Supplement

Characterizing source fingerprints and ageing processes in laboratory-generated secondary organic aerosols using proton-nuclear magnetic resonance (^{1}H-NMR) analysis and HPLC HULIS determination.

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Content:

- Supporting information on source and nature of ambient OA samples.
- NMR spectroscopic data for non-aqueous components of isoprene SOA.
- HPLC fraction distributions for all α-pinene and naphthalene SOA samples.

Origin of ambient samples

The Po Valley samples discussed in Section 4 were collected in San Pietro Capofiume (SPC), a rural site located in the south-eastern sector of the Valley, during the PEGASOS campaign of summer 2012 (Rosati et al., Atmos. Chem. Phys., 16, 7295-7315, 2016). Aerosol particles with ambient aerodynamic diameter < 1 µm were sampled on pre-washed and pre-baked quartz-fiber filters (Whatman, 9 cm size) using a high-volume sampler (model Echo Hivol, Tecora) at a constant nominal flow of 500 l/min located at ground level. Two filters per day were sampled (change at 9 AM and 6 PM local time). Each filter was extracted with 5mL of deionized ultra-pure water (Milli-Q) in a mechanical shaker for 1 hour and the water extract was filtered on PTFE membranes (pore size: 0.45 µm) in order to remove suspended particles. The water extracts were dried by rotary evaporator and were then re-dissolved in 2.15mL of D_2O. An aliquot (0.65mL) was used for proton-nuclear magnetic resonance (^{1}H-NMR) characterization, while a second aliquot (1.5mL) was kept for HPLC analysis and total organic carbon (TOC) analysis. The NMR aliquot was mixed with sodium 3-trimethylsilyl-(2,2,3,3-d4) propionate (TSP-d_4) as internal standard, and with a buffer of potassium formate/formic acid (pH~3.8). The ^{1}H-NMR spectra were acquired at 600MHz with a Varian 600 spectrometer in a 5mm probe. The sample SPC_020712_D was used for comparison with the spectroscopic data of the SOA samples (Figure 7 of the manuscript). The 1H-NMR spectrum of sample SPC_020712_D is shown in Figure S1.

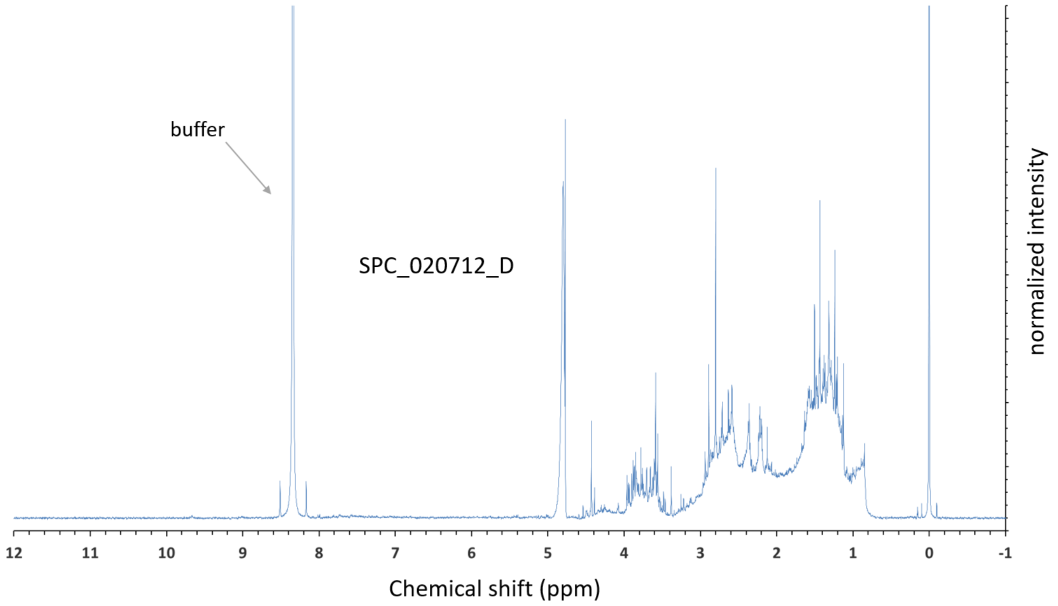

Figure S1. 1H-NMR spectrum of sample SPC_020712_D (after water-extraction) collected in San Pietro Capofiume, a rural site nearby Bologna. Sampling time was 9:00-20:30 (local time).

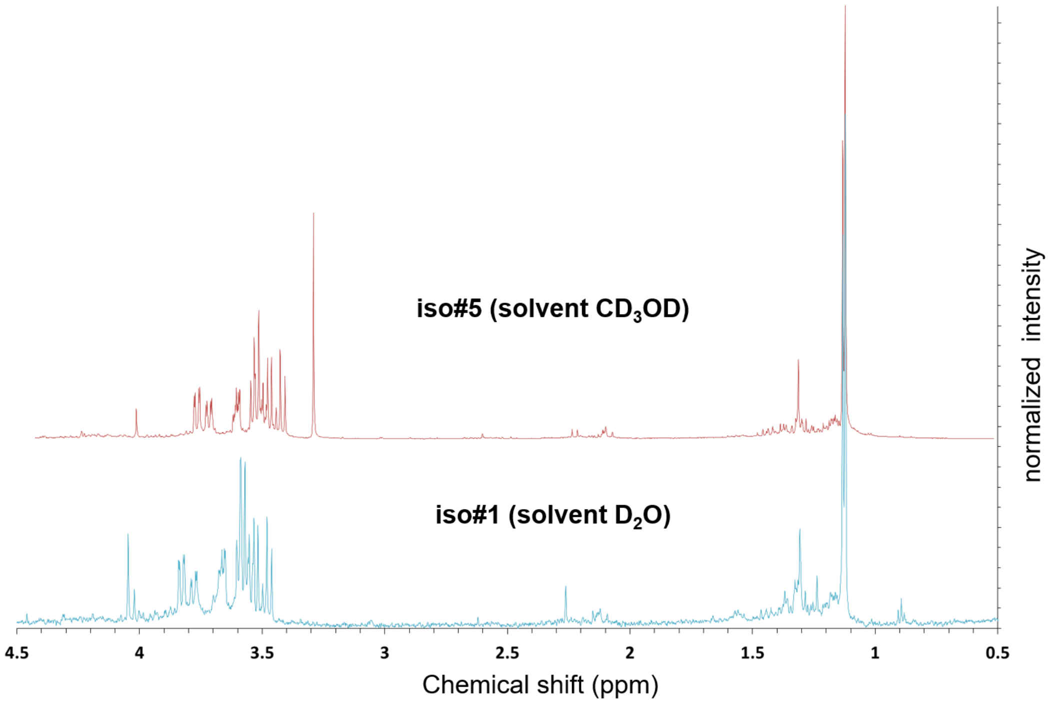

Figure S2. H-NMR spectra (600 MHz) of two isoprene SOA generated with the PAM flow reactor, iso#1 (H-NMR solvent: D_2O) and iso#5 (H-NMR solvent: CD_3OD) samples.

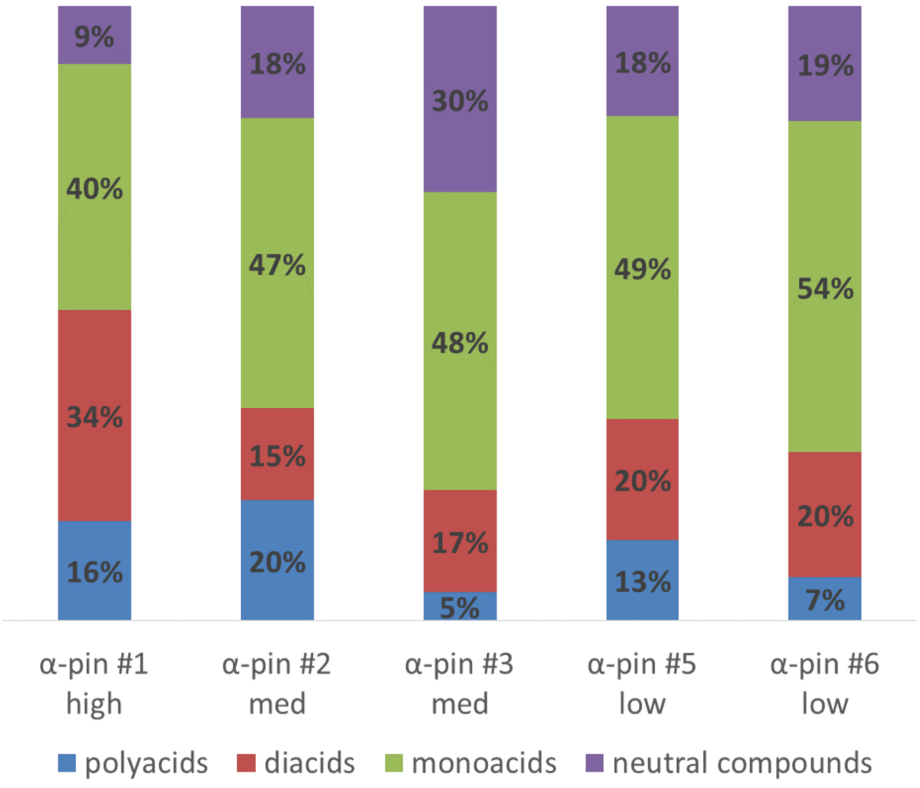

Figure S3. WSOC fractions analyzed by HPLC-TOC for various α-pinene SOA samples generated with the PAM.

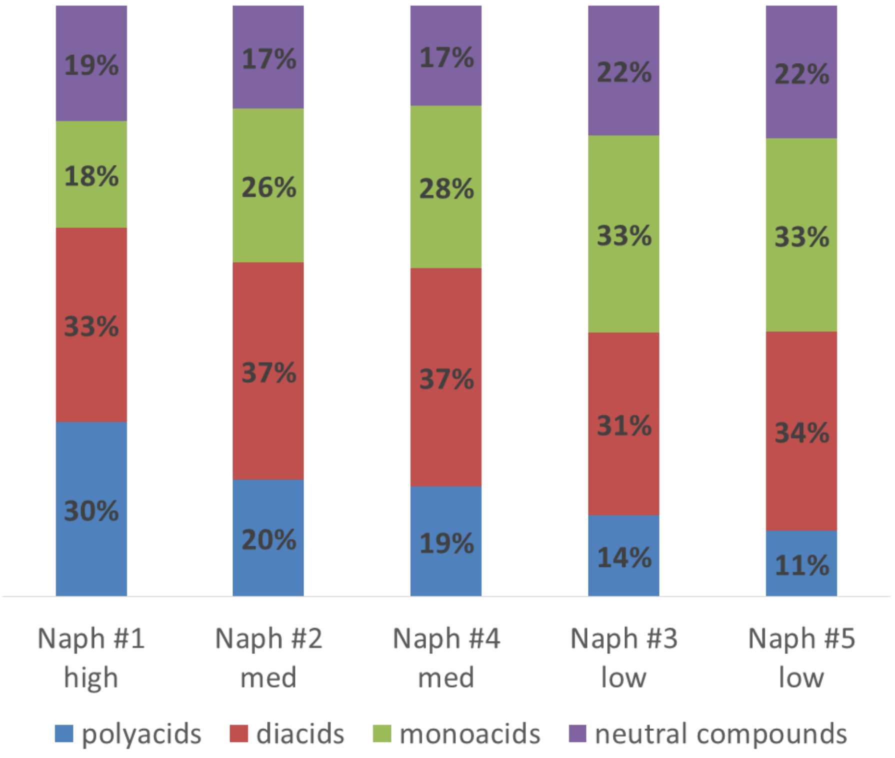

Figure S4. WSOC fractions analyzed by HPLC-TOC for various naphthalene SOA samples generated with the PAM.