



Supplement of

Formation and chemical evolution of secondary organic aerosol in two different environments: a dual-chamber study

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Calibration procedures for the HR-ToF-AMS during the FAIRARI and the SPRUCE22 campaigns

AMS in the Po Valley: For the HR-ToF-AMS, an ionization efficiency (IE) calibration was run at the beginning of the measurements period (11/02/2022). The calibration was performed over 8 data points by scanning nitrate concentrations from zero (HEPA filter) to $45 \mu\text{g m}^{-3}$. At the end of the measurements period a second calibration was done in order to check that the instrumental sensitivity was not changed over the campaign. The AMS calibration was validated both against offline nitrate measurements on PM_{10} filter samples and SMPS measurements. In both cases, the Pearson correlation coefficients were higher than 0.94 and the regression slopes were within 15% tolerance from the 1:1 line.

Data from IE calibrations were also used to quantify the interference of ammonium nitrate in the CO_2^+ signal following the criteria suggested by Pieber et al. (2016), which resulted negligible even for periods of high inorganic mass fraction during the campaign.

Regarding HR-ToF-AMS particle size calibration, it was performed by following Aerodyne Res. Inc. recommendations, scanning monodispersed ammonium nitrate particles from 70 nm to 500 nm and polystyrene latex spheres (PLS) of 300, 500 and 700 nm. The calibration was verified by comparing the AMS sizing with parallel SMPS measurements.

HR-ToF-AMS detection limits were the following: 0.555, 0.208, 0.113, 0.104 and $0.015 \mu\text{g m}^{-3}$ for HROrg, HRNO₃, HRSO₄, HRNH₄ and HRChl, respectively.

AMS in Pertouli: At the beginning of the SPRUCE-22 campaign, three calibrations were conducted on the HR-ToF-AMS: a flow rate calibration, a particle size calibration, and an ionization efficiency calibration. The standard procedures were followed for each calibration. Ammonium nitrate was chosen as the calibrant due to its efficient vaporization, minimal particle bounce, ability to form spherical particles and its simple fragmentation pattern. The ammonium nitrate was atomized, dried, and passed through a Differential Mobility Analyzer (DMA) to produce monodisperse aerosols, which were then introduced into the AMS.

For the particle size calibration (velocity calibration), monodisperse aerosols of various diameters were generated. For the ionization efficiency calibration, a specific particle size of 300 nm was used. The ionization efficiency calibration was performed using the Brute Force Single Particle (BFSP) method.

The high-resolution (HR) peak fitting was conducted using the Pika module, designed for analyzing AMS data. Specific ions, represented with custom peak shape functions, were fitted at each m/z value based on the resulting residuals. An ion was included in the fitting process if its addition significantly reduced the residuals; otherwise, it was excluded. At the conclusion of the HR fitting process, diagnostic checks were performed, including a comparison between results from the Pika and Squirrel modules.

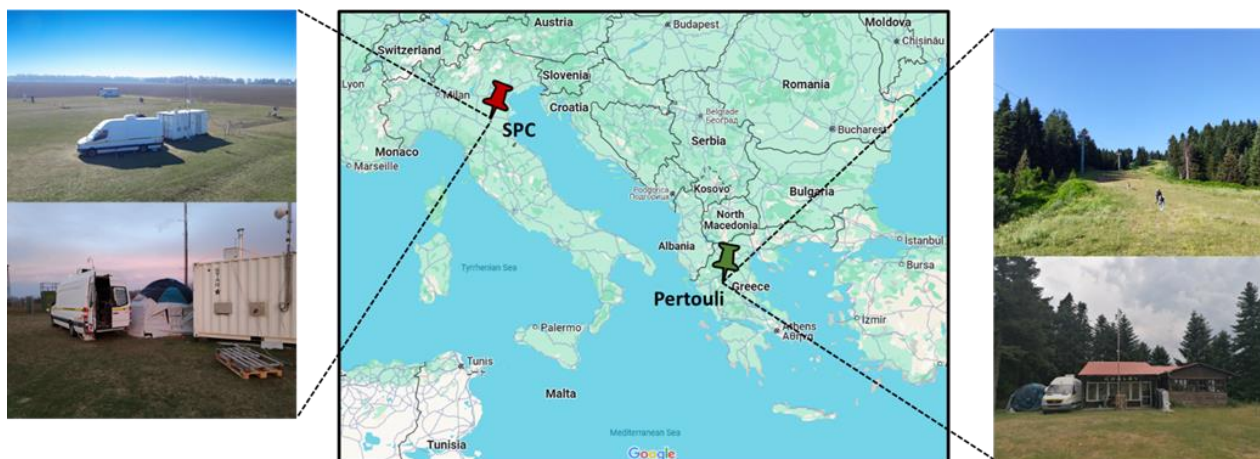


Figure S1: The sites where the two field campaigns took place. The site in San Pietro Capofiume (SPC), northern Italy is shown on the left, while the site in Pertouli where the SPRUCE-22 campaign took place is shown on the right (map from © Google Maps 2024).

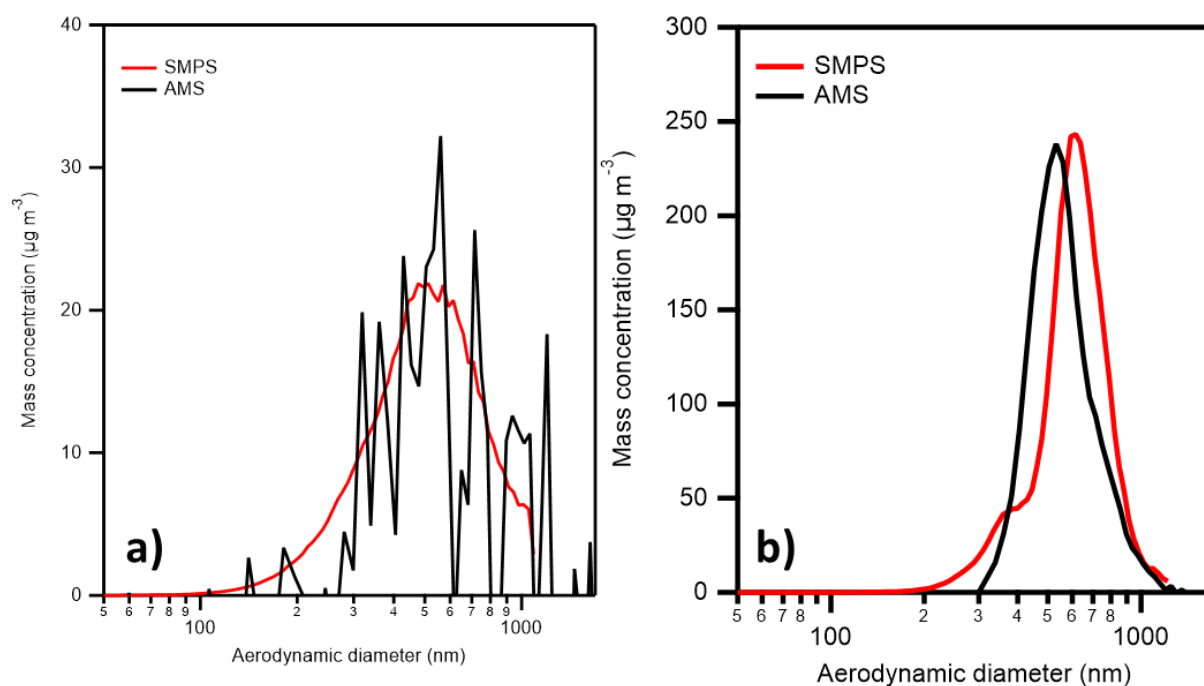


Figure S2: Example of CE corrected mass size distributions of PM_{10} measured by the AMS and the SMPS for a) the characterization period and b) the SOA formation period during Exp. 7 in Po Valley.

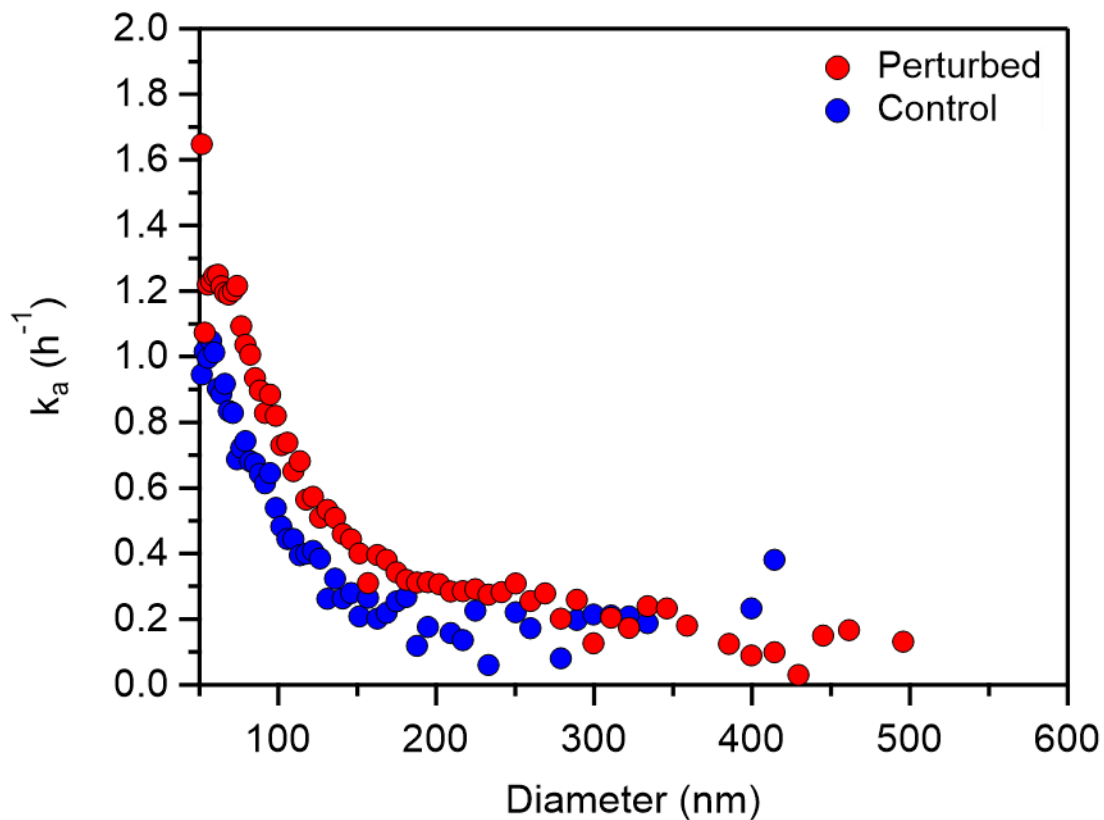


Figure S3: Size dependent wall-loss rate constant measured during Exp. 3 (5-3-2022).

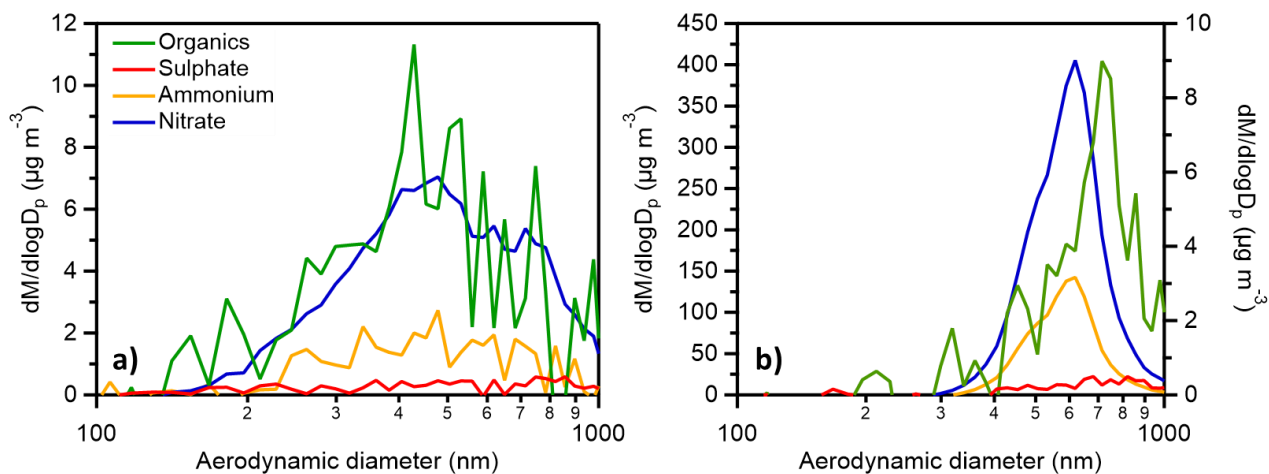


Figure S4: Mass size distributions of the various compounds measured by the AMS for a) the characterization period and b) the SOA formation period during a typical experiment.

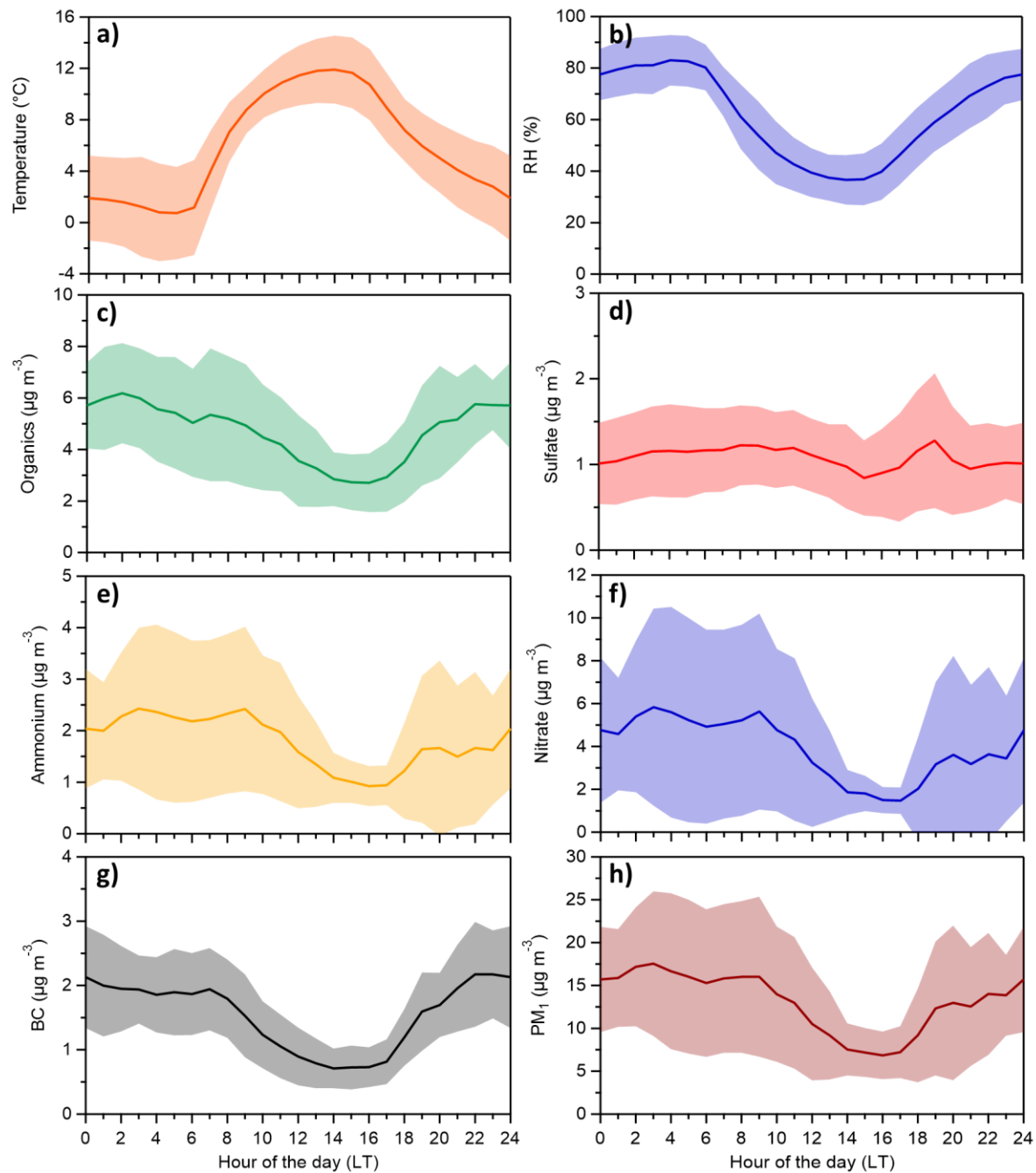


Figure S5: Diurnal profiles of the ambient a) temperature, b) relative humidity, c) organics, d) sulfate, e) ammonium, f) nitrate, g) black carbon and h) the PM₁ concentrations measured by the AMS during the chamber experiments period (2-17 March 2022) in Po Valley. The shaded areas correspond to one standard deviation.

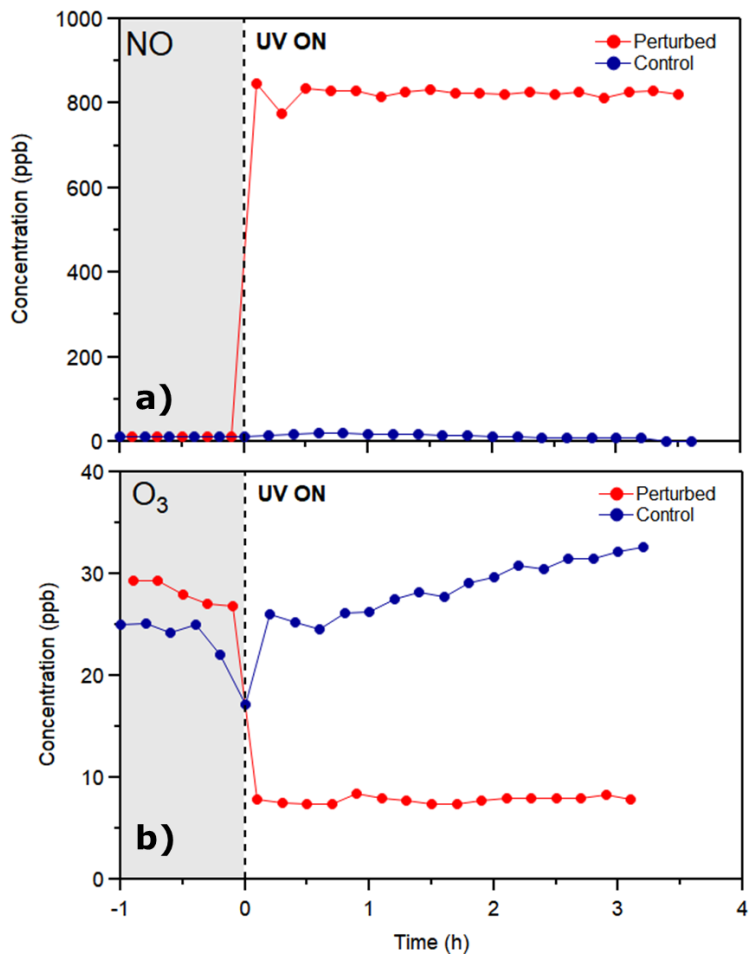


Figure S6: Concentration of a) NO and b) O₃ in the perturbed and the control chamber during the experiment of 10-3-2022.

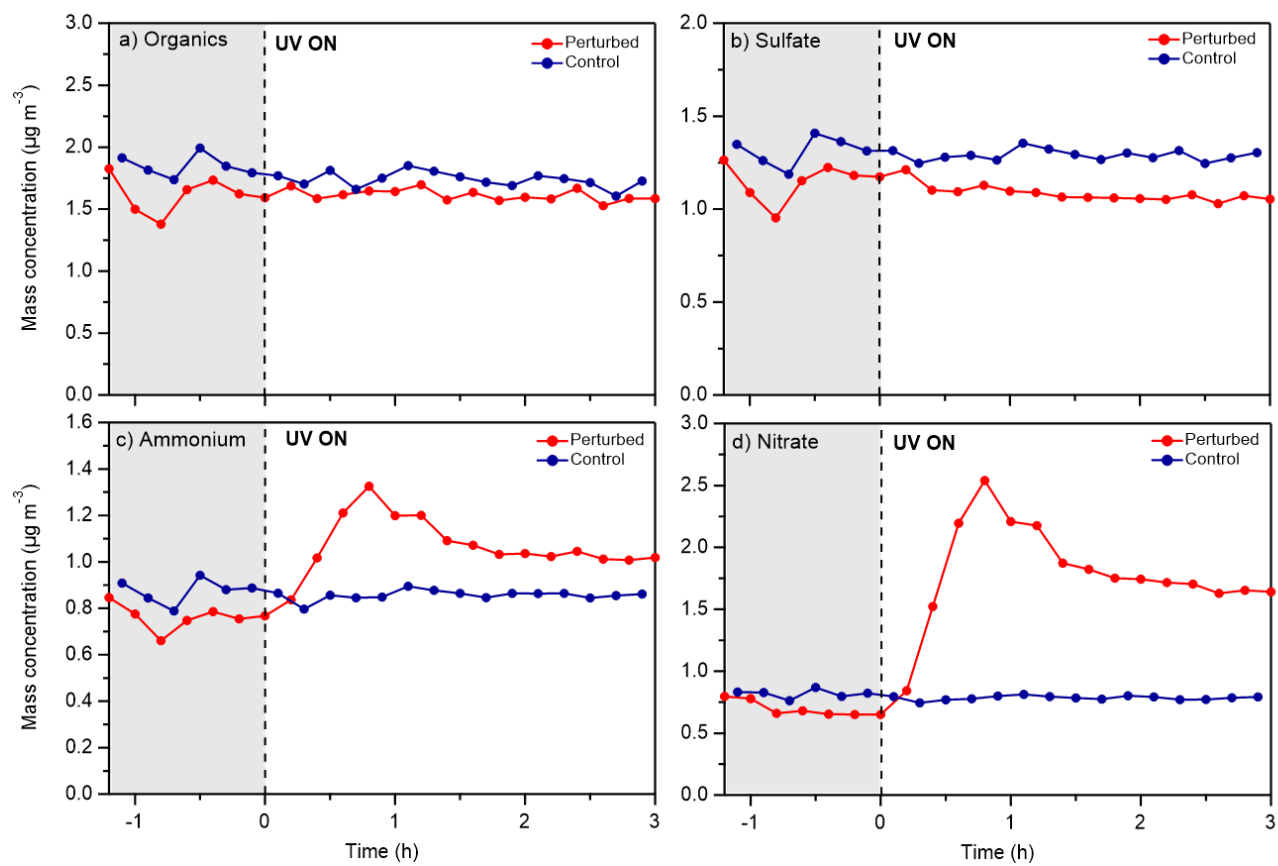


Figure S7: Wall-loss (perturbed: $k_{ac}=0.24 \text{ h}^{-1}$, control: $k_{ac}=0.2 \text{ h}^{-1}$) and CE corrected mass concentrations of a) organics, b) sulfate, c) ammonium and d) nitrate in the perturbed and the control chambers during the Exp. 2 (7/3/2022).

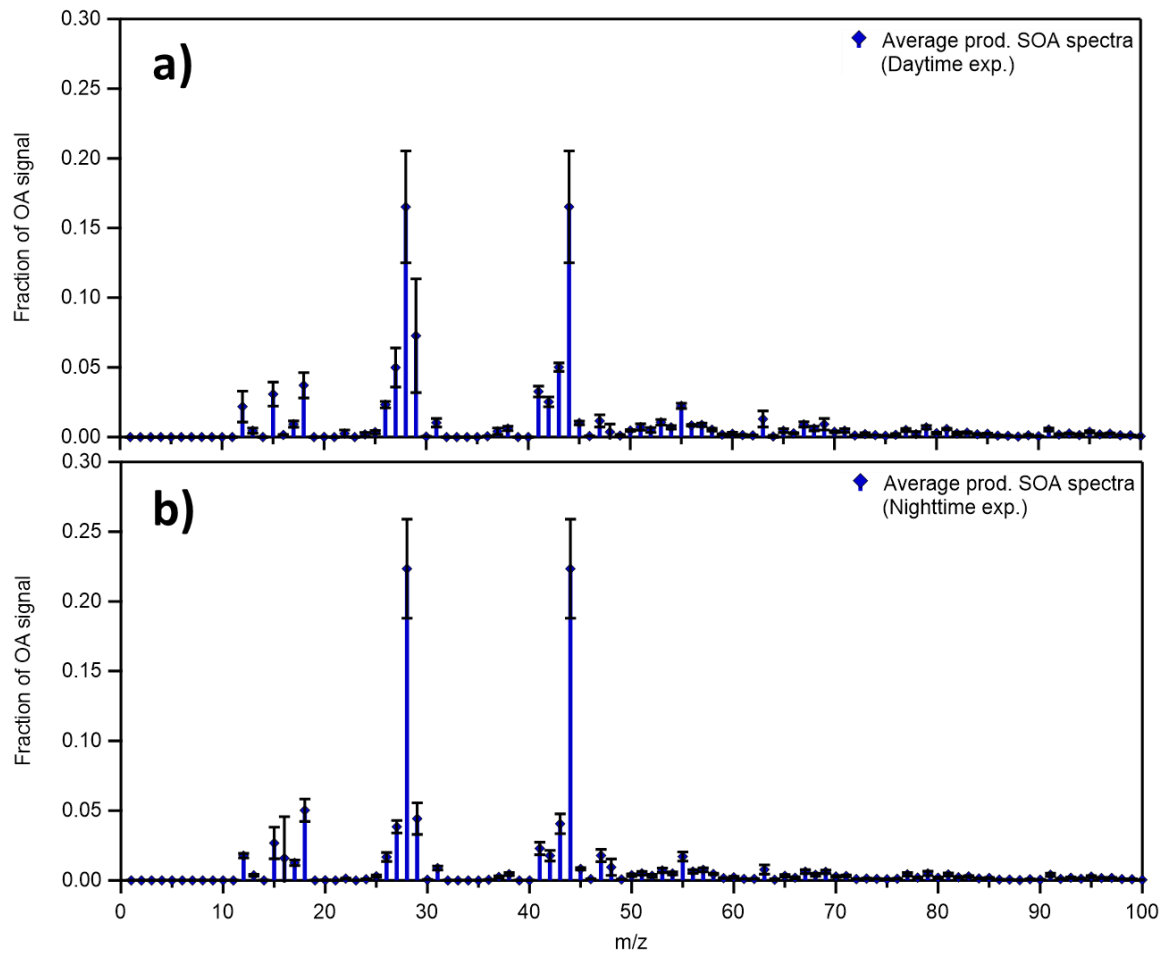


Figure S8: Average mass spectra of the produced SOA during the a) daytime and b) nighttime experiments in the Po Valley. The error bars represent one standard deviation. The θ angle between the daytime experiments ranged from 5.2° to 15.5° and between the nighttime experiments from 2.4° to 19° .

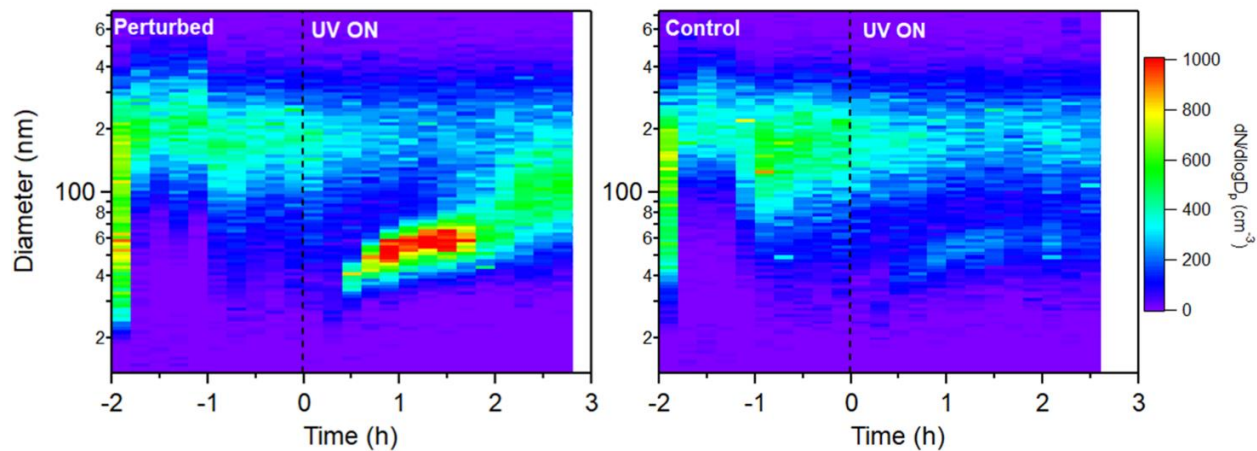


Figure S9: Particle number size distributions in the perturbed and the control chamber during the Exp. 3 (5/3/2022).

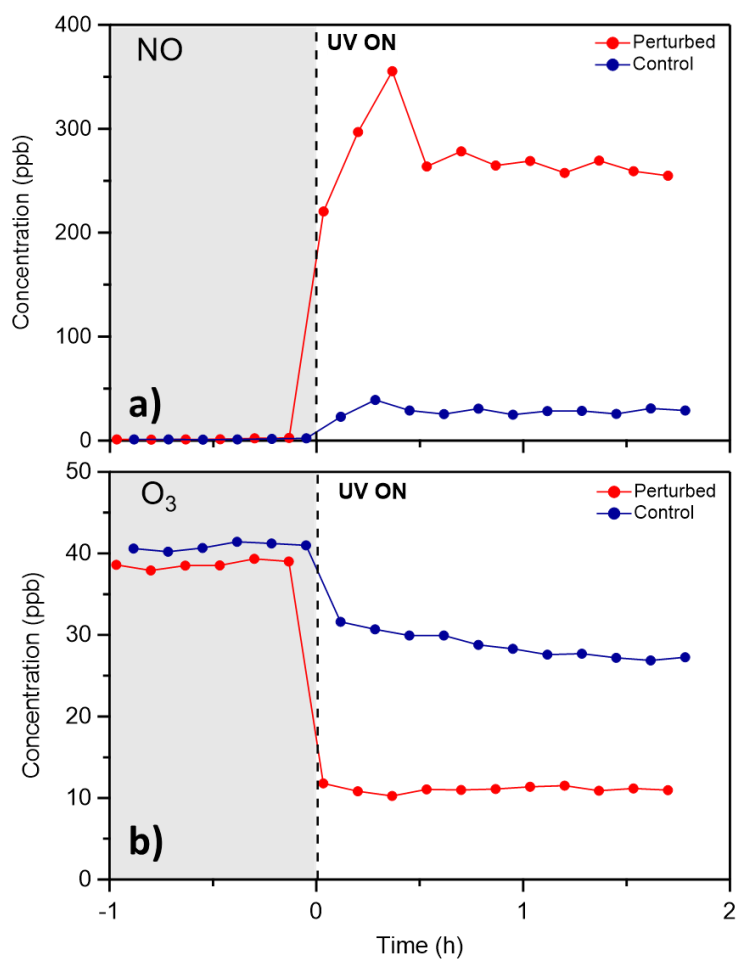


Figure S10: Concentration of a) NO and b) O₃ in the perturbed and the control chamber during the experiment of 10-7-2022.

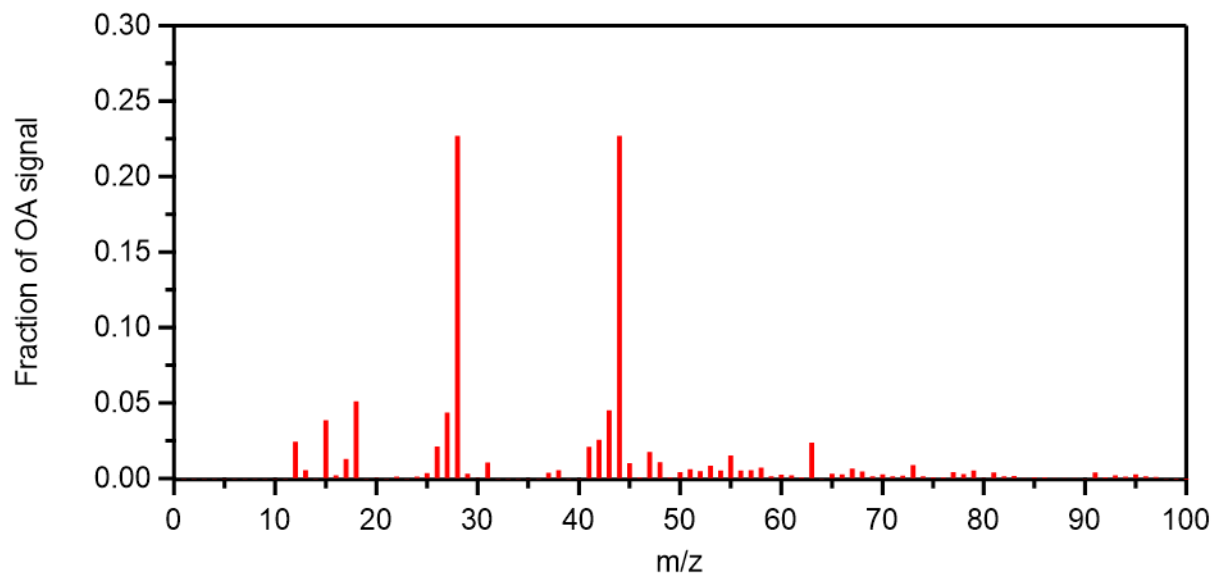


Figure S11: Mass spectrum of the produced SOA during Exp. 1 in Pertouli.

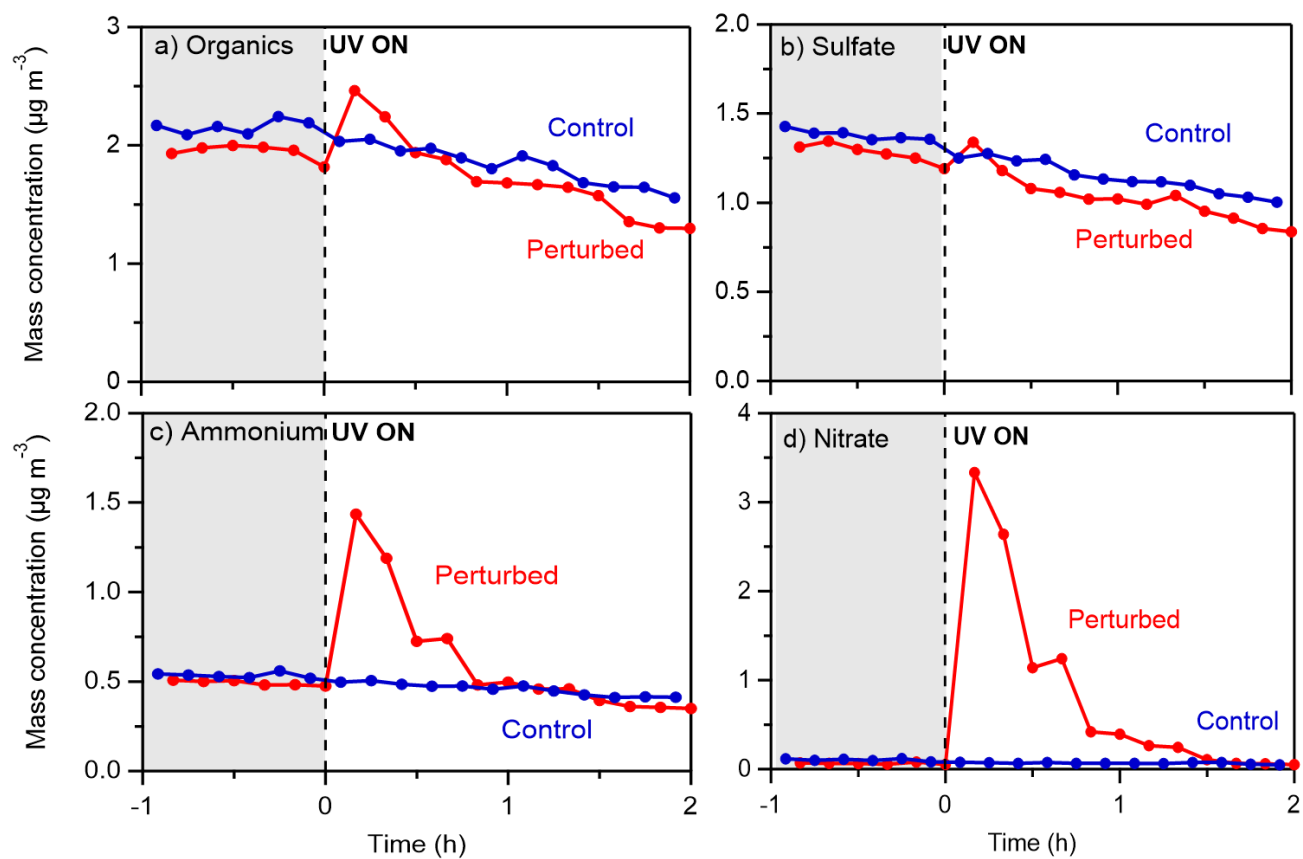


Figure S12: Mass concentrations of a) organics, b) sulfate, c) ammonium and d) nitrate in the perturbed and the control chambers during Exp. 2 (12-7-2022) in Pertouli.

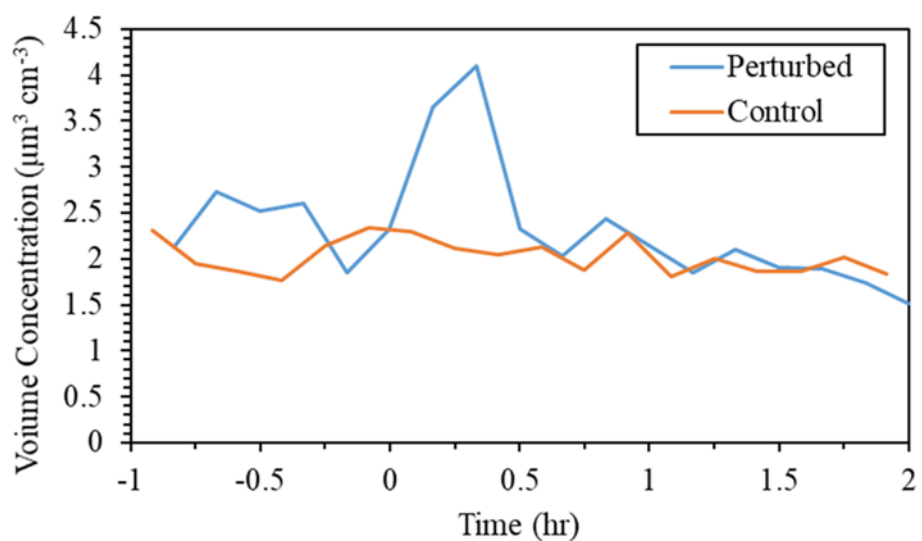


Figure S13: Aerosol volume concentration for the perturbed and control chambers during Exp. 2 (12-7-2022) in Pertouli measured by the SMPS.

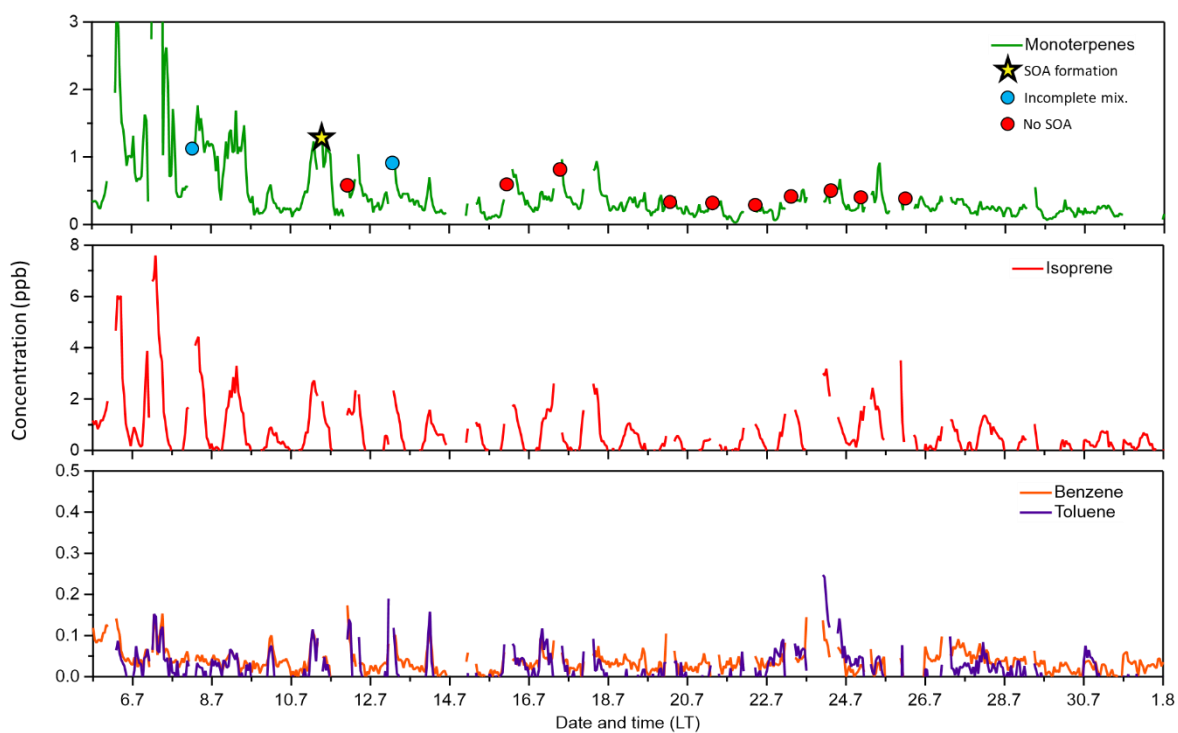


Figure S14: Ambient concentrations of the monoterpenes, isoprene and benzene and toluene during the SPRUCE-22 campaign.

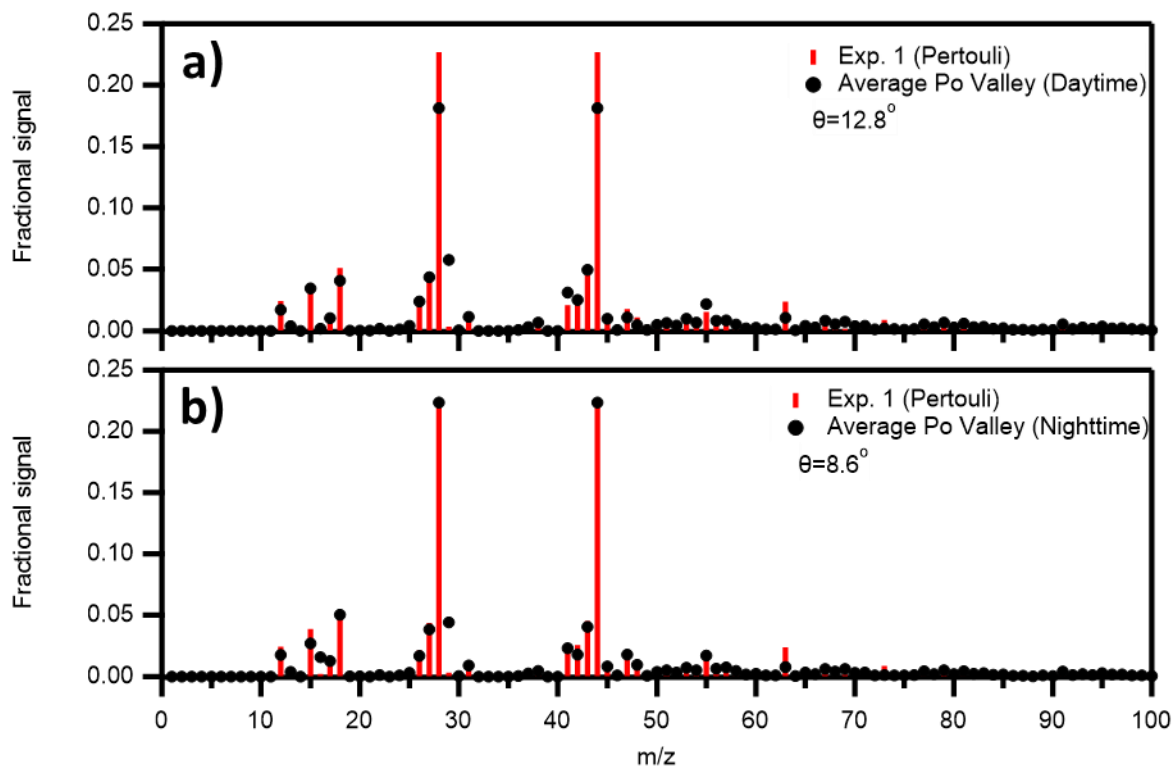


Figure S15: Average fractional signal of the produced SOA during a) Exp. 1 in Pertouli and the daytime (average) experiments in the Po Valley and b) Exp. 1 in Pertouli and the nighttime (average) experiments in the Po Valley.

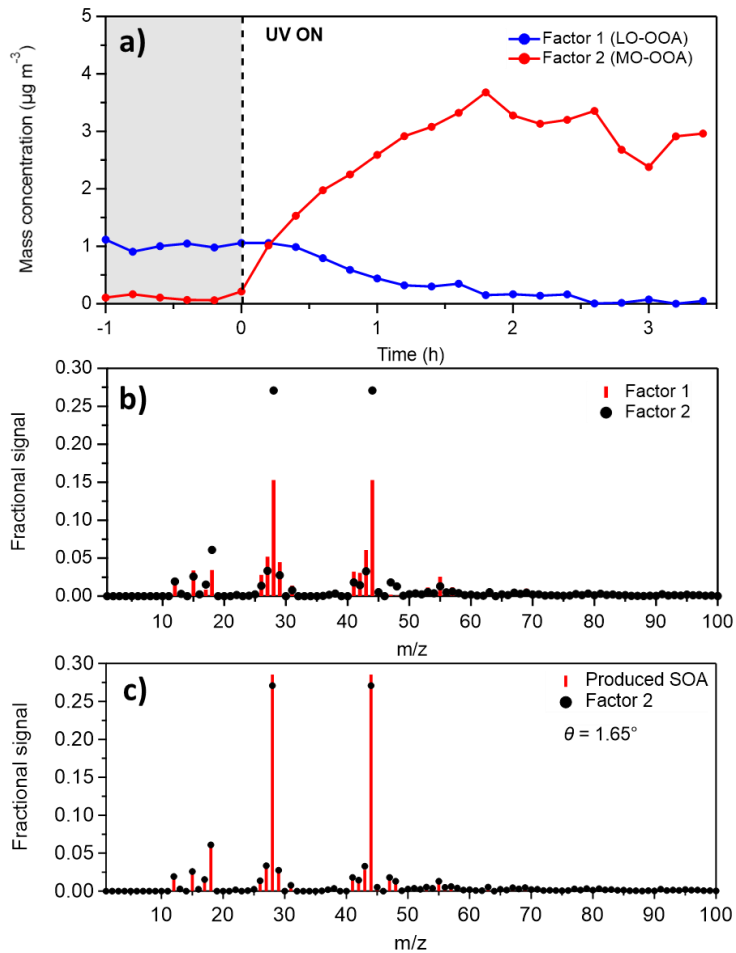


Figure S16: Results from the PMF analysis done for Exp. 1 in the Po Valley, including a) the timeseries of the two different identified factors, b) the comparison of their mass spectra and c) the comparison of the calculated mass spectra of the produced SOA and Factor 2.