

Dynamic light absorption of biomass burning organic aerosol photochemically aged under natural sunlight

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Supplementary Materials

Number of Documents: 1

Number of Figures: 4

Document S1. Chamber operation and characterization of photooxidation of pure levoglucosan

Levoglucosan (99% purity, Aldrich) solid particles was dissolved in HPLC grade water to make 0.02 M aqueous solution. Levoglucosan aerosol was generated from the aqueous solution using a constant output atomizer. After the injection of levoglucosan to East outdoor chamber, chamber air was mixed for five minutes using a mixing fan. HONO was introduced to the chamber by passing the clean air through a flask in which 10 mL of 0.1 M NaNO_2 and 10 mL of 10 % H_2SO_4 reacted to produce HONO. HONO was estimated as the difference in NO_x concentration which were measured by a NO_x analyzer with and without a base denuder (coated using 1% Na_2CO_3 + 1% glycerol in ethanol) (Febo and Perrino, 1991). The initial chamber concentration of levoglucosan was $121 \mu\text{g}/\text{m}^3$, HONO 50 ppb, and NO_x 124 ppb.

A filter sample was collected using a 13mm Teflon-coated borosilicate filter. For each filter sample, $5\mu\text{L}$ of bornyl acetate solution ($2.4\text{mg}/\text{mL}$ in acetonitrile), an internal standard, was added. Both levoglucosan and oxidation products were extracted by sonicating the filter sample with 5mL acetonitrile for one hour. The extracted solution was concentrated to 1 mL using a dry air stream and transferred to a GC vial. In order to derivatize alcohol, phenol, and carboxylic acid, 35 mL of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) solution and 15mL pyridine were added to the GC vial. The solution was stood at 70°C for 1 hour.

Gaseous products from oxidation of levoglucosan were collected using a XAD-coated denuder, which was located upstream the filter. After the sample collection, the denuder was extracted using 125mL of acetonitrile. The extracted solution was concentrated to 1 mL using a rotary evaporator, transferred to a GC vial, and derivertized with BSTFA as described above.

The derivatized products were analyzed using a gas chromatography ion trap mass spectrometer (GC-ITMS). The GC temperature profile in this study was 80°C for 1 minute ramp to 100°C at $5^\circ\text{C minute}^{-1}$; ramp to 280°C at $10^\circ\text{C minute}^{-1}$ and hold for 8 minutes. For the identification of new products, samples were analyzed in both electron impact (EI) and chemical ionization (CI) modes. Acetonitrile was used as the chemical ionization reagent.

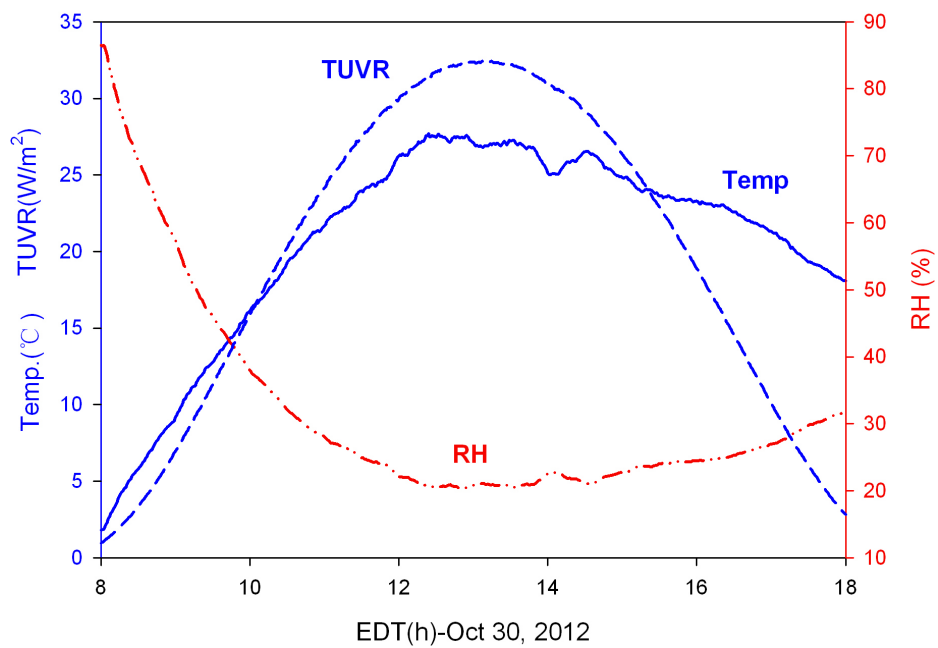


FIGURE S1. Time profile of sunlight total ultra-violet radiation (TUVR), temperature and relative humidity measured in the UF-APHOR east chamber on October 30, 2012.

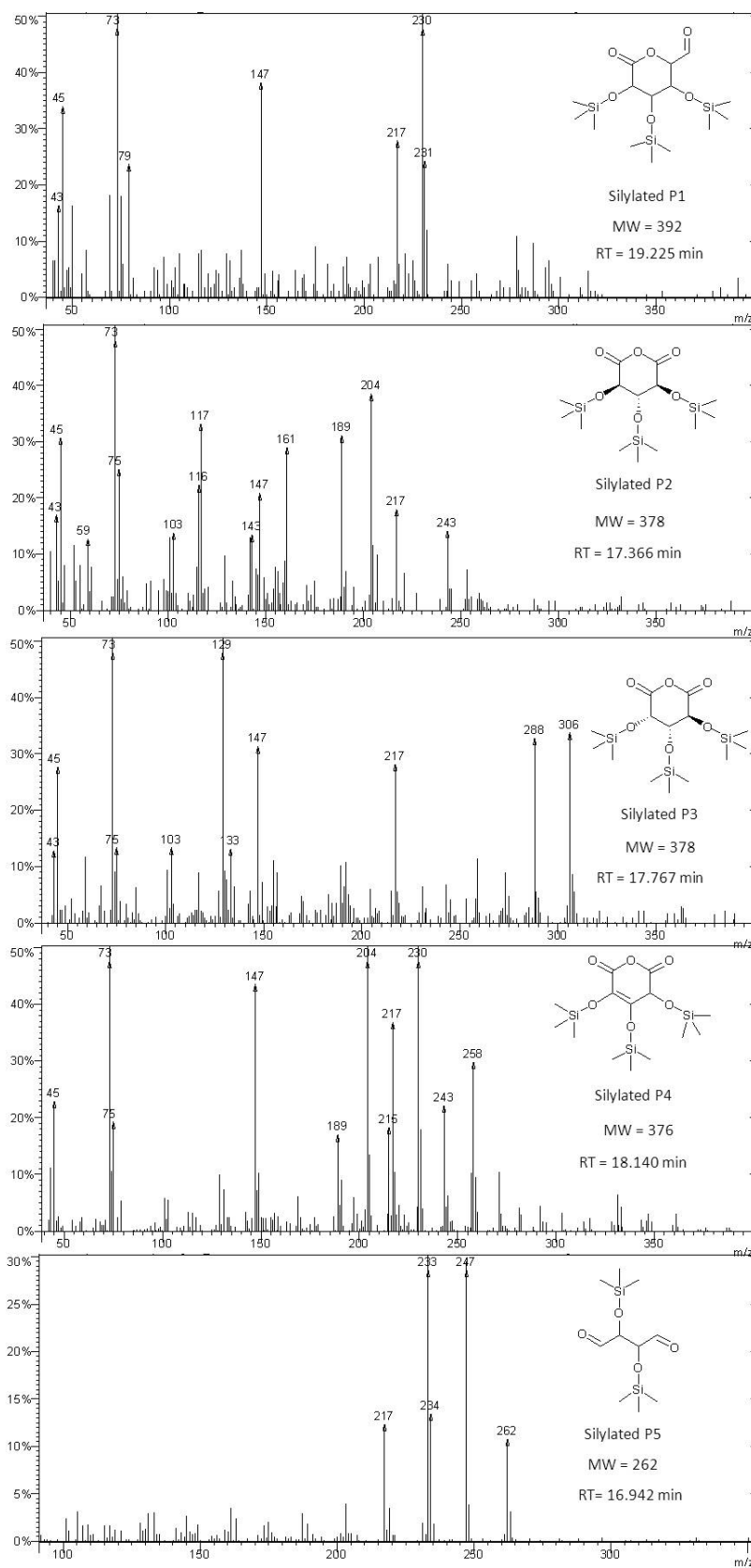


FIGURE S2. Mass fragmentation patterns of BSTFA-derivatives of levoglucosan oxidation products in EI mode. RT is retention time.

In Figure S2, the mass peak at $m/z = 217$ and $m/z=147$ are the typical mass fragmentation pattern for sugar types of compounds. All products show these two peaks in mass fragmentation patterns.

P1. The molecular structure was tentatively identified based on the molecular ion peak shown in the CI spectrum in Figure S3.

P2. The mass peak at $m/z = 243$ corresponds with M-45 (COOH)

P3. The mass peak at $m/z = 306$ and $m/z = 288$ originate from M-72 [Si(CH₃)₃+1] and M-88(OSi(CH₃)₃+1), respectively.

P4. The molecular structure was tentatively identified based on the molecular ion peak shown in the CI spectrum in Figure S3.

P 5. The mass peak at $m/z = 262$ is the molecular ion peak. The mass peaks at $m/z=247$ and $m/z=233$ correspond with M-15 (CH₃) and M-29 (CHO), respectively.

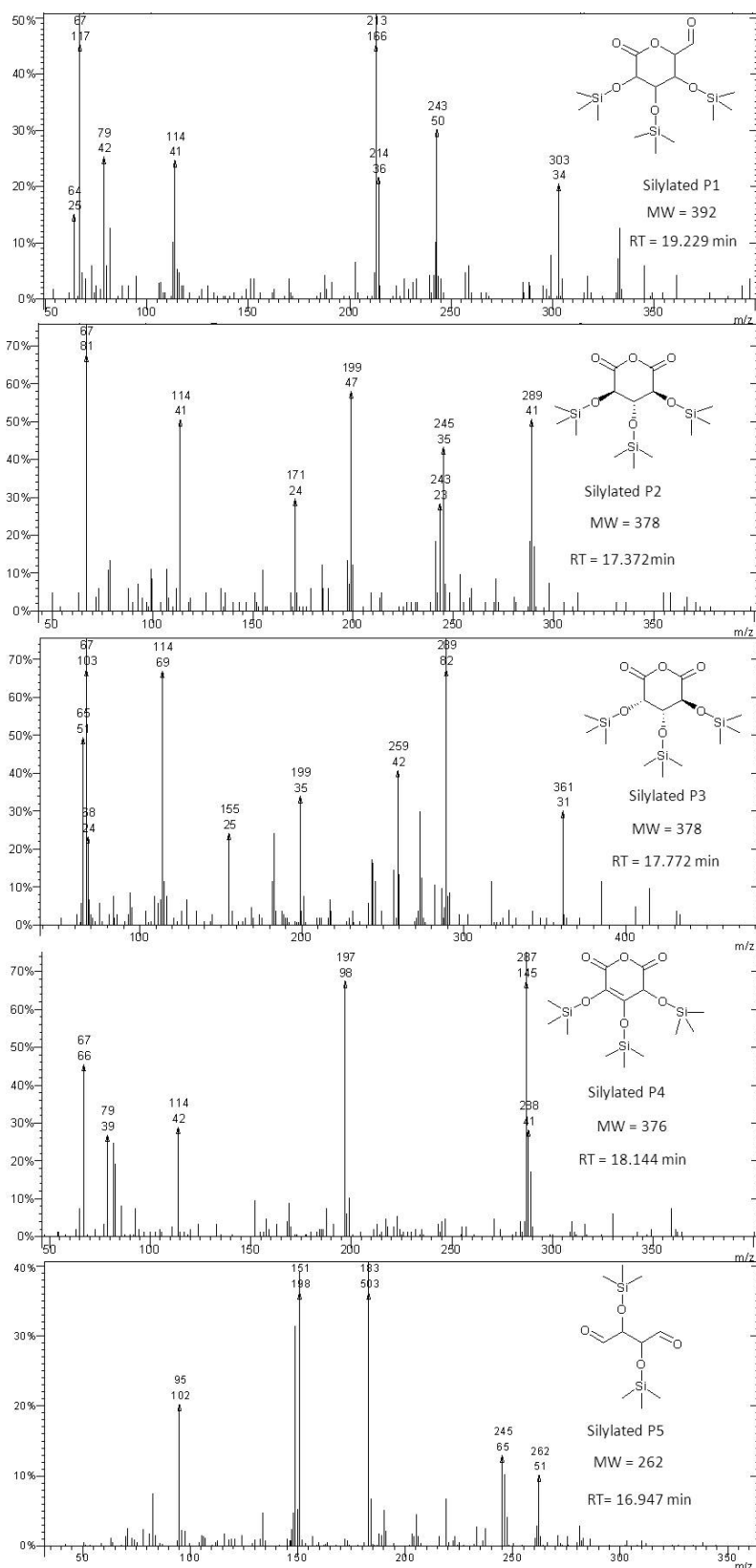


FIGURE S3. Mass fragmentation patterns of BSTFA-derivatives of levoglucosan oxidation products in CI mode. RT is retention time.

P1. The mass peak at $m/z = 303$ corresponds with M-89 [$\text{OSi}(\text{CH}_3)_3$].

P2. The mass peaks at $m/z=289$, $m/z=245$, and $m/z=199$ correspond with M-89 [$\text{OSi}(\text{CH}_3)_3$], M-89-44 [$\text{OSi}(\text{CH}_3)_3$ and CO_2] and M-89-90 [$2 \text{OSi}(\text{CH}_3)_3-1$], respectively.

P3. The mass peak at $m/z = 289$ and $m/z=199$ correspond with M-89 [$\text{OSi}(\text{CH}_3)_3$] and M-89-90 [$2 \text{OSi}(\text{CH}_3)_3-1$], respectively. P3 is isomer of P2.

P4. The mass peak at $m/z = 287$ and $m/z=197$ correspond with M-89 [$\text{OSi}(\text{CH}_3)_3$] and M-89-90 [$2 \text{OSi}(\text{CH}_3)_3-1$], respectively.

P 5. The mass peak at $m/z = 262$ is the molecular ion peak.

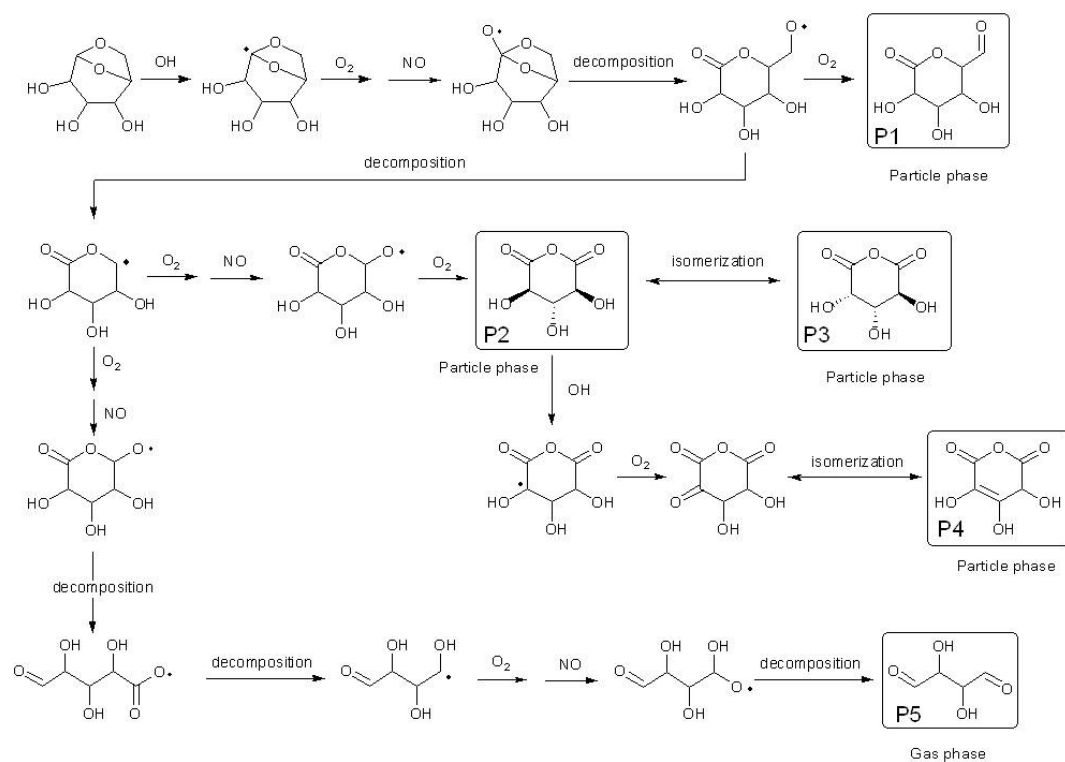


FIGURE S4. Reaction pathways for levoglucosan decomposition

References

Febo, A., and Perrino, C.: Prediction and experimental evidence for high air concentration of nitrous acid in indoor environments, *Atmospheric Environment. Part A. General Topics*, 25, 1055-1061, [http://dx.doi.org/10.1016/0960-1686\(91\)90147-Y](http://dx.doi.org/10.1016/0960-1686(91)90147-Y), 1991.