Both | Neither | Total Ion Signal |
|---|---|---|---|---|---|---|
| (-) ESI Mode | No Photolysis | 6.2 | 8.2 | 74.0 | 11.6 | 28000 |
| | 2 hr Photolysis | 5.7 | 12.5 | 62.2 | 19.6 | 28500 |
| | 24 hr Photolysis | 4.4 | 11.3 | 64.5 | 19.9 | 15500 |
| (+) ESI Mode | No Photolysis | 8.1 | 13.9 | 69.3 | 8.7 | 29500 |
| | 2 hr Photolysis | 4.7 | 25.4 | 55.7 | 14.2 | 24000 |
| | 24 hr Photolysis | 3.2 | 19.1 | 58.0 | 19.7 | 5000 |
| | **0.5 ppm** | Carbonyl | Carboxyl | Both | Neither | Total Ion Signal |
| (-) ESI Mode | No Photolysis | 6.0 | 9.3 | 73.0 | 11.9 | 28000 |
| | 2 hr Photolysis | 4.4 | 14.0 | 65.5 | 16.1 | 28500 |
| | 24 hr Photolysis | 4.6 | 12.1 | 63.5 | 19.9 | 15500 |
| (+) ESI Mode | No Photolysis | 7.4 | 16.7 | 66.6 | 9.4 | 29500 |
| | 2 hr Photolysis | 4.1 | 31.8 | 52.7 | 11.4 | 24000 |
| | 24 hr Photolysis | 8.9 | 20.7 | 51.7 | 18.7 | 5000 |
| | **0.1 ppm** | Carbonyl | Carboxyl | Both | Neither | Total Ion Signal |
| (-) ESI Mode | No Photolysis | 4.2 | 11.2 | 70.0 | 14.6 | 19500 |
| | 2 hr Photolysis | 3.9 | 13.9 | 66.5 | 15.7 | 16500 |
| (+) ESI Mode | No Photolysis | 5.6 | 22.7 | 64.1 | 7.6 | 18000 |
| | 2 hr Photolysis | 7.9 | 30.7 | 47.5 | 13.9 | 8000 |
| | **0.05 ppm** | Carbonyl | Carboxyl | Both | Neither | Total Ion Signal |
| (-) ESI Mode | No Photolysis | 4.3 | 13.4 | 65.4 | 16.8 | 11500 |
| | 2 hr Photolysis | 5.6 | 20.3 | 55.3 | 18.9 | 6000 |
| (+) ESI Mode | No Photolysis | 8.4 | 21.0 | 51.7 | 18.8 | 6000 |
| | 2 hr Photolysis | 12.9 | 27.8 | 37.3 | 21.9 | 3000 |

**Table S4.** Average values of O/C, H/C, DBE and percent ion current calculated for limonene SOA compounds after 2 hours of photolysis **directly on a filter** (the corresponding table for the aqueous extract of SOA is given in the text). The SOA compounds have been grouped according to their ratio of relative abundance in the photolyzed mass spectra to relative abundance in non-photolyzed mass spectra. The top and bottom sections of the table were calculated from ESI (-) and (+) mass spectra, respectively. On the whole, the trends for the on-filter and aqueous photolysis are similar.

| | | 1ppm Filter 2 hr Photolysis | | | | 0.5 ppm Filter 2 hr Photolysis | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\langle$O/C$\rangle$ | $\langle$H/C$\rangle$ | $\langle$DBE$\rangle$ | % Ion Current | $\langle$O/C$\rangle$ | $\langle$H/C$\rangle$ | $\langle$DBE$\rangle$ | % Ion Current |
| Negative ESI Mode | New Compounds | 0.50 | 1.49 | 5.98 | 7 | 0.49 | 1.52 | 5.10 | 1 |
| | Increased Relative Abundance | 0.54 | 1.51 | 5.09 | 14 | 0.54 | 1.48 | 4.48 | 2 |
| | No Change | 0.53 | 1.54 | 3.90 | 75 | 0.54 | 1.53 | 3.87 | 71 |
| | Decreased Relative Abundance | 0.44 | 1.41 | 3.78 | 3 | 0.46 | 1.55 | 3.88 | 23 |
| | Destroyed Compounds* | 0.48 | 1.59 | 4.01 | 10* | 0.48 | 1.59 | 4.27 | 11* |
| Positive ESI Mode | New Compounds | 0.44 | 1.58 | 5.17 | 8 | 0.43 | 1.61 | 4.52 | 10 |
| | Increased Relative Abundance | 0.47 | 1.62 | 3.15 | 12 | 0.45 | 1.64 | 3.00 | 39 |
| | No Change | 0.44 | 1.59 | 3.96 | 66 | 0.43 | 1.60 | 4.11 | 41 |
| | Decreased Relative Abundance | 0.35 | 1.58 | 4.27 | 5 | 0.30 | 1.57 | 3.68 | 2 |
| | Destroyed Compounds* | 0.40 | 1.52 | 6.75 | 11* | 0.38 | 1.40 | 7.39 | 9* |