Atmospheric
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Supplement of

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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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 ^{1}H-NMR spectrum of sample SPC_020712_D is shown in Figure S1a.

The Amazonian sample discussed in the same Section 4 of the manuscript was collected at Fazenda Nossa Senora (FNS) (10°45'44''S, 62°21'27''W, 315 m a.s.l.) in Rondônia, Brazil, during the SMOCC field campaign (Tagliavini et al. 2006) from 12 to 14 November 2002 using a High Volume Dichotomous Sampler (HVDS) equipped with pre-baked quartz-fiber filters. A fraction of the PM1 filter was extracted with 30 ml of ultrapure (milliQ) water for 60 min with stirring. The aqueous solution was filtered on 0.45 μm hydrophobic PTFE-membrane (Sartorius Minisart SRP 15) filters. An aliquot of the filtered solution was evaporated to dryness under vacuum, collected with 0.7 mL of D_2O containing sodium 3-trimethylsilyl-(2,2,3,3-d4)-propionate (TSP-d_4, 0.24 mM), and used for ^{1}H-NMR analysis. The NMR spectra were obtained with a Varian Inova 600 at 600 MHz. The residue HOD peak was suppressed by presaturation using a PRESAT pulse sequence. The ^{1}H-NMR spectrum of sample SMOCC_55H is shown in Figure S1b.
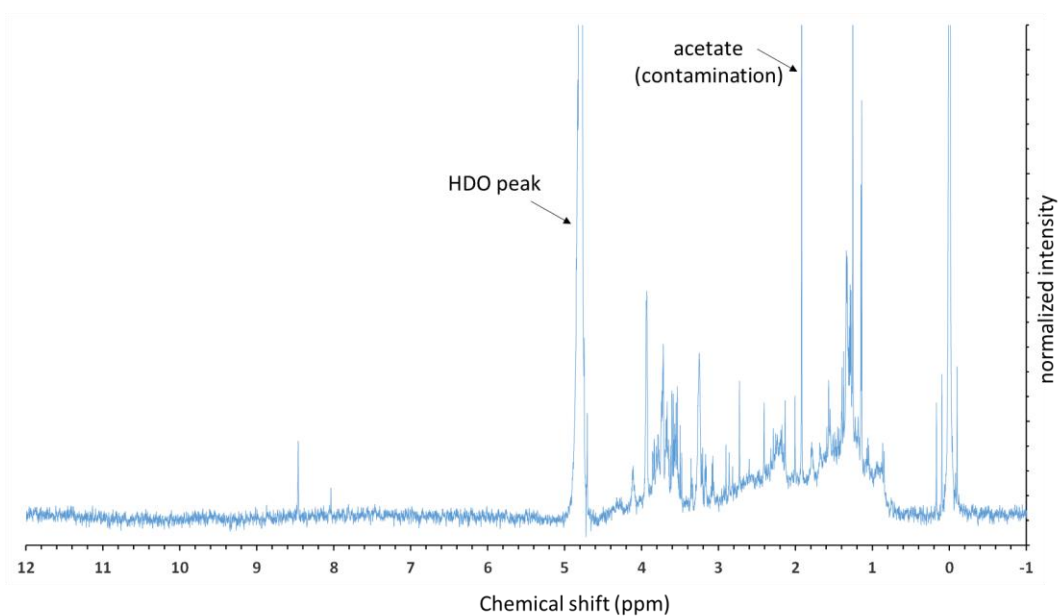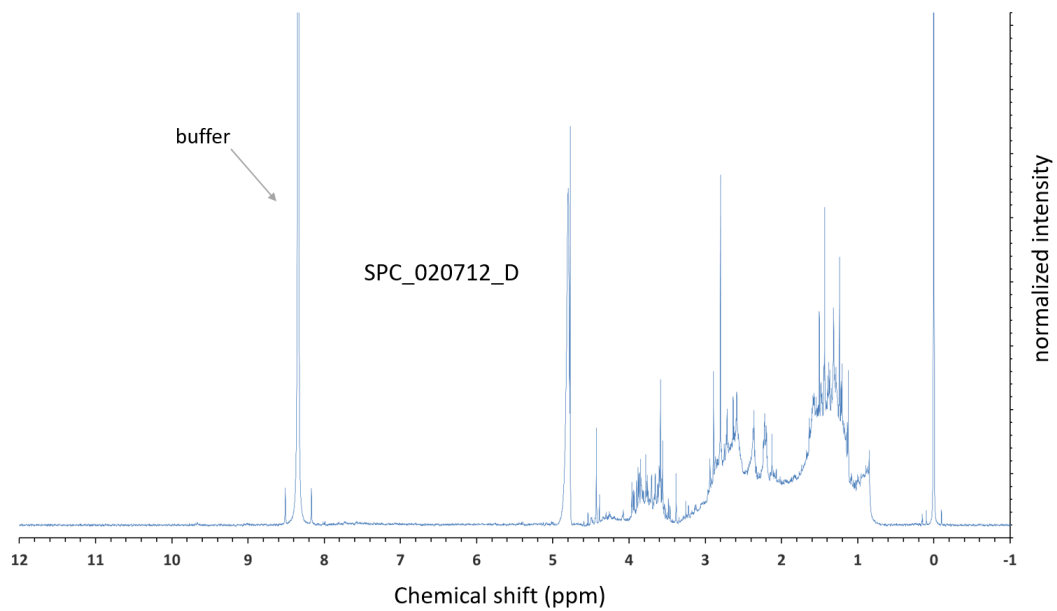
Figure S1. a) (top) ^{1}H-NMR spectrum of sample SPC_020712_D (after water-extraction) collected in San Pietro Capofiume, a rural site nearby Bologna. Sampling time was 9:00-20:30 (local time). b) (bottom) ^{1}H-NMR spectrum of sample SMOCC_55H (after water-extraction) collected in Fazenda Nossa Senora, a rural site in Rondônia, Brazil. Sampling was performed at different times of the day between 12 and 14 Nov. 2012.
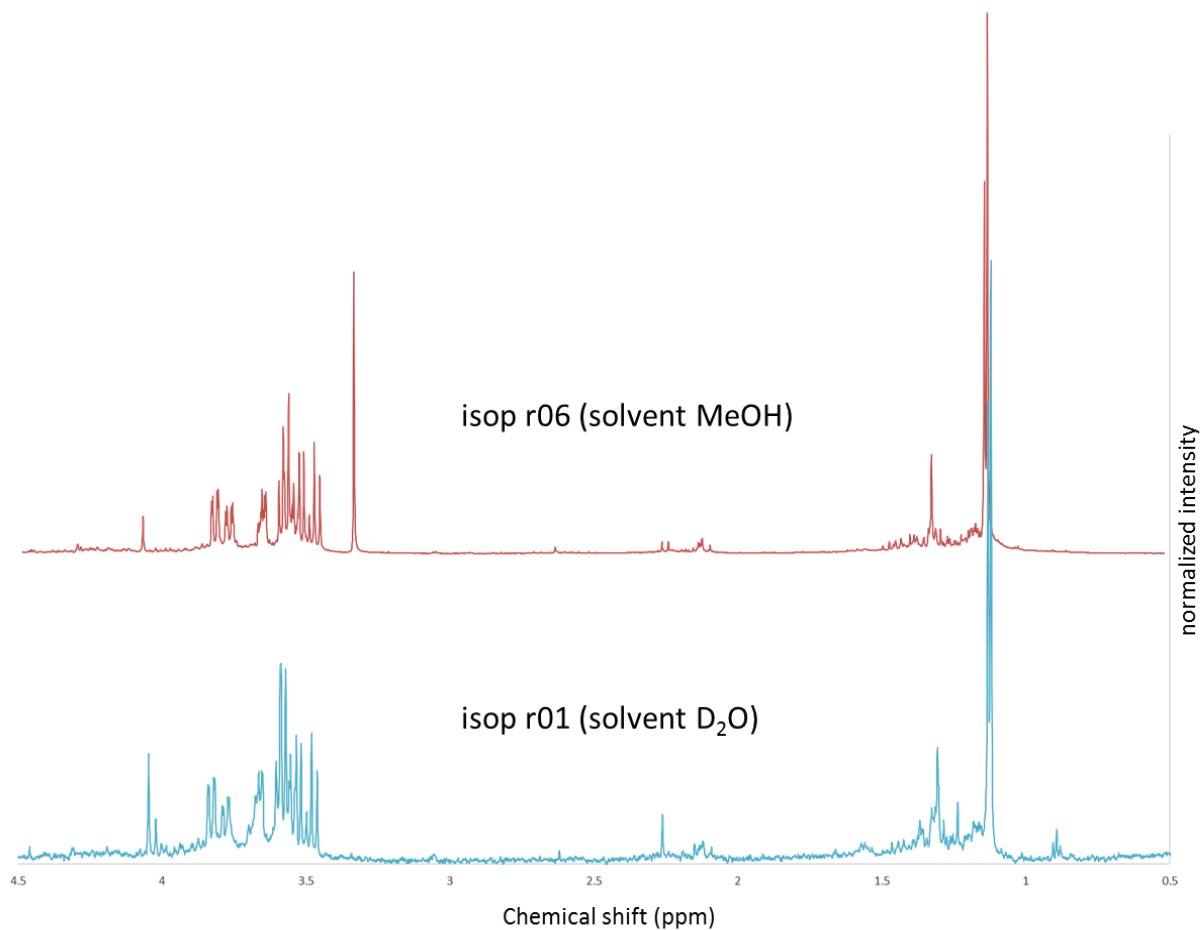
Figure S2. H-NMR spectra (600 MHz) of two isoprene SOA generated with the PAM flow reactor, R01 (H-NMR solvent: D_2O) and R06 (H-NMR solvent: MeOH) samples.
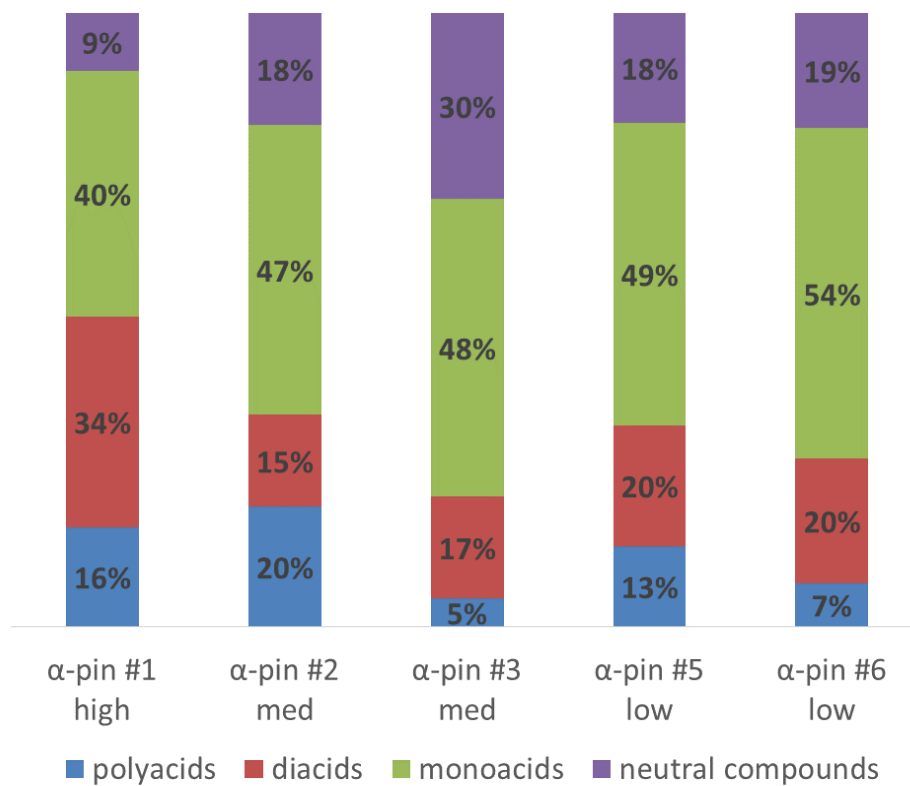
Figure S3. WSOC fractions analyzed by HPLC-TOC for various alpha-pinene SOA samples generated with the PAM.
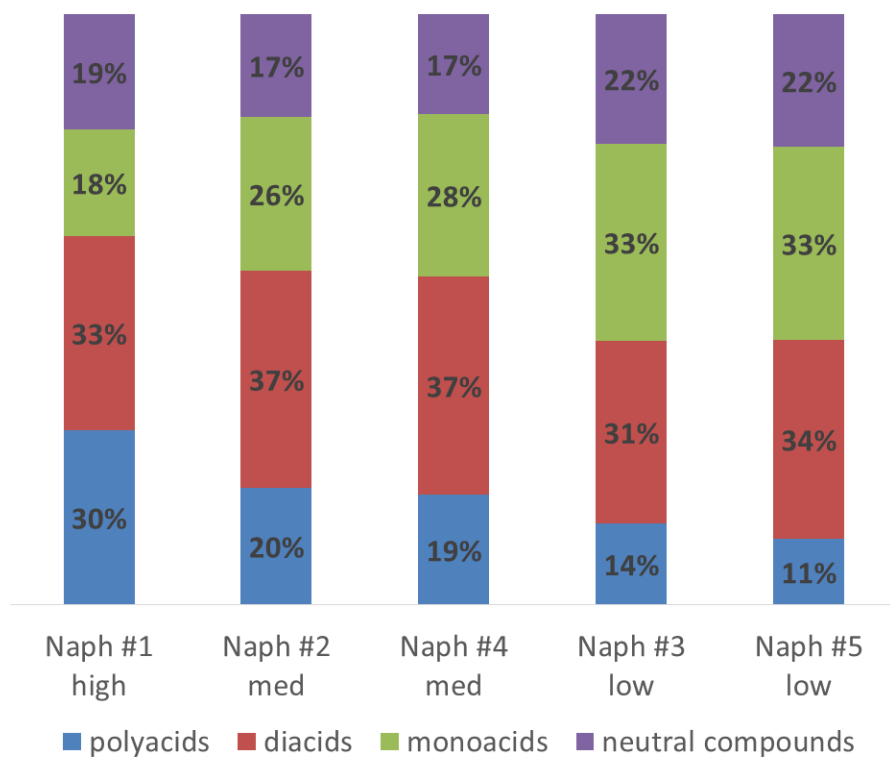
Figure S4. Figure S3. WSOC fractions analyzed by HPLC-TOC for various naphthalene SOA samples generated with the PAM.
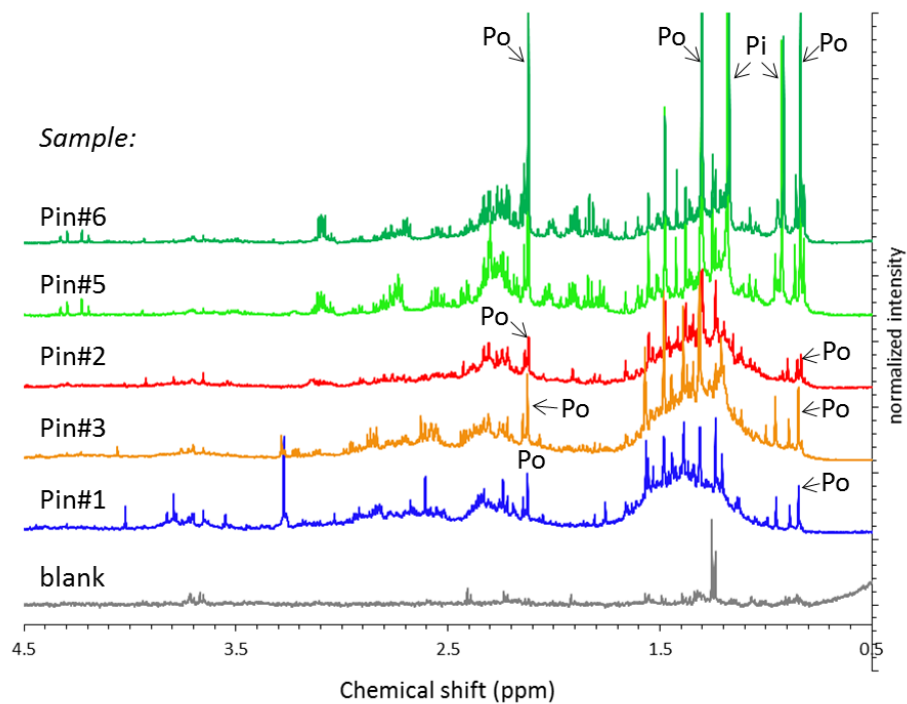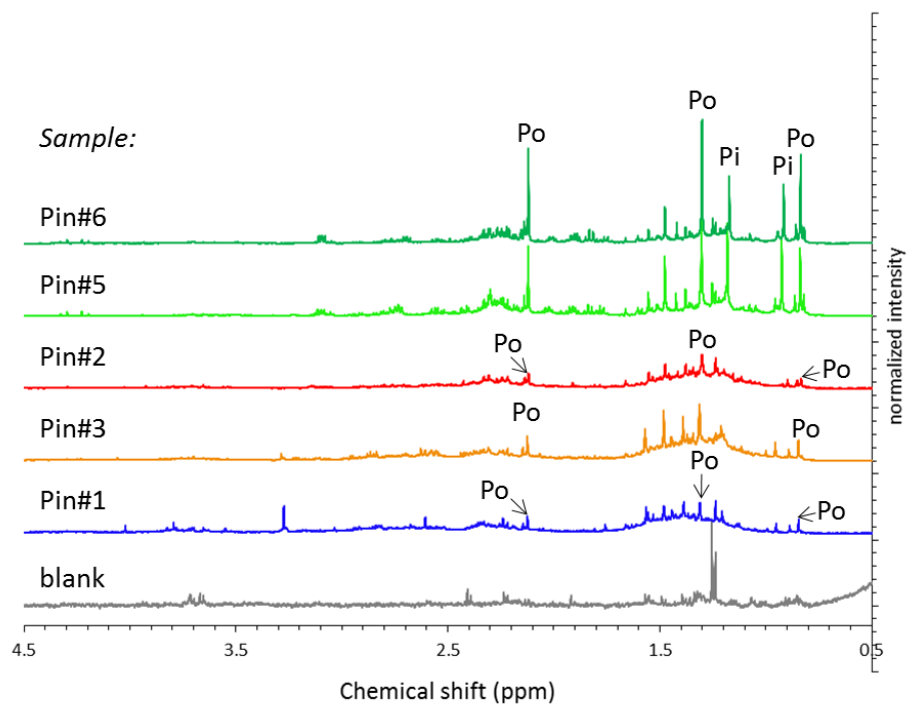
Figure S5. ^{1}H-NMR spectra of α-pinene SOA. Same as in Figure 1 but with a close-up view on the aliphatic region. Two different vertical scales are used to visualize the main individual resonances (from compounds such as pinonic acid "Po" and pinic acid "Pi") (on top) and the background unresolved bands (on the bottom).
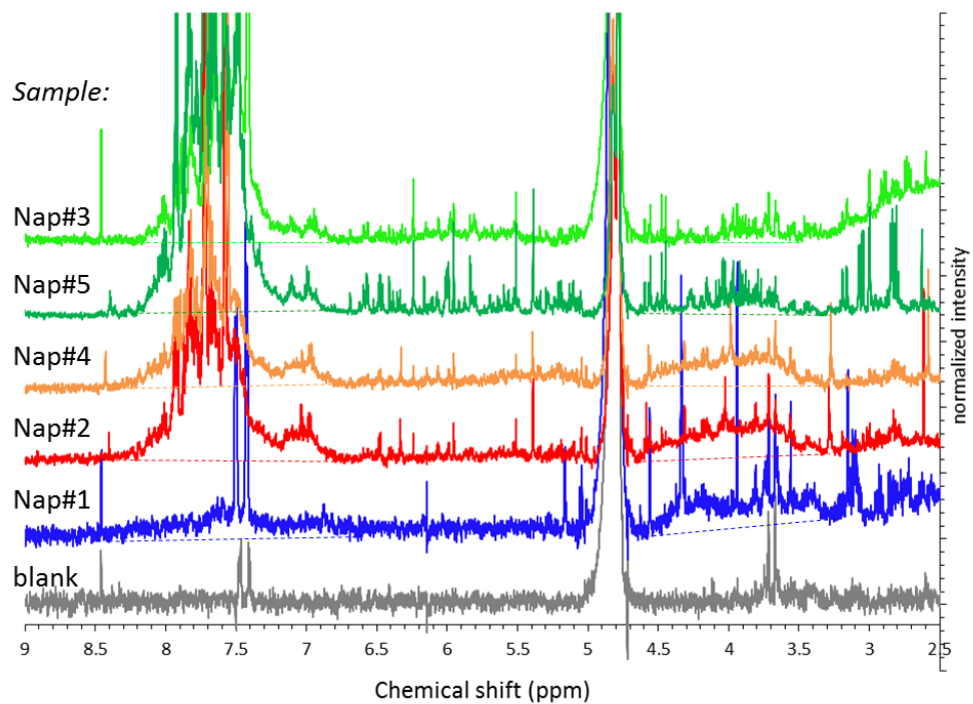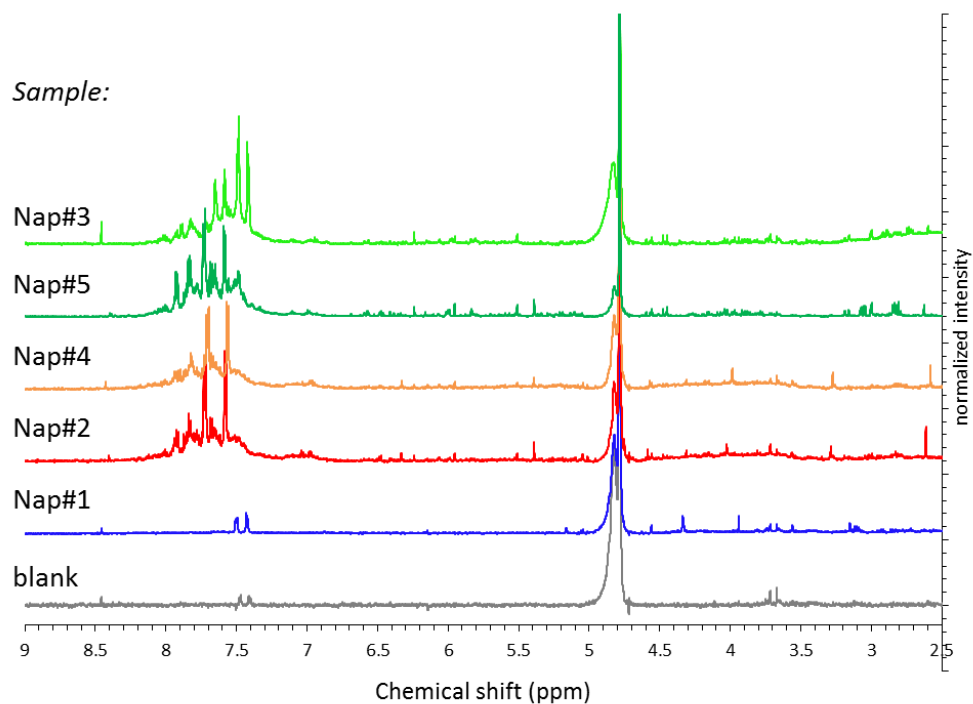
Figure S6. ^{1}H-NMR spectra of naphthalene SOA. Same as in Figure 2 but with a close-up view on the chemical shift region between 2.5 and 9.0 ppm (outside the region < 2.5 ppm where most bands from contaminants and interferences are found). Two different vertical scales are used to visualize the main individual resonances of aromatic compounds (on top) and the background unresolved bands (on the bottom). Dashed lines indicate the approximate baseline underlying

broad bands of aromatic compounds (6.5 – 8.5 ppm of chemical shift) and of oxygenated functional groups (3.5 – 4.5 ppm).