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Diurnal aging of biomass burning emissions: impacts on secondary organic aerosol formation and oxidative potential

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Supplementary Information

S1: Water-soluble oxidative potential (WS-OP) measurements of fresh and aged biomass burning emissions

The custom made system used for the WS-OP measurements (Fig. S1) is equipped with two programmable syringe pumps: one with a 12-way distribution rotary valve and a 10 mL glass syringe capacity (VersaPump 6, Norgren Kloehn, Inc.), and a second with a 6-way valve and a 250 μL glass syringe capacity (VersaPump 3, Norgren Kloehn, Inc.), an autosampler (14-port rotary valve, model Cheminert C25Z-31814D) connected to a multiposition actuator control module (model EMHCA-CE, VICI Valco Instrument Co., Inc.), a 10 cm liquid waveguide capillary cell (LWCC-M-100, World Precision Instruments, Inc.), and an online spectrophotometer. The spectrophotometer consisted of a light source (DH-mini Deuterium-Halogen UV-VIS-NIR, Ocean Insight) and a multi-wavelength light detector (Flame-T UV-VIS miniature spectrometer, Ocean Optics, Inc.). This custom system adopts a simplified yet analytically precise approach (Dominutti et al., 2025) to perform the original dithiothreitol assay developed by Cho et al. (2005). This assay mimics the electron transfer mechanism by utilizing the catalytic ability of redox-active PM species to transfer electrons from DTT to oxygen (Rao et al., 2020).

Prior to the WS-OP analysis, punches (1.5 cm^2) of the collected PM filter samples were extracted with 5 mL of Milli-Q water (18.2 MΩ) through a 30 min ultrasonication (ultrasonic heated bath, Elmasonic S30H). The extracts were filtered using PTFE syringe filters (0.45 μm pore size, 25 mm diameter) to remove insoluble components. Subsequently, 3.5 mL of the aqueous extracts were incubated, with a use of a thermomixer (Eppendorf ThermoMixer), in a potassium phosphate buffer where the DTT was also added under controlled conditions (T = 37 °C and pH = 7.4).

The DTT is depleted over time as it is oxidized by the ROS of the sample. The reaction follows pseudo-first order kinetics and the rate of DTT oxidation, commonly defined as DTT activity, is proportional to the ROS aqueous concentration (Jiang et al., 2020). Thus, DTT activity can be determined by measuring the DTT consumption at specific time intervals (4, 13, 23, 30 and 41 min). The remaining amount of DTT in the samples was quantified by adding DTNB reagent (5,5-Dithioben (2-nitrobenzoic acid) which forms the light absorbing derivative 2-nitrobenzoic acid (TNB). The spectrophotometer detected the TNB product by measuring absorption at 412 nm. Simultaneously, TNB absorption at 700 nm was also recorded, serving as the baseline absorbance due to the product minimal absorption at this wavelength. Light

absorbance readings were taken every minute at both wavelengths using the SpectraSuite data acquisition software by Ocean Optics, Inc. Absorption measurements at 412 nm were subsequently corrected by subtracting the baseline measurements obtained at 700 nm.

The rate of DTT consumption, in nmol min^{-1}, was calculated using linear regression of the TNB absorbance data against time, based on the average of 2 duplicate readings. Subsequently the WS-OP of the aerosol extract was calculated by subtracting the consumption rate of the blank sample, which accounts for any non-specific reactions or interference, from the DTT consumption rate of each aerosol extract. All reported data were blank corrected. The net DTT consumption rates are expressed in nmol min^{-1} μg^{-1} (OC mass normalized DTT activity – DTT_m) representing the per unit OC mass activity of the samples (Fang et al., 2015).

For the precision control of the semi-automated system, a phenanthrequinone (PQN) solution of known concentration was used as an external standard for each analyzed sequence (a total of 12 aerosol samples in every sequence). The system was routinely calibrated by preparing twelve samples containing all the necessary reagents and known DTT concentrations, ranging from 0.01 mM to 0.14 mM, without utilizing the programmable syringe pumps. The exact methodology applied for OP measurement, standard testing analysis, reagents preparation and the pre-treatment of the PM samples is described in detail in the work of Fang et al. (2015) and Paraskevopoulou et al. (2019).

OC, used to normalize DTT_m activity, as well as the EC content of the samples were quantified using thermal-optical analysis (Sunset Laboratory Inc., Model M5L) following the NIOSH-870 protocol. For instrument calibration, low volumes of sucrose solutions with carbon mass concentrations ranging from 0.34 to 6.74 μg C μL^{-1} were utilized. Additional details regarding OC/EC measurement methodology and instrument calibration can be found in Karanasiou et al. (2015), Panteliadis et al. (2015) and Brown et al. (2019). Based on replicate analyses the relative standard deviations for OC and EC measurements were 15 ± 5% and 20 ± 5%, respectively.

S2: ΔCO_2 normalization of fresh olive wood and mixed with pine VOCs emissions

To investigate the potential net effect of pine kindling on VOC emissions from olive wood burning, the concentrations (in ppb) of the measured VOC species in all experiments were normalized according to the relative difference in carbon dioxide concentration (ΔCO_2, in ppm; values included in Table S1) observed in the chamber before and after the injection of fresh emissions. The absolute and ΔCO_2 normalized average concentrations of the identified VOCs

in fresh olive wood burning emissions and fresh olive-pine mixed emissions, along with their percentage contribution to the total measured VOCs are summarized and compared in Fig. S5.

Lower levels of aldehydes and ketones were observed in experiments ND7 and ND8, which can be attributed to a distinct emission profile. However, these levels fall within the measurement uncertainty range of the other experiments, making their statistical significance questionable. In contrast, monoterpenes (*m/z* 137) and their fragments (*m/z* 81) showed a significant increase in fresh olive-pine mixed emissions, rising from 1.5 ppb to 7 ppb and from 1.4 ppb to 2.1 ppb, respectively. A high contribution of terpenes (70-90%) in VOCs emissions from pine burning has also been reported by Pohleven et al. (2019).

Despite the lower concentrations of most of the aromatic compounds in olive-pine emissions, their proportion to the total VOCs emissions was higher (19.4%), than that of olive wood emissions (9.3%), suggesting differences in pyrolysis pathways between the two wood types (i.e., different thermal degradation mechanisms). Some aromatic hydrocarbons, such as benzene (*m/z* 79), toluene (*m/z* 93), and styrene (*m/z* 105) remained relatively stable across both wood fuel types, while heavier PAHs, such as naphthalene (*m/z* 129), increased in the mixed emissions, rising from 1.4 ppb to 2.5 ppb (79%). Nyström et al. (2017) observed that pine, even at high burn rates (as in our examined cases), produced the lowest organic-to-elemental carbon (OC/EC) ratio (0.83 ± 0.48) along with elevated concentrations of PAHs and oxy-PAHs compared to other fuels. Similarly, significantly lower OA/BC ratios were observed in both experiments (0.4 in ND7 and 0.9 in ND8), representing the lowest values among all conducted experiments.

S3: Calculation of reacted VOC fractions

The theoretical reacted fractions and lifetimes of most of the consumed species were also calculated for the 2-h daytime oxidation period, assuming a first-order reaction of specific VOCs with OH and O_3. These theoretical values were then compared to the daytime observed relative changes in VOC concentrations. The k_{OH} and k_{O3} values for the different species (in molecule^{-1} cm^3 s^{-1}) were obtained from the literature. Details regarding these calculations are provided in Tables S4 and S5.

S4: Statistical analysis of WS-OP measurements

Statistical analysis of the WS-OP results was performed by applying the independent samples t-test to compare and determine if there is a significant difference between the means ($\bar{\mu}_1$ and $\bar{\mu}_2$; $\bar{\mu}_1 > \bar{\mu}_2$) of two independent groups (fresh, day-aged, night-aged) of WS-OP

measurements (e.g., test scores of two different classes). First two hypotheses were formulated: the null hypothesis (H_0), which assumes no difference between the group means (e.g., $\bar{\mu}_1 = \bar{\mu}_2$), and the alternative one (H_1) that implies difference between the two comparable groups of values (e.g., $\bar{\mu}_1 \neq \bar{\mu}_2$). For each group of OP measurements (x_i) the standard deviation (σ^2) was calculated based on the sample's size (n) and its mean value ($\bar{\mu}$), by applying the equation (S1).

$$\sigma^2 = \frac{1}{n-1}\sum_i (x_i - \bar{\mu})^2 \quad \text{(S1)}$$

Then the absolute value of the test statistic (t_0) was calculated based on equation (S2):

$$t_0 = \sqrt{\left(\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}\right)} \frac{(\bar{\mu}_1 - \bar{\mu}_2)}{\sqrt{(n_1 - 1)\sigma_1^2 + (n_2 - 1)\sigma_2^2}} \quad \text{(S2)}$$

where the term $(n_1 + n_2 - 2)$ represents the degrees of freedom. In case the sizes of the two groups of samples are equal $(n_1 = n_2)$ then equation (S2) is simplified in the following form:

$$t_0 = \sqrt{n}\, \frac{\bar{\mu}_1 - \bar{\mu}_2}{\sqrt{(\sigma_1^2 + \sigma_2^2)}} \quad \text{(S3)}$$

Subsequently, using a t-distribution table, the critical t-value (ct) was estimated based on the chosen significance level (here $\alpha = 0.05$) and the degrees of freedom of each group of values. If the absolute value of the test statistic is greater than the critical value ($t_0 > ct$), the null hypothesis is rejected (Hypothesis H_1 acceptable). If the absolute value of the test statistic is less than or equal to the critical value ($t_0 \leq ct$), the null hypothesis is accepted. Table S6 summarizes the results of all examined hypotheses.

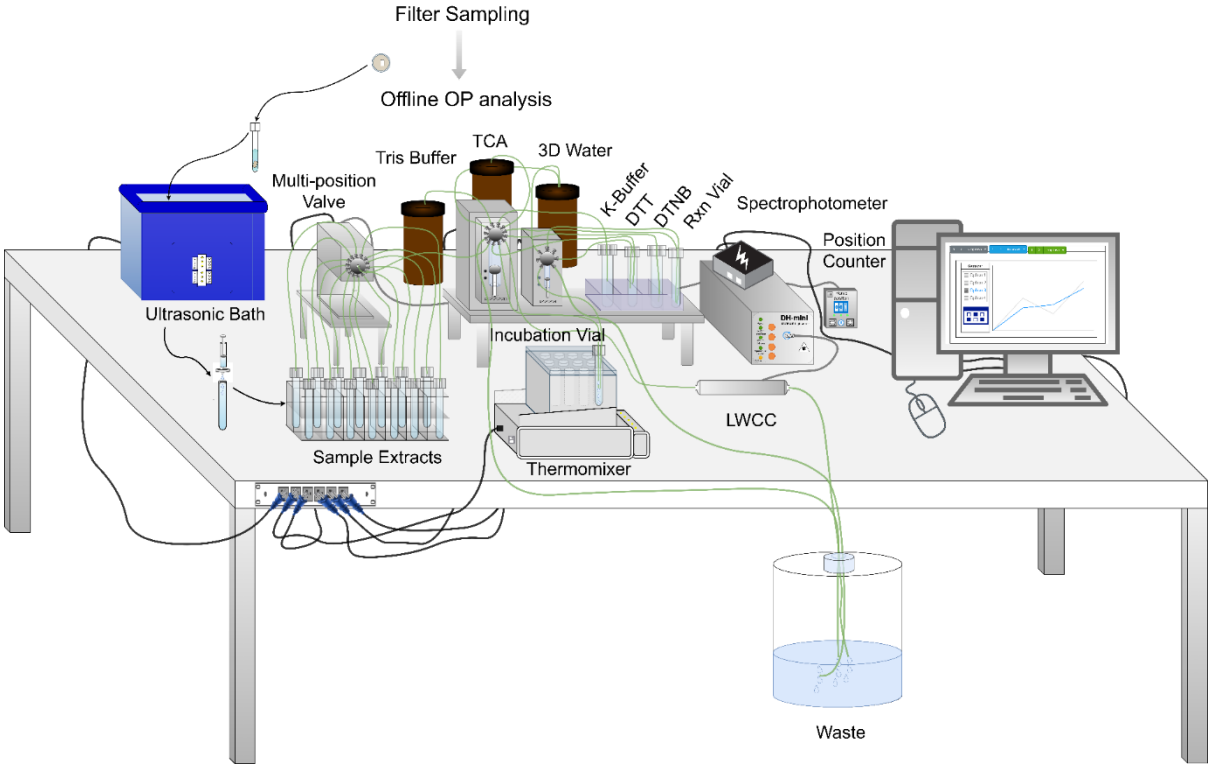

Figure S1: Semi automated spectrophotometric system used for the offline water-soluble oxidative potential (WS-OP) analysis.

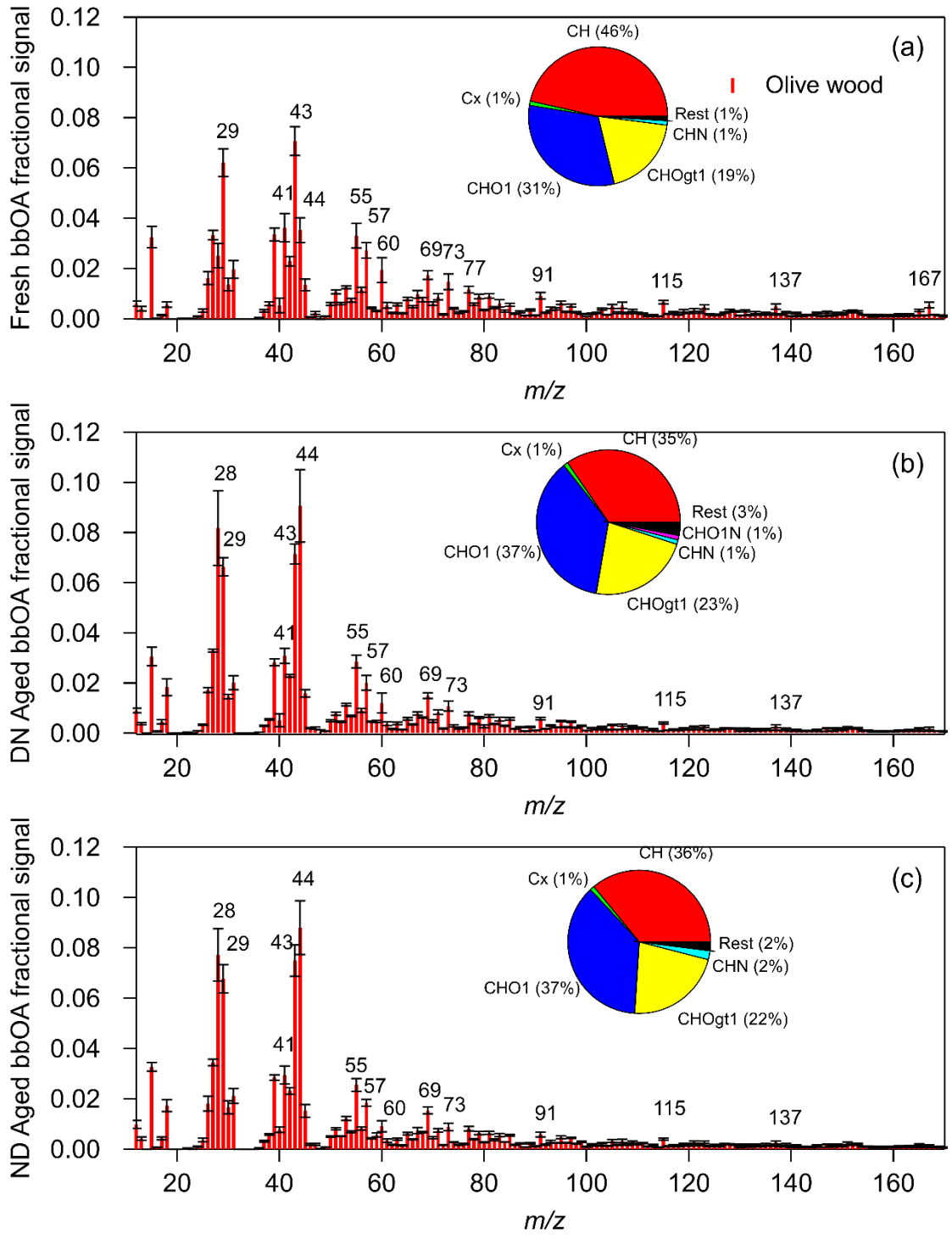

Figure S2: Average high-resolution normalized mass spectra of (a) fresh bbOA, (b) aged bbOA after DN oxidation, and (c) aged bbOA after ND oxidation, obtained from AMS, in case of olive logs burning (DN1-DN8, ND1-ND6). Error bars indicate the one standard deviation of each mass-to-charge (*m/z*) normalized signal across experiments. Embedded pie charts indicate the average contribution of the main aerosol components to the total fractional signal. All the other families are presented in black colour.

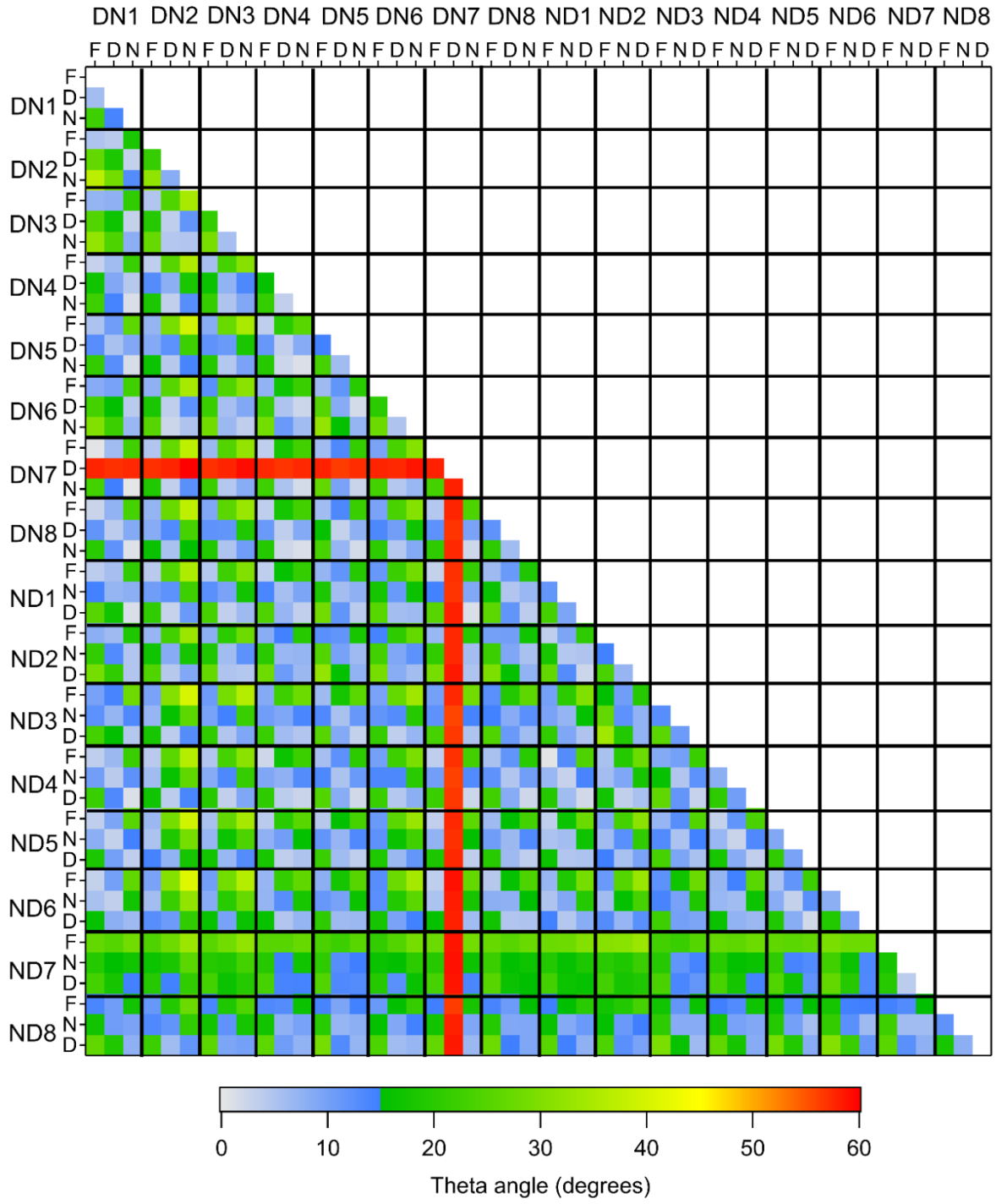

Figure S3: The theta angle (θº, degrees) of fresh and aged bbOA mass spectra obtained by AMS analysis between all possible pairs of conducted experiments.

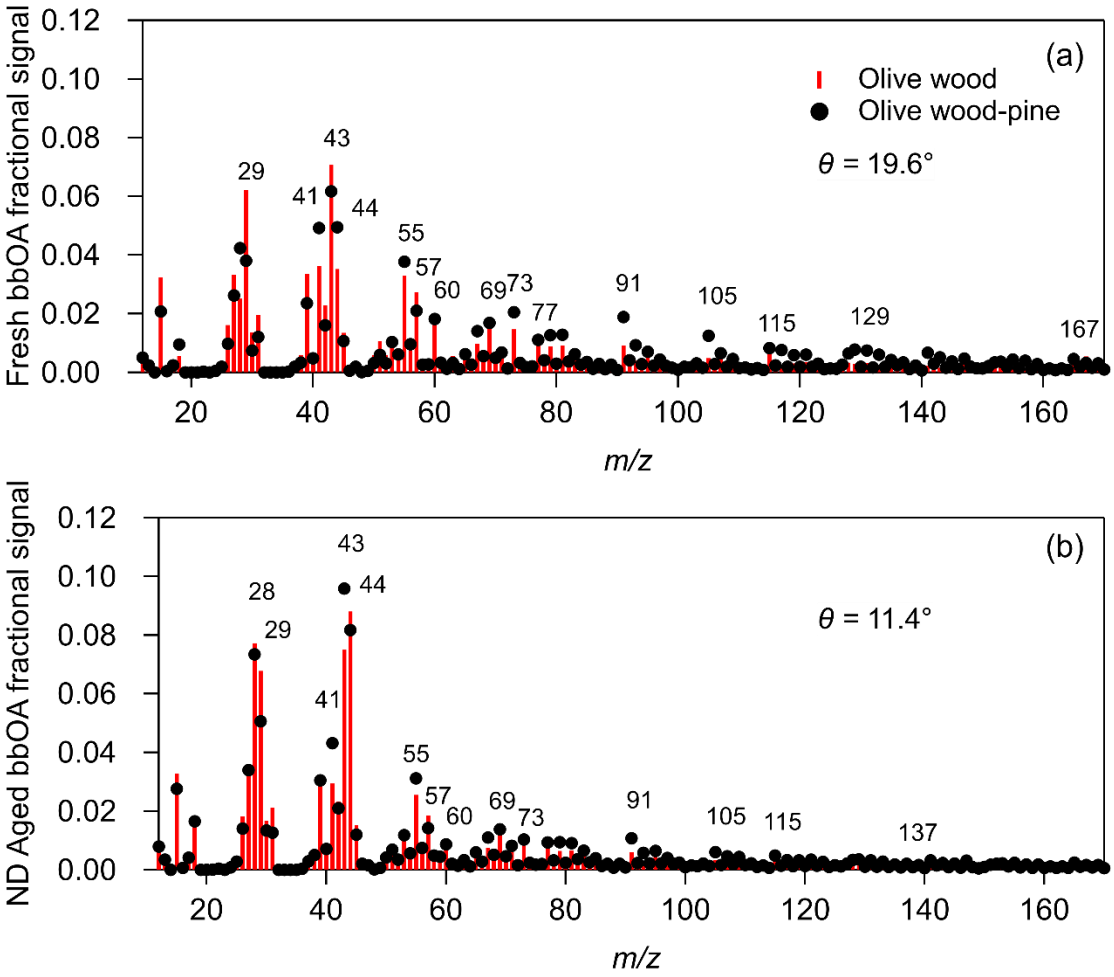

Figure S4: Average high-resolution normalized mass spectra of (a) fresh bbOA and (b) ND aged bbOA from olive logs burning (DN1-DN8, ND1-ND6) (red sticks) compared to the corresponding spectra (black circles) from the burning of olive logs mixed with pine kindling (ND7, ND8). The theta angle of the two average fresh spectra in graph (a) was 19.6°, while the theta angle of the two ND aged spectra in graph (b) was approximately 11°.

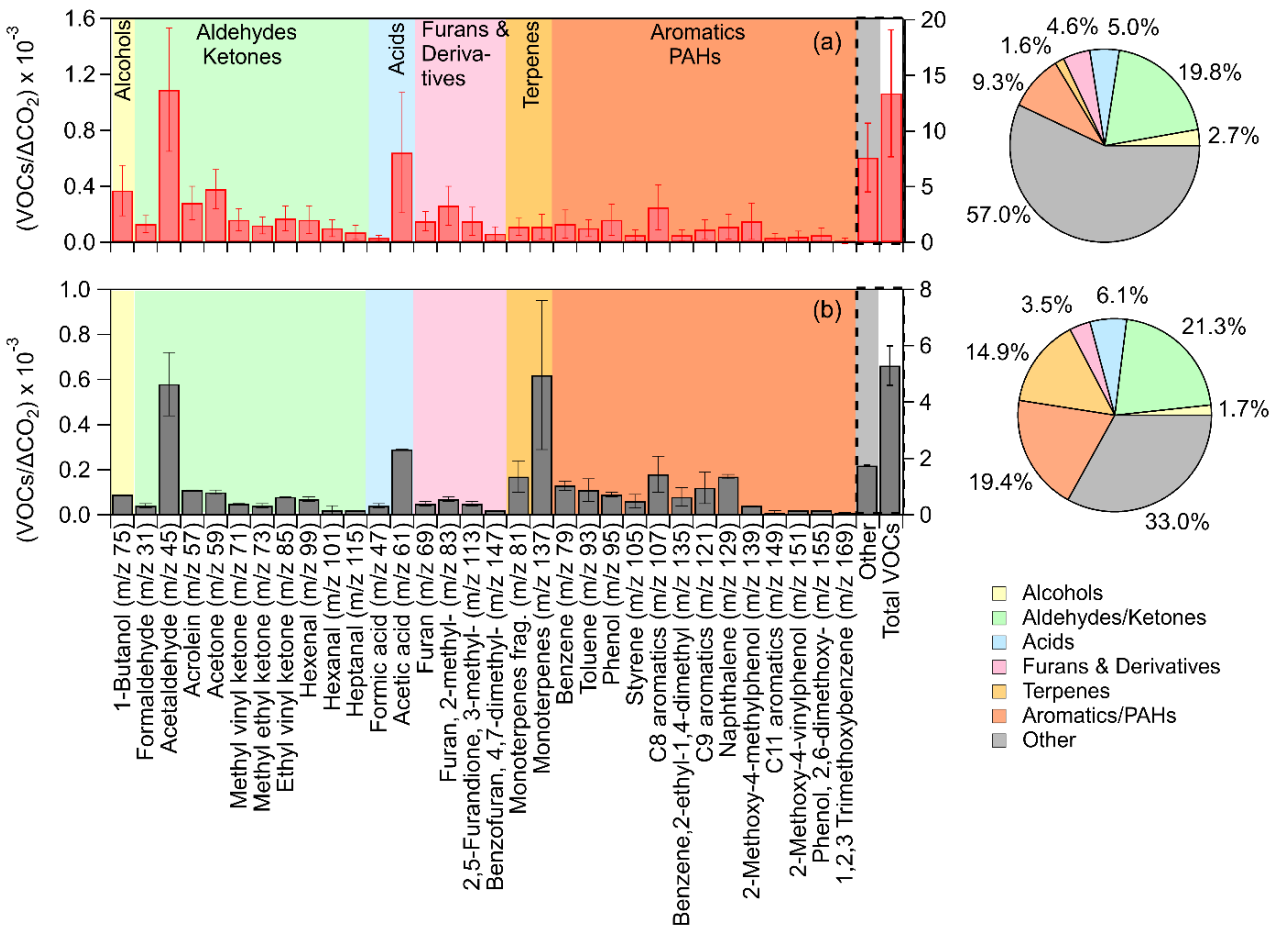

Figure S5: ΔCO_2-normalized average concentrations of the identified VOCs in (a) fresh olive wood burning emissions (red bars) and (b) fresh olive-pine mixed emissions (grey bars), along with their percentage contribution to the total VOCs concentration measured by PTR-QMS. The protonated *m/z* for each compound is shown in parentheses on the x-axis. The left y-axis shows the ΔCO_2-normalized concentrations of identified VOCs, while the right y-axis displays the concentrations of the sum of the unidentified VOCs (other) and the total measured VOCs.

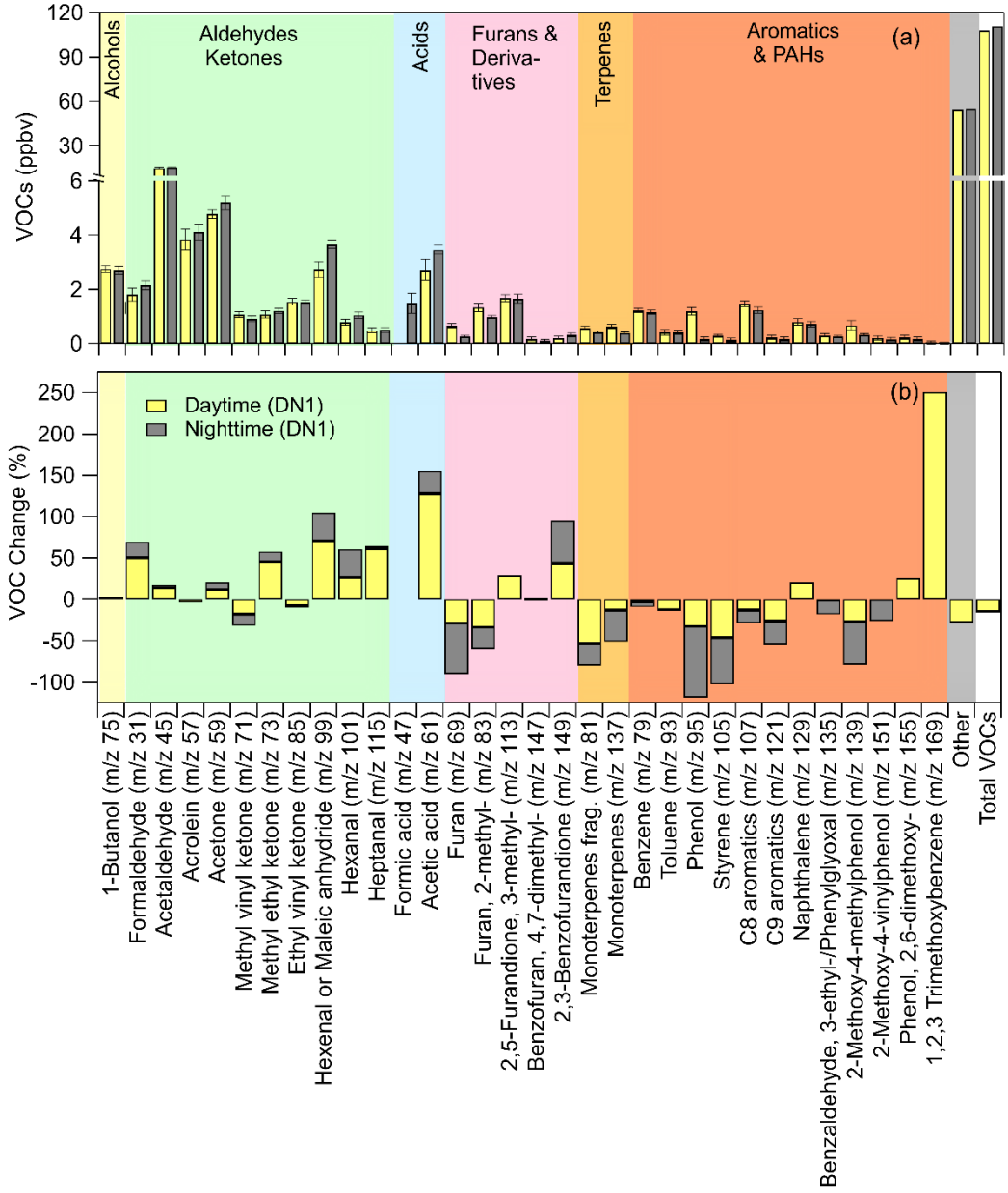

Figure S6: (a) Absolute (in ppm) and (b) percentage (%) changes in identified VOC concentrations during each oxidation phase in the typical DN1 experiment. Daytime percentage changes (yellow bars) were calculated based on the difference in concentration relative to the average value measured in the fresh emissions, while nighttime percentage changes (grey stacked bars) were determined relative to the daytime values. The protonated *m/z* for each compound is shown in parentheses on the x-axis.

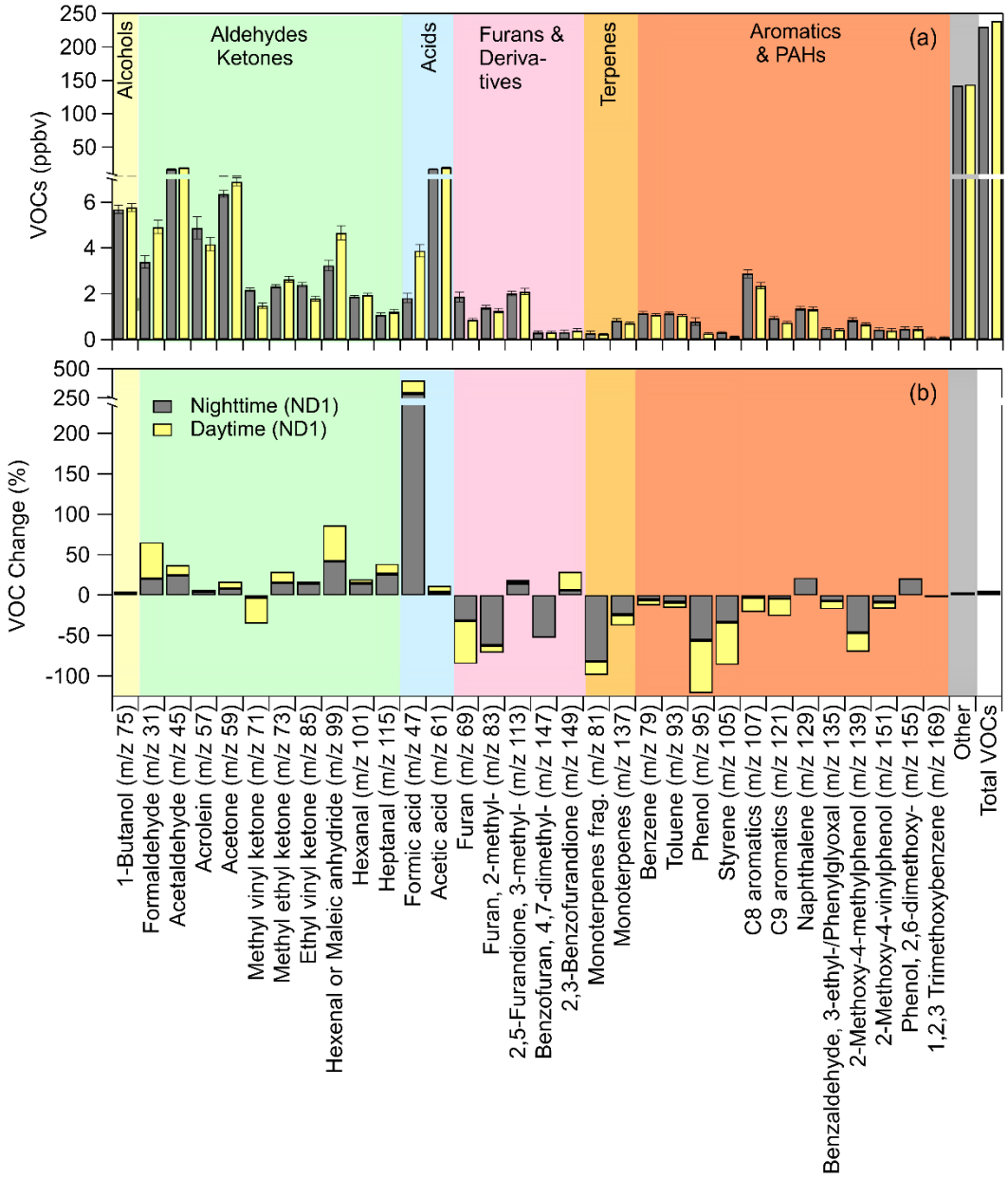

Figure S7: (a) Absolute (in ppm) and (b) percentage (%) changes in identified VOC concentrations during each oxidation phase in the typical ND1 experiment. Nighttime percentage changes (grey bars) were calculated based on the difference in concentration relative to the average value measured in the fresh emissions, while daytime percentage changes (yellow stacked bars) were determined relative to the daytime values. The protonated *m/z* for each compound is shown in parentheses on the x-axis.

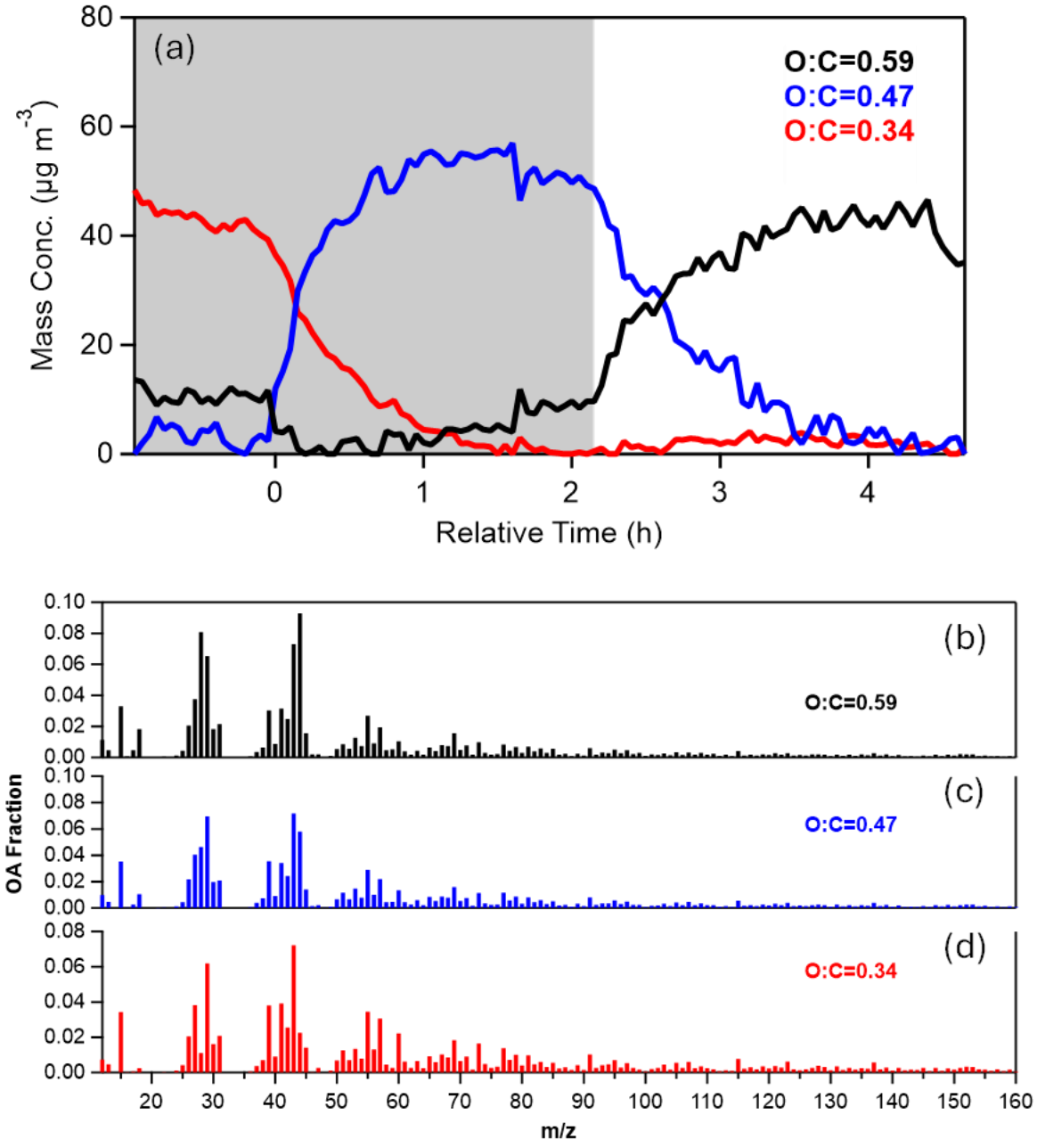

Figure S8: Positive matrix factorization (PMF) 3-factor solution for a typical night-to-day oxidation experiment (ND4), showing: (a) the temporal evolution of OA mass concentration and the changing relative contributions of fresh (red line), less-oxidized (blue line), and a more-oxidized factors (black line); and the high-resolution normalized mass spectra of (b) fresh, (c) less-oxidized (LO-OOA), and (d) more-oxidized OA (MO-OOA). Identical results were obtained using Multilinear Engine analysis (ME-2) for the 3-factor solution.

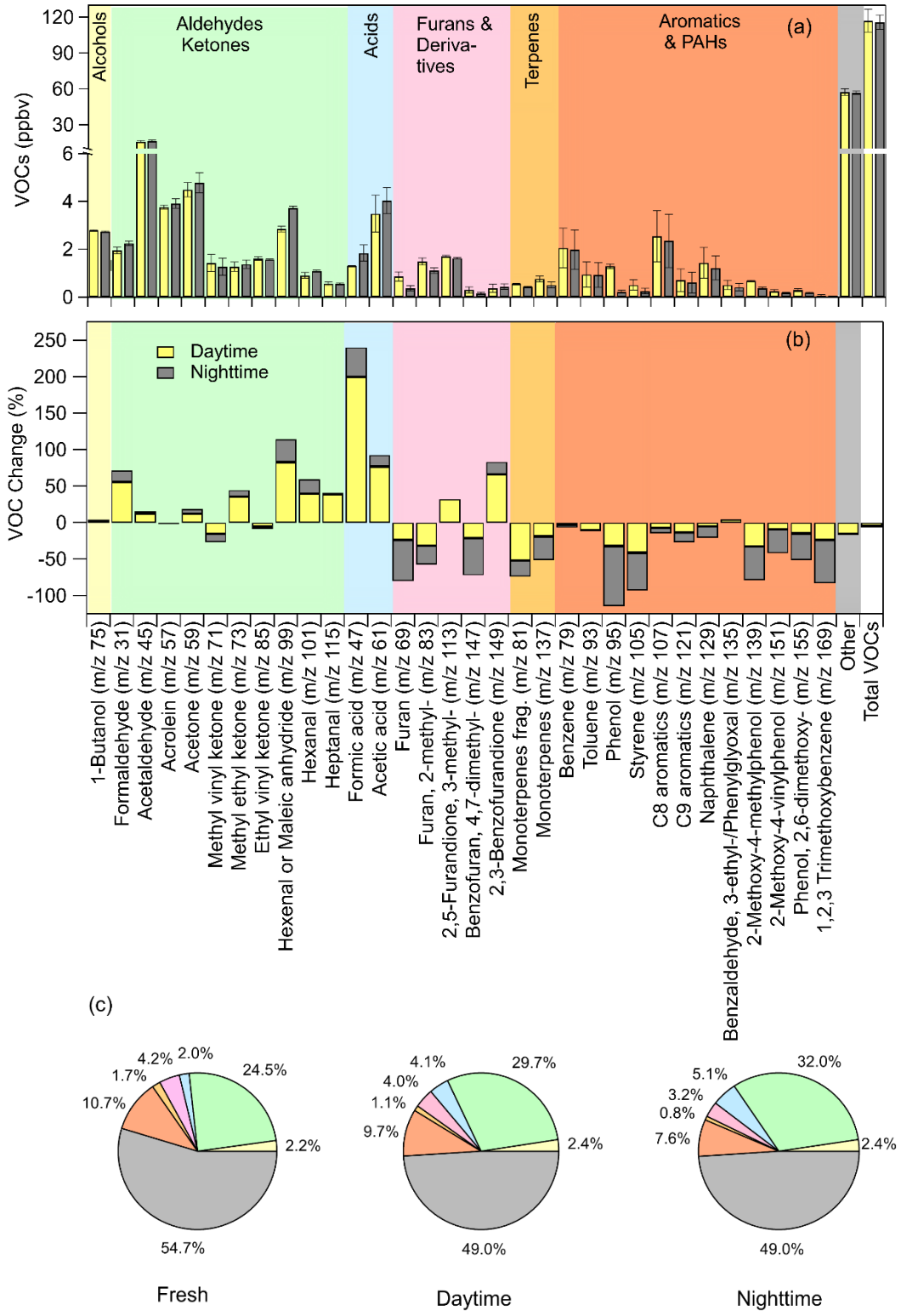

Figure S9: (a) Absolute (in ppm) and (b) percentage (%) changes in identified VOC concentrations after one day-to-night oxidation cycle, considering all DN experiments, along with (c) the average composition of fresh and aged emissions composition. The protonated *m/z* for each compound is shown in parentheses on the x-axis.

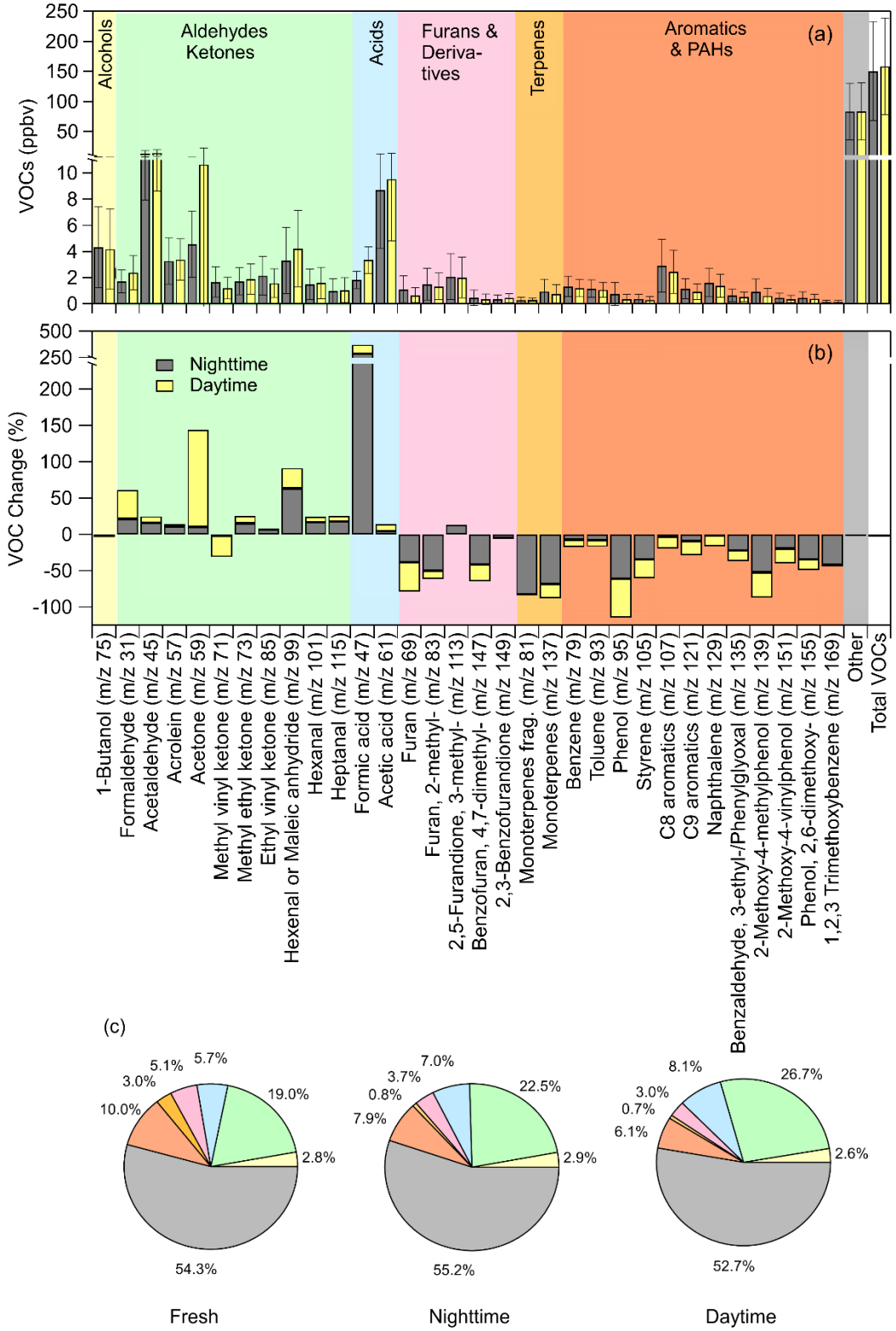

Figure S10: (a) Absolute (in ppm) and (b) percentage (%) changes in identified VOC concentrations after one night-to-day oxidation cycle, considering all ND experiments, along with (c) the average composition of fresh and aged emissions composition. The protonated *m/z* for each compound is shown in parentheses on the x-axis.

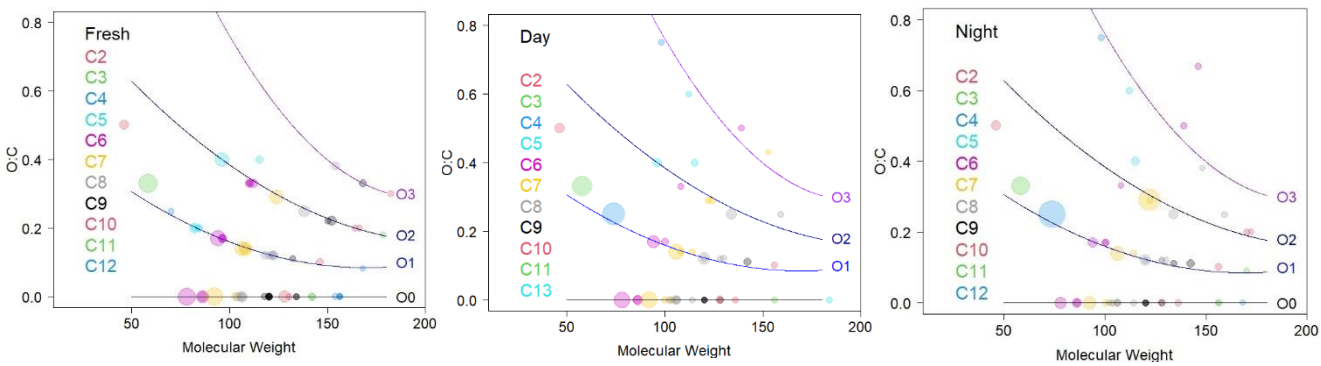

Figure S11: Average VOCs/IVOCs per experiment phase as detected by the Tenax tubes in terms of the molecule oxygenation and the molecular weight (experiment DN4). Color indicates the carbon number, while the depicted lines the oxygen number. The size is proportional to the concentration on a logarithmic scale.

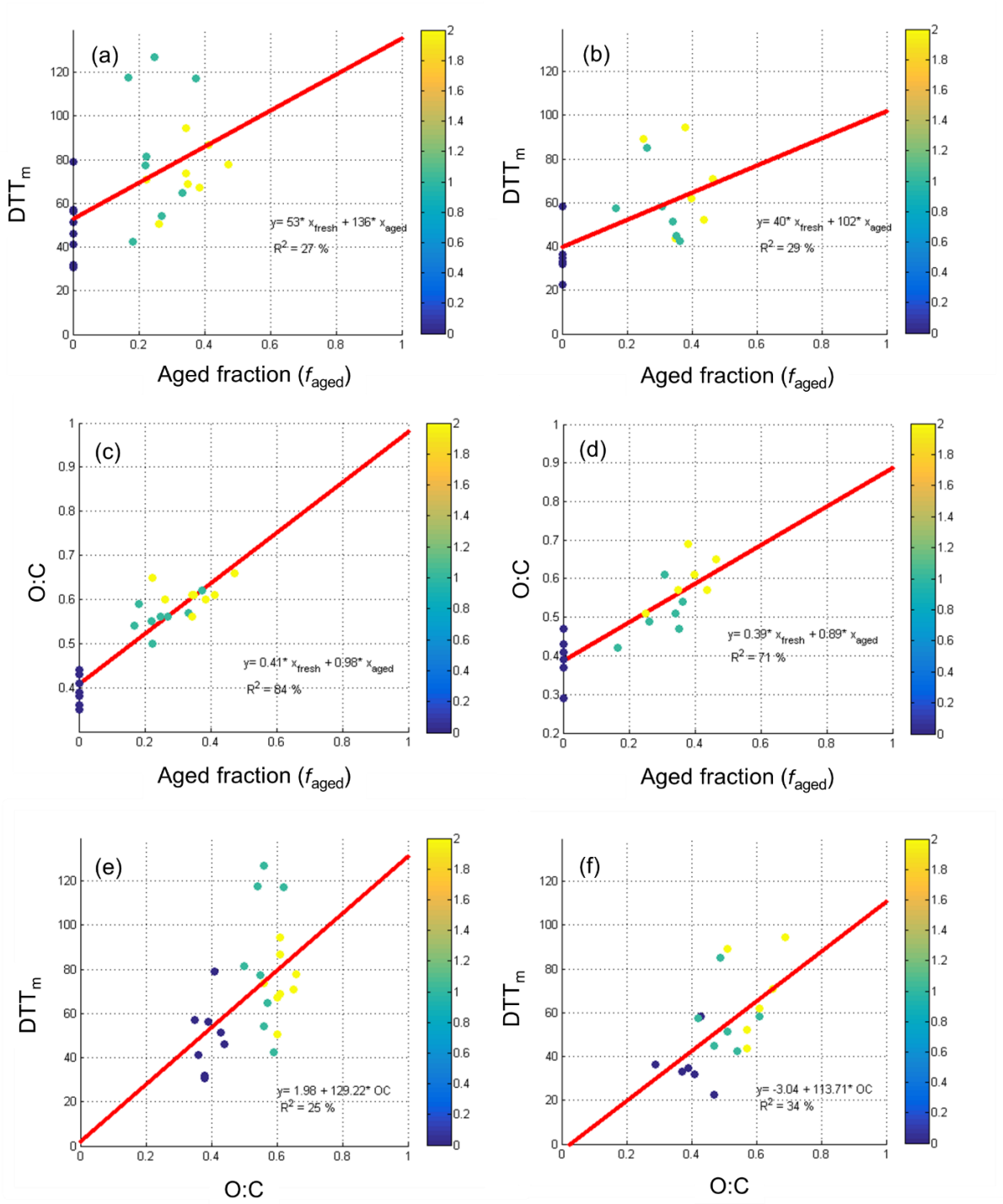

Figure S12: (a, b) Correlation between WS-OP, expressed as DTT_m activity (pmol min^{-1} μg^{-1}), and the aged fraction of OA for DN (a) and ND (b) oxidation cycles. (c, d) Correlation between the O:C ratio and the aged fraction of OA for DN (c) and ND (d) oxidation cycles. (e, f) Correlation between WS-OP and the O:C ratio for DN (e) and ND (f) oxidation cycles. Color bars on the right of each diagram indicate oxidation stages, where 0, 1, and 2 correspond to fresh aerosol, first-stage oxidation, and second-stage oxidation, respectively. For fresh OA, the aged fraction is zero.

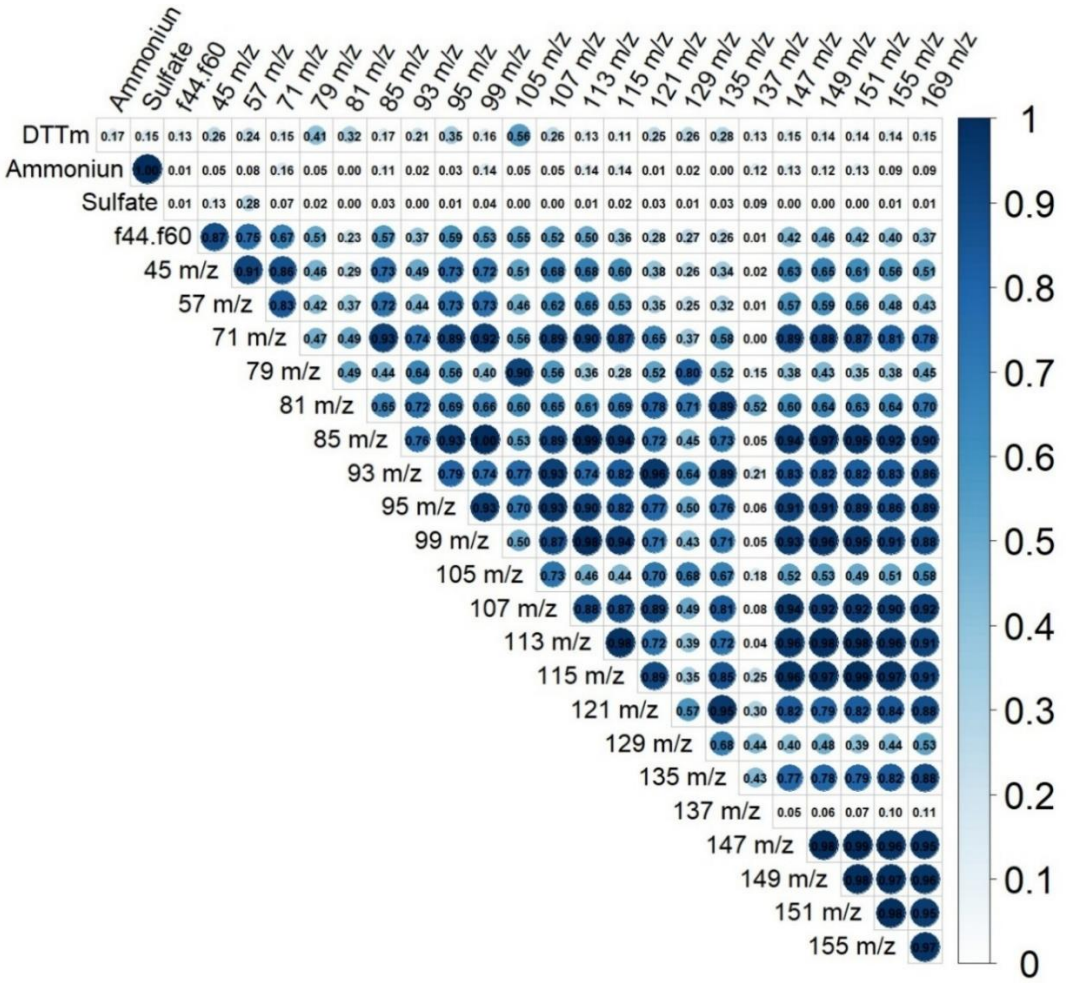

Figure S13: Correlation (R^2) of fresh WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) with selected aerosol components (Table 1) and VOC species (Table S1) from fresh emissions. Only correlations with $R^2 > 0.1$ are shown.

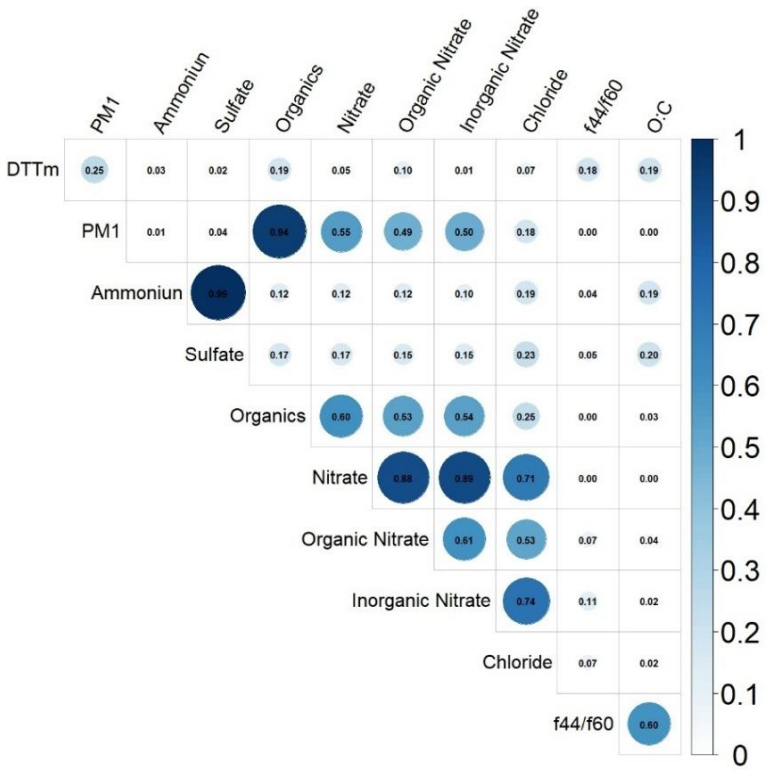

Figure S14: Correlation (R^2) between daytime WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) and aerosol components (Table 2) of aged emissions after first-stage oxidation in the DN cycle.

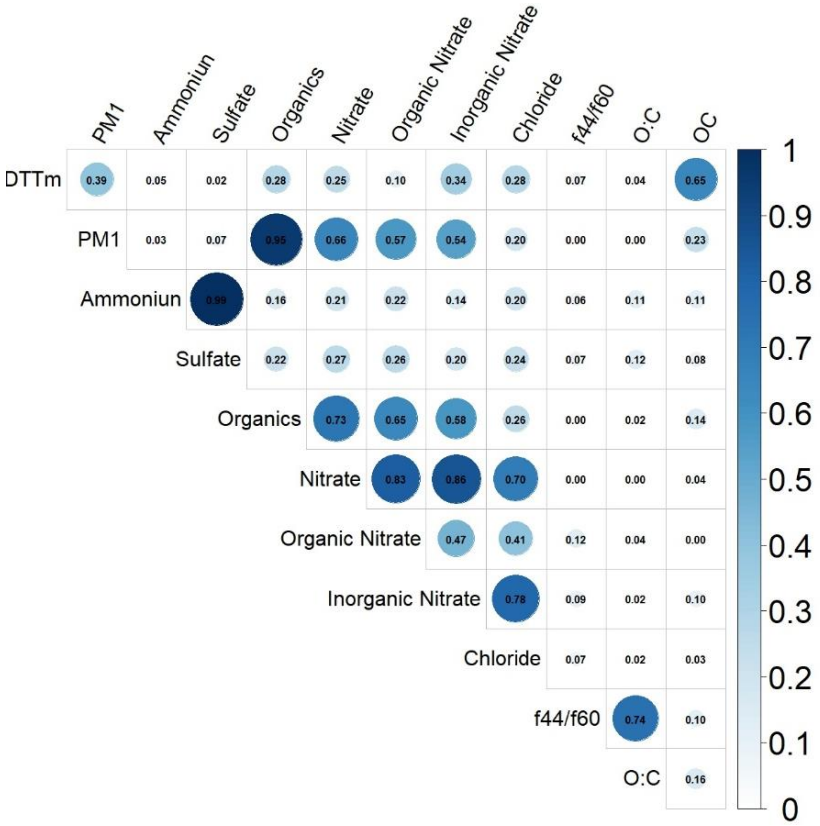

Figure S15: Correlation (R^2) between nighttime WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) and aerosol components (Table 2) of aged emissions after second-stage oxidation in the DN cycle.

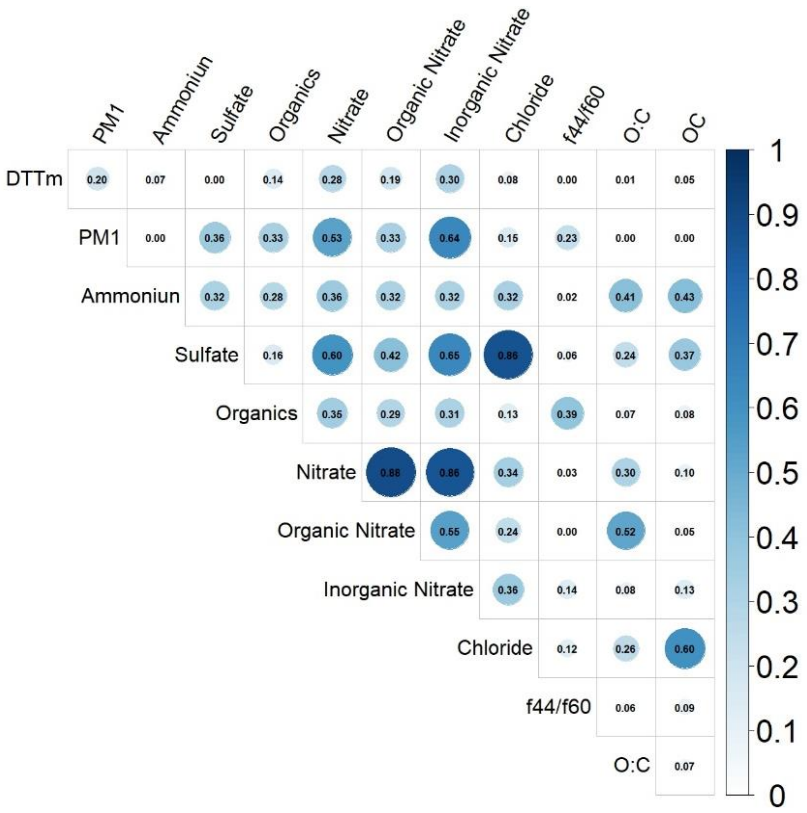

Figure S16: Correlation (R^2) between nighttime WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) and aerosol components (Table 2) of aged emissions after first-stage oxidation in the ND cycle.

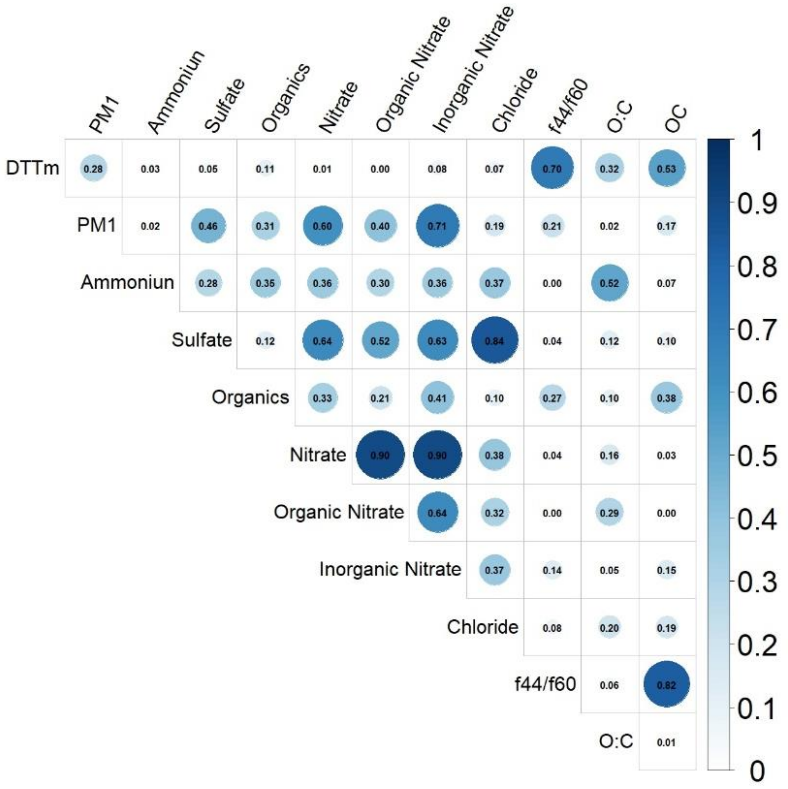

Figure S17: Correlation (R^2) between daytime WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) and aerosol components (Table 2) of aged emissions after second-stage oxidation in the ND cycle.

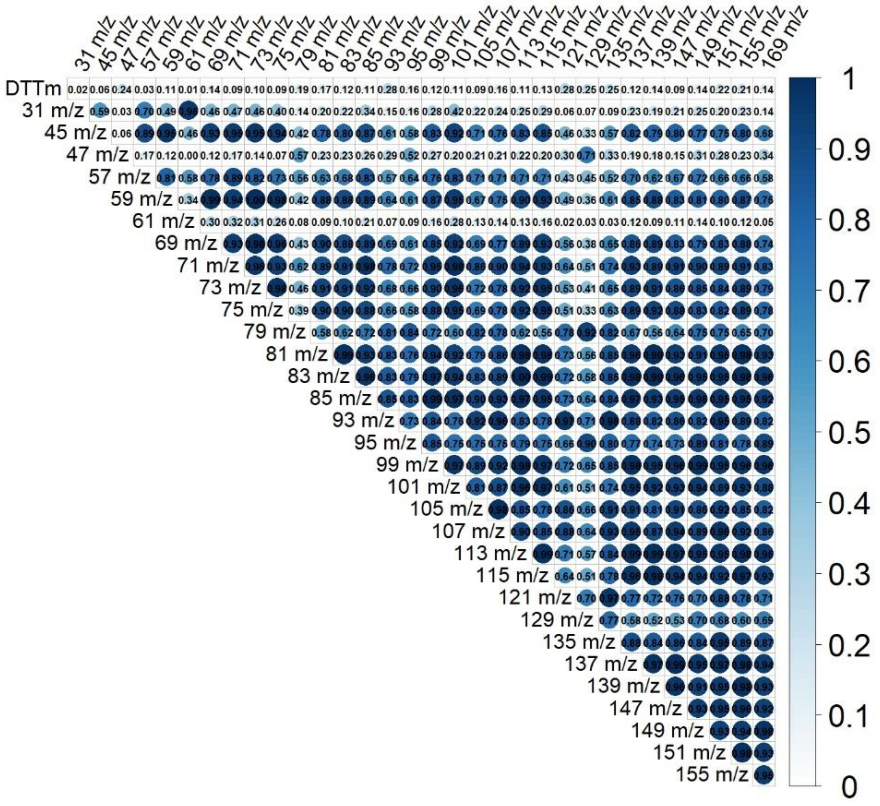

Figure S18: Correlation (R^2) between nighttime WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) and VOC species (Table S1) identified in aged emissions after first-stage oxidation in the ND cycle.

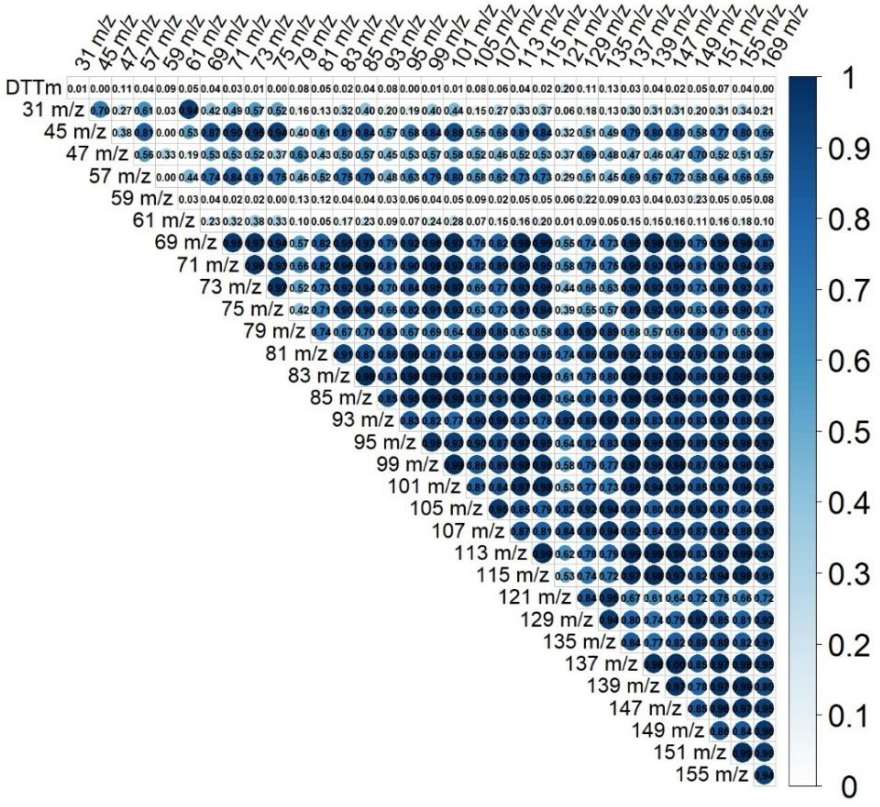

Figure S19: Correlation (R^2) between daytime WS-OP (DTT_m activity, pmol min^{-1} μg^{-1}) and VOC species (Table S1) identified in aged emissions after first-stage oxidation in the ND cycle.

Table S1: Average concentrations (ppb) of both identified and unspecified VOCs measured with PTR-QMS in fresh emissions and aged emissions across all experiments. Oxidation 1 and oxidation 2 refer to the first and second oxidative regime in each diurnal aging cycle. Due to measurement uncertainty, certain protonated mass-to-charge ratios (i.e., *m/z* 21, 30, 32, 37, 181, 211, 225, 247) were excluded from Table S1.

***m/z* [H^+]**	**Identified VOC [ppb]**	**Classification**	**H-Formula**	**Regime/Oxidation stage**	**Olive wood burning emissions**								**Olive wood & pine**	
					DN1	DN8	ND1	ND2	ND3	ND4	ND5	ND6	ND7	ND8
31	Formaldehyde	Carbonyls/Aldehydes	$(CH_2O)H^+$	Fresh	1.20	1.30	2.82	1.05	0.88	1.52	1.14	2.52	0.26	1.04
				Oxidation 1	1.81	2.08	3.40	1.48	1.04	1.73	1.56	2.78	0.52	1.17
				Oxidation 2	2.15	2.35	4.92	1.71	1.56	2.38	2.66	3.87	0.79	1.14
42	1-Butan-d9-ol fragment	-	-	Fresh	6.31	7.14	2.81	3.00	5.29	4.08	4.95	4.69	4.24	4.37
				Oxidation 1	6.10	6.99	2.74	2.99	5.20	3.83	4.95	5.20	4.28	3.50
				Oxidation 2	5.83	6.58	2.71	2.74	5.08	3.52	4.76	4.65	3.86	2.66
45	Acetaldehyde	Carbonyls/Aldehydes	$(C_2H_4O)H^+$	Fresh	13.2	15.1	13.8	6.57	9.34	10.6	15.4	19.0	5.55	10.1
				Oxidation 1	15.1	16.9	17.2	8.39	10.7	11.5	18.6	22.3	6.66	9.56
				Oxidation 2	15.6	17.3	19.3	8.85	12.3	12.7	21.1	23.0	6.93	9.96
47	Formic acid Ethanol	Carboxylic Acids Alcohols	$(CH_2O_2)H^+$ $(C_2H_6O)H^+$	Fresh	BDL	0.44	0.47	0.63	0.15	0.23	0.63	0.68	0.32	0.67
				Oxidation 1	BDL	1.31	1.82	1.82	0.59	1.20	2.19	2.26	1.69	2.96
				Oxidation 2	1.50	2.18	3.89	2.98	1.42	3.06	4.17	4.60	2.41	4.30
57	Acrolein	Carbonyls/Aldehydes	$(C_3H_4O)H^+$	Fresh	4.00	3.70	4.66	1.53	1.47	2.42	4.00	6.03	0.87	2.67
				Oxidation 1	3.85	3.69	4.88	1.69	1.51	3.21	4.17	6.69	1.08	2.96
				Oxidation 2	4.12	3.72	4.17	2.33	1.65	4.17	4.82	6.12	1.32	2.51
59	Acetone	Carbonyls/Ketones	$(C_3H_6O)H^+$	Fresh	4.26	3.74	5.87	2.57	2.48	3.29	7.69	7.87	0.68	2.64
				Oxidation 1	4.79	4.19	6.37	2.68	2.82	3.41	8.34	8.36	1.51	3.05
				Oxidation 2	5.20	4.37	6.89	2.64	3.08	3.90	17.8	8.74	1.90	40.3
61	Acetic acid	Carboxylic Acids	$(C_2H_4O_2)H^+$	Fresh	1.20	2.75	17.1	6.18	6.46	8.97	5.31	13.7	2.23	6.73
				Oxidation 1	2.72	4.26	17.7	7.14	6.93	9.07	6.08	13.7	2.69	6.34
				Oxidation 2	3.48	4.59	19.2	7.48	8.02	9.56	7.88	14.6	3.32	6.22
66	1-Butan-d9-ol (d_9-butanol)	Alcohols	$(C_4D_9OH)H^+$	Fresh	79.9	90.5	26.6	34.4	65.9	45.5	58.0	63.9	54.8	53.8
				Oxidation 1	75.5	87.2	26.6	34.5	66.1	43.4	57.1	61.2	54.5	45.0
				Oxidation 2	71.2	83.6	24.7	30.8	62.7	38.0	53.6	53.7	49.3	32.2
69	Furan Isoprene	Furans Alkadienes	$(C_4H_4O)H^+$ $(C_5H_8)H^+$	Fresh	0.94	1.31	2.72	0.84	0.94	1.31	3.18	3.67	0.32	1.23
				Oxidation 1	0.67	1.05	1.87	0.18	0.29	0.60	2.70	2.59	0.12	0.45
				Oxidation 2	0.26	0.49	0.87	0.14	0.20	0.32	1.64	1.49	0.13	0.41

71	MVK & MACR	Carbonyls/Ketones and Aldehydes	$(C_4H_6O)H^+$	Fresh	1.29	2.09	2.26	0.80	0.70	1.24	3.02	4.00	0.41	1.25
				Oxidation 1	1.07	1.79	2.19	0.76	0.69	1.20	2.99	3.92	0.52	1.16
				Oxidation 2	0.92	1.63	1.49	0.46	0.55	0.84	2.28	2.74	0.42	0.75
73	Methyl ethyl ketone (MEK; 2-Butanone)	Carbonyls/Ketones	$(C_4H_8O)H^+$	Fresh	0.74	1.13	2.01	0.77	0.82	1.17	2.79	2.96	0.25	1.14
				Oxidation 1	1.08	1.46	2.33	0.90	0.96	1.29	3.25	3.32	0.51	1.20
				Oxidation 2	1.21	1.55	2.64	0.97	1.07	1.34	3.64	3.65	0.54	1.28
75	1-Butanol	Alcohols	$(C_4H_{10}O)H^+$	Fresh	2.74	2.71	5.53	2.14	2.86	2.85	9.03	9.51	0.69	2.15
				Oxidation 1	2.76	2.81	5.70	2.26	2.86	2.77	9.16	9.27	0.70	1.93
				Oxidation 2	2.72	2.76	5.77	2.11	2.88	2.64	9.22	8.70	0.67	1.54
79	Benzene	Hydrocarbons, Aromatic	$(C_6H_6)H^+$	Fresh	1.27	2.99	1.24	0.84	0.42	0.64	1.66	3.13	1.16	2.33
				Oxidation 1	1.23	2.89	1.17	0.81	0.40	0.60	1.62	2.96	1.14	1.91
				Oxidation 2	1.16	2.81	1.09	0.76	0.41	0.57	1.51	2.63	1.06	1.49
81	Monoterpenes & Hexenal fragment	Hydrocarbons/Terpenes/ Monoterpenes	$(C_6H_8)H^+$	Fresh	1.22	1.10	1.57	0.61	0.44	0.74	2.18	3.19	1.85	2.26
				Oxidation 1	0.58	0.55	0.29	0.10	0.10	0.12	0.68	0.63	0.12	0.22
				Oxidation 2	0.42	0.45	0.24	0.18	0.25	0.20	0.47	0.52	0.22	0.31
83	Furan, 2-methyl-	Furans	$(C_5H_6O)H^+$	Fresh	2.01	2.35	3.69	1.29	1.61	1.78	6.65	6.83	0.42	1.77
				Oxidation 1	1.34	1.64	1.40	0.60	0.52	0.76	3.50	3.58	0.47	1.20
				Oxidation 2	0.99	1.24	1.27	0.59	0.63	0.77	2.92	3.17	0.39	0.94
85	Ethyl vinyl ketone	Carbonyls/Ketones	$(C_5H_8O)H^+$	Fresh	1.67	1.75	2.09	0.88	0.65	1.22	3.94	4.79	0.64	1.91
				Oxidation 1	1.55	1.68	2.40	0.95	0.78	1.33	3.98	5.02	0.83	1.88
				Oxidation 2	1.54	1.60	1.79	0.67	0.61	0.98	3.18	3.61	0.64	1.14
93	Toluene	Hydrocarbons, Aromatic	$(C_7H_8)H^+$	Fresh	0.48	1.63	1.25	0.62	0.59	0.48	2.07	2.72	1.22	1.25
				Oxidation 1	0.42	1.48	1.14	0.58	0.56	0.45	1.90	2.50	1.20	1.06
				Oxidation 2	0.42	1.45	1.06	0.55	0.56	0.43	1.78	2.17	1.09	0.91
95	Phenol	Hydrocarbons, Aromatic	$(C_6H_6O)H^+$	Fresh	1.77	2.04	1.77	0.68	0.56	0.97	3.30	5.68	0.78	1.77
				Oxidation 1	1.19	1.39	0.79	0.03	0.12	0.25	1.93	2.51	0.08	1.77
				Oxidation 2	0.17	0.30	0.27	BDL	0.09	0.12	0.99	1.00	0.06	0.32
99	Hexenal Maleic anhydride 2-Furanmethanol	Carbonyls/Aldehydes Anhydrides Furans	$(C_6H_{10}O)H^+$ $(C_4H_2O_3)H^+$ $(C_5H_6O_2)H^+$	Fresh	1.60	1.52	2.28	0.83	0.52	1.14	3.99	5.05	0.50	1.87
				Oxidation 1	2.74	2.97	3.24	1.61	1.23	1.66	6.61	8.19	0.87	3.00
				Oxidation 2	3.68	3.80	4.67	2.37	1.92	2.50	8.38	9.54	1.23	3.20
101	Hexanal	Carbonyls/Aldehydes	$(C_6H_{12}O)H^+$	Fresh	0.62	0.68	1.63	0.60	0.48	0.69	2.61	3.22	0.05	0.86
				Oxidation 1	0.79	1.03	1.87	0.79	0.56	0.80	3.00	3.65	0.12	1.05

				Oxidation 2	1.05	1.12	1.96	0.74	0.68	0.90	3.36	3.65	0.22	1.23
105	Styrene	Hydrocarbons, Aromatic	$(C_8H_8)H^+$	Fresh	0.54	1.18	0.47	0.20	0.13	0.25	0.74	1.50	0.65	0.71
				Oxidation 1	0.29	0.72	0.32	0.05	0.09	0.19	0.66	1.18	0.27	0.30
				Oxidation 2	0.13	0.36	0.15	0.05	0.06	0.10	0.58	0.85	0.16	0.30
107	C8 aromatics (xylenes)	Hydrocarbons, Aromatic	$(C_8H_{10})H^+$	Fresh	1.68	3.77	2.96	1.17	1.36	1.35	5.36	7.80	2.00	2.19
				Oxidation 1	1.47	3.60	2.88	1.19	1.37	1.34	4.94	7.32	2.18	2.24
				Oxidation 2	1.24	3.46	2.36	0.89	1.22	1.15	4.15	6.00	1.92	1.90
113	2,5-Furandione, 3-methyl-	Anhydrides	$(C_5H_4O_3)H^+$	Fresh	1.30	1.29	1.76	0.67	0.56	0.89	4.17	4.84	0.33	1.51
				Oxidation 1	1.68	1.75	2.02	0.81	0.70	1.04	4.83	5.20	0.53	1.55
				Oxidation 2	1.66	1.60	2.10	0.76	0.79	1.12	4.69	4.55	0.71	1.40
115	Heptanal	Carbonyls/Aldehydes	$(C_7H_{14}O)H^+$	Fresh	0.31	0.51	0.86	0.28	0.27	0.33	2.14	2.27	BDL	0.54
				Oxidation 1	0.50	0.65	1.09	0.37	0.28	0.37	2.52	2.53	0.01	0.64
				Oxidation 2	0.51	0.59	1.23	0.38	0.36	0.44	2.71	2.51	0.05	0.70
121	C9 aromatics (trimethylbenzene)	Hydrocarbons, Aromatic	$(C_9H_{12})H^+$	Fresh	0.32	1.32	0.99	0.40	0.43	0.36	2.22	3.12	1.52	1.11
				Oxidation 1	0.23	1.18	0.95	0.38	0.41	0.36	1.96	2.59	1.50	1.08
				Oxidation 2	0.17	1.06	0.74	0.28	0.36	0.30	1.48	2.02	1.29	0.96
129	Naphthalene	Hydrocarbons, Aromatic/Naphthalenes	$(C_{10}H_8)H^+$	Fresh	0.66	2.38	1.11	0.53	0.31	0.46	2.15	3.52	1.37	3.65
				Oxidation 1	0.80	2.08	1.36	0.66	0.36	0.55	2.37	3.37	1.30	2.97
	Octanal	Carbonyls/Aldehydes	$(C_8H_{16}O)H^+$	Oxidation 2	0.72	1.71	1.34	0.54	0.41	0.52	2.27	3.01	1.03	1.85
135	Benzene, 1-methyl-2-(1-methylethyl)-;	Hydrocarbons, Aromatic	$(C_9H_{14})H^+$	Fresh	0.32	0.67	0.53	0.19	0.24	0.19	1.44	1.96	0.96	1.00
				Oxidation 1	0.31	0.71	0.49	0.16	0.22	0.17	1.21	1.52	0.63	0.66
	Benzene, 2 ethyl-1,4-dimethyl-	Hydrocarbons, Aromatic	$(C_9H_{10}O)H^+$	Oxidation 2	0.26	0.57	0.44	0.13	0.21	0.16	0.97	1.29	0.55	0.58
	Benzaldehyde, 3-ethyl-Phenylglyoxal	Carbonyls/ Aldehydes	$(C_8H_6O_2)H^+$											
137	Monoterpenes	Hydrocarbons/ Terpenes/ Monoterpenes	$(C_{10}H_{16})H^+$	Fresh	0.73	1.14	1.10	0.36	0.38	0.41	3.42	4.23	7.35	6.75
				Oxidation 1	0.64	0.88	0.84	0.27	0.29	0.32	2.25	2.75	0.26	0.60
				Oxidation 2	0.40	0.63	0.72	0.22	0.30	0.29	1.85	2.00	0.25	0.46

139	Creosol/ Phenol, 2-methoxy-4-methyl-	Hydrocarbons, Aromatic	$(C_8H_{10}O_2)H^+$	Fresh	0.93	1.13	1.62	0.46	0.56	0.60	5.57	5.66	0.26	1.00
				Oxidation 1	0.68	0.71	0.87	0.20	0.29	0.29	2.61	2.51	0.21	0.55
				Oxidation 2	0.33	0.42	0.67	0.13	0.22	0.24	1.65	1.45	0.19	0.34
147	Benzofuran, 4,7-dimethyl-	Hydrocarbons, Aromatic	$(C_{10}H_{10}O)H^+$	Fresh	0.18	0.59	0.68	0.21	0.26	0.23	1.80	2.48	0.15	0.44
				Oxidation 1	0.18	0.43	0.32	0.05	0.10	0.11	1.25	1.61	0.04	0.18
				Oxidation 2	0.10	0.20	0.32	0.06	0.09	0.10	0.96	1.08	0.02	0.17
149	C11 aromatics 2,3-Benzofurandione	Hydrocarbons, Aromatic	$(C_{11}H_{16})H^+$ $(C_8H_4O_3)H^+$	Fresh	0.15	0.31	0.32	0.11	0.12	0.10	0.92	1.16	0.03	0.35
				Oxidation 1	0.21	0.54	0.34	0.20	0.15	0.13	0.75	0.95	0.06	0.40
				Oxidation 2	0.32	0.56	0.41	0.20	0.15	0.16	0.82	1.07	0.19	0.62
151	2-Methoxy-4-vinylphenol	Hydrocarbons, Aromatic	$(C_9H_{10}O_2)H^+$	Fresh	0.21	0.36	0.49	0.12	0.14	0.15	1.39	1.68	0.16	0.34
				Oxidation 1	0.21	0.31	0.45	0.13	0.13	0.12	0.96	1.14	0.29	0.38
				Oxidation 2	0.16	0.20	0.41	0.08	0.13	0.13	0.80	0.83	0.22	0.27
155	Phenol, 2,6-dimethoxy- Naphthalene, 2-ethenyl-	Hydrocarbons, Aromatic Naphthalenes	$(C_8H_{10}O_3)H^+$ $(C_{12}H_{10})H^+$	Fresh	0.19	0.51	0.39	0.09	0.16	0.08	1.93	2.14	0.20	0.51
				Oxidation 1	0.24	0.36	0.48	0.09	0.12	0.02	1.17	1.27	0.13	0.32
				Oxidation 2	0.17	0.21	0.46	0.09	0.14	0.11	0.95	0.92	0.15	0.27
169	Dibenzofuran 1,2,3 Trimethoxybenzene	Furans Hydrocarbons, Aromatic	$(C_{12}H_8O)H^+$ $(C_9H_{12}O_3)H^+$	Fresh	0.01	0.17	0.08	BDL	0.02	0.03	0.54	0.76	0.07	0.21
				Oxidation 1	0.03	0.11	0.08	BDL	0.03	0.01	0.34	0.38	0.00	0.15
				Oxidation 2	0.01	0.04	0.10	BDL	0.03	0.01	0.27	0.33	0.03	0.12
Other measured/unspecified species														
33	Various species including methanol			Fresh	59.4	37.1	99.8	32.1	52.2	49.5	93.6	109.5	1.99	18.8
				Oxidation 1	37.8	37.4	100.6	32.3	51.3	47.0	91.9	105.4	1.97	18.9
				Oxidation 2	37.8	36.0	101.0	31.3	50.8	45.5	102.0	98.3	3.33	18.2
41	Various fragments			Fresh	2.95	6.08	4.87	2.41	3.94	3.75	5.63	6.50	3.27	3.74
				Oxidation 1	2.56	5.51	4.43	2.21	3.79	3.76	5.32	6.42	3.12	3.24
				Oxidation 2	2.33	5.20	3.40	2.17	3.63	3.84	4.91	5.37	2.95	2.70
43	Various species			Fresh	9.22	12.6	30.3	12.3	15.4	18.3	16.3	27.5	7.26	14.5
				Oxidation 1	10.5	13.5	31.9	13.6	16.0	18.9	18.3	29.3	8.10	13.5
				Oxidation 2	10.9	13.5	34.4	13.8	17.1	19.0	20.8	30.3	8.55	12.4
63	Various species			Fresh	0.11	0.18	0.16	0.08	0.13	0.09	0.16	0.18	0.12	0.13
				Oxidation 1	0.20	0.28	0.15	0.12	0.14	0.11	0.18	0.24	0.14	0.16
				Oxidation 2	0.22	0.31	0.22	0.14	0.20	0.17	0.26	0.31	0.16	0.18
87	Various species			Fresh	2.41	2.15	3.79	1.41	1.34	1.92	5.92	6.43	0.46	2.09

		Oxidation 1	2.37	2.12	4.07	1.51	1.45	2.01	6.40	6.81	0.60	1.95
		Oxidation 2	2.33	1.96	3.87	1.36	1.48	1.85	6.06	5.96	0.61	1.58
88	Various species	Fresh	0.14	0.11	0.20	0.05	0.05	0.12	0.27	0.38	BDL	0.10
		Oxidation 1	0.14	0.12	0.22	0.06	0.08	0.11	0.38	0.36	0.03	0.12
		Oxidation 2	0.14	0.11	0.23	0.07	0.08	0.11	0.33	0.28	0.02	0.08
91	Various species	Fresh	0.77	BDL	BDL	0.06	BDL	BDL	BDL	BDL	BDL	BDL
		Oxidation 1	0.48	BDL	BDL	0.03	BDL	BDL	BDL	BDL	BDL	BDL
		Oxidation 2	0.75	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
103	Various species	Fresh	0.33	0.68	0.50	0.19	0.12	0.14	1.22	1.68	0.41	0.72
		Oxidation 1	0.41	0.65	0.65	0.19	0.10	0.16	1.35	1.86	0.53	0.63
		Oxidation 2	0.51	0.56	0.77	0.20	0.17	0.26	1.38	1.82	0.46	0.55
163	Various species	Fresh	0.05	0.15	0.11	0.07	0.04	0.01	0.50	0.64	0.04	0.15
		Oxidation 1	0.06	0.20	0.09	0.03	0.06	0.02	0.33	0.45	0.03	0.10
		Oxidation 2	0.06	0.11	0.11	0.03	0.05	0.03	0.32	0.44	0.05	0.12
Total VOCs (excluding *m/z* 42 and *m/z* 66 related to 1-Butan-d9-ol)		Fresh	123.1	122.8	225.8	82.9	109.5	120.5	235.9	300.4	46.7	104.1
		Oxidation 1	105.6	127.0	230.4	87.4	110.1	119.0	234.3	289.4	42.7	92.0
		Oxidation 2	107.8	123.0	237.0	88.5	115.9	123.1	258.0	274.4	46.2	123.7
$\Delta CO_2 \times 1000$ (ppb) *			14.7	8.7	14.5	36.4	8.0	7.2	15.5	14.2	7.7	22.9

*ΔCO_2= CO_2 (after emissions injection) - CO_2 (before emissions injection).

Table S2: Prominent species detected by TD-GCMS for a typical experiment (DN4).

MW	Name	Neutral Formula	Fresh	Frac. %	Day	Night
94	Phenol	C_6H_6O	0.84		0.45	0.35
108	Phenol, 2-methyl-	C_7H_8O	0.61		-	-
108	Phenol, 4 methyl-	C_7H_8O	0.33		0.03	-
122	Phenol, 2,5-dimethyl-	$C_8H_{10}O$	0.26		-	-
122	Phenol, 2,3-dimethyl-	$C_8H_{10}O$	0.15		-	-
122	Phenol, 2-ethyl-	$C_8H_{10}O$	0.02		-	-
124	Phenol, 2-methoxy-	$C_7H_8O_2$	0.71	33%	0.10	-
138	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	0.37		-	-
150	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	0.04		-	-
152	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	0.21		-	-
154	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	0.15		-	-
164	3-Allyl-6-methoxyphenol	$C_{10}H_{12}O_2$	0.02		-	-
166	Phenol, 2-methoxy-4-propyl-	$C_{10}H_{14}O_2$	0.04		-	-
139	Phenol, 2-nitro-	$C_6H_5NO_3$	-	-	0.04	0.06
153	Phenol, 4-methyl-2-nitro-	$C_7H_7NO_3$	-	-	0.01	-
120	Acetophenone	C_8H_8O	-	-	0.40	0.51
134	Phenylglyoxal	$C_8H_6O_2$	-	-	0.28	0.36
128	Naphthalene	$C_{10}H_8$	0.4		0.11	0.10
142	Naphthalene, 2-methyl-	$C_{11}H_{10}$	0.1		-	-
142	Naphthalene, 1-methyl-	$C_{11}H_{10}$	0.09		-	-
154	Naphthalene, 2-ethenyl-	$C_{12}H_{10}$	0.05	6%	-	-
156	Naphthalene, 2,6-dimethyl-	$C_{12}H_{12}$	0.05		-	-
156	Naphthalene, 1,7-dimethyl-	$C_{12}H_{12}$	0.02		-	-
156	Naphthalene, 1,3-dimethyl-	$C_{12}H_{12}$	0.01		-	-
156	Naphthalene, 2,3-dimethyl-	$C_{12}H_{12}$	0.01		-	-
118	Benzofuran	C_8H_6O	0.12		-	-
146	Benzofuran, 4,7-dimethyl-	$C_{10}H_{10}O$	0.09	2%	-	-
168	Dibenzofuran	$C_{12}H_8O$	0.005		0.02	-
148	2,3-Benzofurandione	$C_8H_4O_3$	-	-	0.01	0.01
82	Furan, 2-methyl-	C_5H_6O	0.24		-	-
96	Furfural	$C_5H_4O_2$	0.62		0.15	-
96	Furan, 2,5-dimethyl-	C_6H_8O	0.17		-	-
98	2-Furanmethanol	$C_5H_6O_2$	*	11%		
110	2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	0.16		-	-
110	Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	0.05		-	-
110	Furan, 2-ethyl-5-methyl-	$C_6H_6O_2$	0.03		-	-
110	Furan, 2,3,5-trimethyl-	$C_7H_{10}O$	0.01		-	-
98	Maleic anhydride	$C_4H_2O_3$	-	-	0.03	0.05
112	2,5-Furandione, 3-methyl-	$C_5H_4O_3$	-	-	0.03	0.03
78	Benzene	C_6H_6	1.18		0.82	0.59
92	Toluene	C_7H_8	1.21		0.93	0.77
103	Benzonitrile	C_7H_5N	0.15	34%	0.09	0.06
104	Styrene	C_8H_8	0.19		0.02	0.04
106	p-Xylene	C_8H_{10}	0.36		0.16	0.14

106	Ethylbenzene	C_8H_{10}	0.16		0.13	0.13
106	o-Xylene	C_8H_{10}	0.11		0.09	0.07
118	.alpha.-Methylstyrene	C_9H_{10}	0.07		-	-
120	Benzene, 1,2,3-trimethyl-	C_9H_{12}	0.08		-	-
120	Benzene, (1-methylethyl)-	C_9H_{12}	0.07		0.04	0.03
120	Benzene, 1,2,4-trimethyl-	C_9H_{12}	0.07		0.03	0.03
120	Benzene, propyl-	C_9H_{12}	0.03		-	-
120	Benzene, 1,3,5-trimethyl-	C_9H_{12}	0.02		-	-
120	Benzene, 1-ethyl-2-methyl-	C_9H_{12}	0.02		-	-
130	2-Methylindene	$C_{10}H_{10}$	0.04		-	-
134	Benzene, 1-methyl-2-(1-methylethyl)-	C_9H_{14}	0.03		-	-
134	Benzene, 2-ethyl-1,4-dimethyl-	C_9H_{14}	0.02		-	-
168	1,2,3-Trimethoxybenzene	$C_9H_{12}O_3$	0.09		-	-
108	p-Benzoquinone	$C_6H_4O_2$	-	-	0.04	0.02
131	Benzeneacetonitrile, .alpha.-oxo-	C_8H_5NO	-	-	-	<0.01
120	Benzaldehyde, 4-methyl-	C_8H_8O	0.1		-	-
106	Benzaldehyde	C_7H_6O	0.68	7%	0.80	1.09
132	Cinnamaldehyde, (E)-	C_9H_8O	0.04		-	-
120	Benzeneacetaldehyde	C_8H_8O	-	-	0.04	0.04
122	Benzaldehyde, 2-hydroxy-	$C_7H_6O_2$	-	-	0.04	0.04
134	Benzaldehyde, 3-ethyl-	$C_9H_{10}O$	-	-	-	0.03
100	Hexanal	$C_6H_{12}O$	-	-	0.08	0.07
114	Heptanal	$C_7H_{14}O$	-	-	0.03	0.04
128	Octanal	$C_8H_{16}O$	-	-	0.04	0.06
142	Nonanal	$C_9H_{18}O$	-	-	0.10	0.18
156	Decanal	$C_{10}H_{20}O$	-	-	0.06	0.08
170	Undecanal	$C_{11}H_{22}O$	-	-	-	0.01
74	1-Butanol	$C_4H_{10}O$	-	-	2.30	6.63

*Coeluted with other species.

Table S3: Evolution of the water soluble oxidative potential (WS-OP), expressed as per mass normalized DTT activity (DTT_m), organic carbon (OC) of the samples, and the average oxygen-to-carbon ratio (O:C) for the sampling period, across experiments and for both diurnal oxidation cycles.

Exp.	DTT_m [pmol min^{-1} μg^{-1}]			Organic Carbon (OC) [µg]			Oxygen to carbon (O:C)		
	Fresh	**Daytime**	**Nighttime**	**Fresh**	**Daytime**	**Nighttime**	**Fresh**	**Daytime**	**Nighttime**
	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD
DN1	51.42 ± 4.73	77.58 ± 6.32	68.70 ± 5.97	3.33 ± 0.31	5.01 ± 0.4	4.09 ± 0.35	0.43 ± 0.003	0.55 ± 0.024	0.61 ± 0.003
DN2	56.25 ± 5.18	117.14 ± 8.98	77.63 ± 7.11	3.59 ± 0.35	6.33 ± 0.49	3.77 ± 0.36	0.39 ± 0.002	0.62 ± 0.019	0.66 ± 0.006
DN3	21.23 ± 5.68	102.86 ± 17.97	68.44 ± 4.66	7.76 ± 0.67	1.22 ± 0.22	1.46 ± 0.210	0.38 ± 0.003	0.59 ± 0.015	0.65 ± 0.007
DN4	30.71 ± 2.99	117.49 ± 11.84	50.46 ± 12.93	2.96 ± 0.3	2.72 ± 0.29	0.66 ± 0.18	0.38 ± 0.004	0.54 ± 0.011	0.60 ± 0.005
DN5	57.23 ± 4.92	81.63 ± 6.18	73.63 ± 11.11	3.85 ± 0.35	2.21 ± 0.17	1.35 ± 0.22	0.35 ± 0.003	0.50 ± 0.016	0.56 ± 0.003
DN6	41.28 ± 4.68	64.97 ± 6.51	86.90 ± 16.17	1.55 ± 0.24	2.68 ± 0.29	4.05 ± 0.29	0.36 ± 0.002	0.57 ± 0.013	0.6 ± 0.004
DN7	79.03 ± 11.29	127.13 ± 13.06	94.34 ± 6.72	4.28 ± 0.41	4.73 ± 0.44	5.29 ± 0.46	0.41 ± 0.002	0.56 ± 0.014	0.61 ± 0.014
DN8	46.18 ± 4.46	54.33 ± 5.09	67.44 ± 5.95	2.18 ± 0.26	2.68 ± 0.28	1.00 ± 0.20	0.44 ± 0.003	0.56 ± 0.017	0.60 ± 0.003
	Fresh	**Nighttime**	**Daytime**	**Fresh**	**Nighttime**	**Daytime**	**Fresh**	**Nighttime**	**Daytime**
	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD	mean ± SD
ND1	31.84 ± 2.80	42.48 ± 3.10	70.97 ± 5.74	3.97 ± 0.34	7.95 ± 0.54	5.00 ± 0.39	0.41 ± 0.002	0.54 ± 0.007	0.65 ± 0.010
ND2	22.63 ± 2.35	58.16 ± 5.36	94.55 ± 13.71	2.68 ± 0.29	3.15 ± 0.31	0.94 ± 0.15	0.47 ± 0.002	0.61 ± 0.009	0.69 ± 0.006
ND3	36.18 ± 3.67	57.56 ± 6.56	89.04 ± 9.80	2.54 ± 0.27	2.03 ± 0.24	2.14 ± 0.25	0.29 ± 0.003	0.42 ± 0.009	0.51 ± 0.009
ND4	34.56 ± 2.46	85.14 ± 6.97	43.55 ± 3.20	7.81 ± 0.52	6.97 ± 4.37	7.5 ± 0.51	0.39 ± 0.006	0.49 ± 0.007	0.57 ± 0.009
ND5	33.23 ± 3.33	44.95 ± 3.63	52.03 ± 4.04	3.11 ± 0.31	3.63 ± 5.98	6.91 ± 0.5	0.37 ± 0.002	0.47 ± 0.007	0.57 ± 0.011
ND6	58.27 ± 4.25	51.61 ± 3.81	61.92 ± 4.51	7.95 ± 0.55	3.81 ± 8.53	8.38 ± 0.57	0.43 ± 0.002	0.51 ± 0.007	0.61 ± 0.009
ND7	44.71 ± 3.96	46.84 ± 3.90	39.68 ± 3.27	3.48 ± 0.32	3.90 ± 4.43	4.5 ± 0.37	0.23 ± 0.002	0.36 ± 0.008	0.41 ± 0.006
ND8	41.07 ± 3.41	48.68 ± 3.81	51.60 ± 4.23	4.55 ± 0.37	3.81 ± 5.99	5.37 ± 0.41	0.35 ± 0.002	0.47 ± 0.008	0.53 ± 0.007

Table S4: Theoretical calculation of reacted fractions and lifetimes of selected VOCs during their reaction with OH in typical experiments DN1 and ND1.

VOCs	*m/z* [H^+]	Reaction with OH			DN1				ND1			
		Expression (296-340K)	Reference	k_{OH} [molecules^{-1} cm^3 s^{-1}]	Daytime OH = 3.21×10^6 [molecule cm^{-3}]				Daytime OH = 4.18×10^6 [molecule cm^{-3}]			
					*C/Co	**1-C/Co	Observed reacted fraction	***Life time [h]	C/Co	1-C/Co	Observed reacted fraction	Life time [h]
Acrolein	57	1.96×10^{-11}	MCM (v3.3.1)[1]	1.96E-11	63.6%	36.4%	3.7%	4	55.4 %	44.6%	14.6 %	3
Isoprene	69	$2.7\times10^{-11}\exp(390/T)$	MCM (v3.3.1)	1.00E-10	9.8%	90.2%	28.7%	1	4.9%	95.1%	53.3 %	1
Furan	69	$1.32\times10^{-11}\exp(334/T)$	NIST database[2]; (Atkinson, 1986; Bierbach et al., 1995)	4.06E-11	39.1%	60.9%	28.7%	2	29.4 %	70.6%	53.3 %	2
MACR	71	$8.0\times10^{-12}\exp(380/T)$	MCM (v3.3.1)	2.88E-11	51.4%	48.6%	17.5%	3	42.1 %	57.9%	32.2 %	2
MVK	71	$3.29\times10^{-12}\exp(514/T)$	(Atkinson, 1986)	1.86E-11	65.1%	34.9%	17.5%	5	57.2 %	42.8%	32.2 %	4
Benzene	79	$2.33\times10^{-12}\exp(-193/T)$	(Calvert et al., 2002; Seinfeld and Pandis, 2016)	1.22E-12	97.2%	2.8%	2.9%	71	96.4 %	3.6%	6.8%	55
Monoterpenes frag.	81	$4.2\times10^{-12}\exp(565/T)$	NIST database	2.81E-11	52.2%	47.8%	52.8%	3	42.9 %	57.1%	17%	2
Methyl furan (3-methylfuran)	83	$3.2\times10^{-12}\exp(310/T)$	NIST database; (Aschmann et al., 2011)	9.09E-12	81.1%	18.9%	33.3%	10	76.1 %	23.9%	9.3%	7
Ethyl vinyl ketone	85	$4.36\times10^{-14}(T/298)^{3.92}\exp(1725/T)$	NIST database; (Paul et al., 2018)	1.43E-11	71.8%	28.2%	7.5%	6	65.0 %	35.0%	25.5 %	5
Toluene	93	$1.8\times10^{-12}\exp(340/T)$	(Calvert et al., 2002; Seinfeld and Pandis, 2016)	5.66E-12	87.7%	12.3%	11.9%	15	84.3 %	15.7%	6.8%	12
Phenol	95	$4.7\times10^{-13}\exp(1220/T)$	MCM (v3.3.1); IUPAC database[3]	2.86E-11	51.7%	48.3%	32.5%	3	42.3 %	57.7%	65.3 %	2

[1] MCM(v3.3.1): https://mcm.york.ac.uk/MCM/browse
[2] NIST database: https://webbook.nist.gov
[3] IUPAC database: https://iupac.aeris-data.fr/

Styrene		105	$1.02\times10^{-11}\exp(532/T)$	NIST database; (Cho et al., 2014)	6.12E-11	24.3%	75.7%	46.1%	1	15.9 %	84.1%	52.6 %	1
C8 aromatics	o-xylene	107	1.36×10^{-11} (at 298 K)	(Seinfeld and Pandis, 2016)	1.36E-11	73.0%	27.0%	12.7%	6	66.4 %	33.6%	17.9 %	5
	m-xylene		$1.66\times10^{-11}\exp(115/T)$	NIST database; (Atkinson, 1986)	2.44E-11	56.8%	43.2%		4	47.9 %	52.1%		3
	p-xylene		1.43×10^{-11} – 1.52×10^{-11}	MCM (v3.3.1); (Seinfeld and Pandis, 2016)	1.43E-11	71.9%	28.1%		6	65.0 %	35.0%		5
C9 aromatics	1,2,3 TMB	121	$3.61\times10^{-12}\exp(620/T)$	NIST database; (Bohn and Zetzsch, 2012)	2.91E-11	51.0%	49.0%	25.7%	3	41.6 %	58.4%	21.7 %	2
	1,2,4 TMB		$2.73\times10^{-12}\exp(730/T)$	NIST database; (Bohn and Zetzsch, 2012)	3.19E-11	47.9%	52.1%		3	38.3 %	61.7%		2
	1,3,5 TMB		$4.4\times10^{-12}\exp(738/T)$	NIST database; (Aschmann et al., 2006)	5.28E-11	29.5%	70.5%		2	20.4 %	79.6%		1
Naphthalene		129	2.17×10^{-11} (at 298 K)	NIST database	2.17E-11	60.6%	39.4%	-	4	52.0 %	48.0%	0.84 %	3
Monoterpenes (α-pinene)		137	$1.2\times10^{-11}\exp(440/T)$	MCM (v3.3.1)	5.28E-11	29.5%	70.5%	12.9%	2	20.4 %	79.6%	13.7 %	1
Creosol/2-methoxy-4-methylphenol		139	$(9.45\pm0.59)\times10^{-11}$	(Coeur-Tourneur et al., 2010)	8.86E-11	12.9%	87.1%	27%	1	6.9%	93.1%	23.3 %	1
Dibenzofuran		169	3.4×10^{-11} - 3.5×10^{-12} (at 298 K)	NIST database; (Atkinson, 1987; Brubaker and Hites, 1998)	3.4 E-11	45.6%	54.4%	-	3	35.9 %	64.1%	-	2

*The remaining fraction was calculated assuming first order reaction of the VOCs species with OH by applying the equation $C/Co=\exp(-k_{OH}[OH]t)$, for t=2h; **The reacted fraction using the relationship 1-C/Co. OH reaction rates (k_{OH}) calculated at T = 298 ± 2 K; P = 1 atm; ***Lifetimes were determined as the reciprocal of the product of OH concentration and the reaction rate constant for each VOC with OH (k_{OH}).

Table S5: Theoretical calculation of reacted fractions and lifetimes of selected VOCs during their daytime reaction with O_3 in typical experiments DN1 and ND1.

VOCs		*m/z* [H+]	Reaction with O_3			DN1				ND1			
			Expression	Reference	k_{O3} [molecules^{-1} cm^3 s^{-1}]	Daytime $O_3 = 8.15\times10^{11}$ [molecule cm^{-3}]				Daytime $O_3 = 3.77\times10^{12}$ [molecule cm^{-3}]			
						C/Co	1-C/Co	Observed reacted fraction	Life time [h]	C/Co	1-C/Co	Observed reacted fraction	Life time [h]
Acrolein		57	2.9×10^{-19}	MCM (v3.3.1)	2.90E-19	99.8%	0.2%	3.7%	1176	99.2%	0.8%	14.6%	254
Isoprene		69	7.86×10^{-15}exp(-1913/T)	(Seinfeld and Pandis, 2016)	1.26E-17	92.9%	7.1%	28.7 %	27	71.1%	28.9 %	53.3%	6
Furan		69	2.42×10^{-18}	NIST database	2.42E-18	98.6%	1.4%	28.7 %	141	93.6%	6.4%	53.3%	30
Methacrolein (MACR)		71	1.4×10^{-15}exp(-2100/T)	MCM (v3.3.1)	1.19E-18	99.3%	0.7%	17.5 %	286	96.8%	3.2%	32.2%	62
Methyl vinyl ketone (MVK)		71	8.5×10^{-16}exp(-1520/T)	MCM (v3.3.1)	5.10E-18	97.1%	2.9%	17.5 %	67	87.1%	12.9 %	32.2%	14
Benzene		79	1.72×10^{-22}	NIST database	1.72E-22	>99.9%	<0.01 %	2.9%	1982649	100%	0.0%	6.8%	428001
Methylfuran (3-methylfuran)		83	2.00×10^{-17}	MCM (v3.3.1)	2E-17	88.9%	11.1%	33.3 %	17	58.1%	41.9 %	9.3%	4
Ethyl vinyl ketone		85	6.04×10^{-18}	NIST database	6.04E-18	96.5%	3.5%	7.5%	56	84.9%	15.1 %	25.5%	12
Toluene		93	3.9×10^{-22}	IUPAC database	3.90E-22	100%	0.0%	11.9 %	874399	100%	0.0%	6.8%	188759
Phenol		95	1.2×10^{-19}	(Atkinson et al., 1992)	1.20E-19	99.9%	0.1%	32.5 %	2842	99.7%	0.3%	65.3%	613
Styrene		105	1.7×10^{-17}	MCM (v3.3.1)	1.70E-17	90.5%	9.5%	46.1 %	20	63.0%	37.0 %	52.6%	4
C8 aromatics	o-xylene	107	1.72×10^{-21}	NIST database	1.72E-21	100%	0.0%	12.7 %	198265	100%	0.0%	17.9%	42800
	m-xylene		8.48×10^{-22}	NIST database	8.48E-22	100%	0.0%		402141	100%	0.0%		86811
	p-xylene		1.36×10^{-21}	NIST database	1.36E-21	100%	0.0%		250747	100%	0.0%		54129
C9 aro	1,2,3 TMB	121	1.60×10^{-21}	NIST database	1.60E-21	100%	0.0%	25.7 %	213135	100%	0.0%	21.7%	46010

matics	1,3,5 TMB		2.19×10^{-21}	NIST database	2.19E-21	100%	0.0%		155715	100%	0.0%		33615
Naphthalene		129	$< 3.01\times10^{-19}$	NIST database	3.01E-19	99.8%	0.2%	-	1133	99.2%	0.8%	0.84%	245
Monoterpenes (α-pinene)		137	$1.01\times10^{-15}\exp(-732/T)$	(Seinfeld and Pandis, 2016)	8.60E-17	60.4%	39.6%	12.9 %	4.0	9.7%	90.3 %	13.7%	0.9
Dibenzofuran		169	$< 8\times10^{-20}$	IUPAC database	8.00E-20	100%	0.0%	-	4263	99.9%	0.1%	-	3681

Table S6: WS-OP statistical analysis results of independent samples T-test for the examined hypotheses.

	Day-to-night oxidation					
	t-test 1		t-test 2		t-test 3	
Hypotheses	H_0: Fresh = UV oxidized WS-OP H_1: UV oxidized > fresh WS-OP		H_0: Fresh = NO_3 oxidized WS-OP H_1: NO_3 oxidized > fresh WS-OP		H_0: UV oxidized = NO_3 oxidized WS-OP H_1: UV oxidized > NO_3 oxidized WS-OP	
WS-OP measurements	Fresh	UV aged	Fresh	NO_3 aged	NO_3 aged	UV aged
DN1	51.42	77.58	51.42	68.70	68.70	77.58
DN2	56.25	117.14	56.25	77.63	77.63	117.14
DN3	21.23	102.86	21.23	68.44	68.44	102.86
DN4	30.71	117.49	30.71	50.46	50.46	117.49
DN5	57.23	81.63	57.23	73.63	73.63	81.63
DN6	41.28	64.97	41.28	86.90	86.90	64.97
DN7	79.03	127.13	79.03	94.34	94.34	127.13
DN8	46.18	54.33	46.18	67.44	67.44	54.33
Sample size	$n_2 = 8$	$n_1 = 8$	$n_2 = 8$	$n_1 = 8$	$n_2 = 8$	$n_1 = 8$
Mean value	$\bar{\mu}_2 = 47.92$	$\bar{\mu}_1 = 92.89$	$\bar{\mu}_2 = 47.92$	$\bar{\mu}_1 = 92.89$	$\bar{\mu}_2 = 47.92$	$\bar{\mu}_1 = 92.89$
SD	$\sigma_2^2 = 313.1$	$\sigma_1^2 = 727.5$	$\sigma_2^2 = 313.1$	$\sigma_1^2 = 178.2$	$\sigma_2^2 = 727.5$	$\sigma_1^2 = 178.2$
$\sqrt{SD}$	$\sigma_2 = 17.70$	$\sigma_1 = 26.97$	$\sigma_2 = 17.70$	$\sigma_1 = 13.35$	$\sigma_2 = 27.00$	$\sigma_1 = 13.30$
t_0	3.943		3.257		1.828	
Degrees of freedom	14		14		14	
F(ct)	0.95		0.95		0.95	
α	0.05		0.05		0.05	
ct	1.761		1.761		1.761	
Check	$t_0 > ct$		$t_0 > ct$		$t_0 > ct$	
Hypothesis accepted	H_1		H_1		H_1	
	Night-to-day oxidation					
	t-test 1		t-test 2		t-test 3	
Hypotheses	H_0: Fresh =NO_3 oxidized WS-OP H_1: NO_3 oxidized > fresh WS-OP		H_0: Fresh = UV oxidized WS-OP H_1: UV oxidized > fresh WS-OP		H_0: UV oxidized = NO_3 oxidized WS-OP H_1: UV oxidized > NO_3 oxidized WS-OP	
WS-OP measurements	Fresh	NO_3 aged	Fresh	UV aged	NO_3 aged	UV aged
ND1	31.84	42.48	31.84	70.97	42.48	70.97
ND2	22.63	58.16	22.63	94.55	58.16	94.55
ND3	36.18	57.56	36.18	89.04	57.56	89.04
ND4	34.56	85.14	34.56	43.55	85.14	43.55
ND5	33.23	44.95	33.23	52.03	44.95	52.03
ND6	58.27	51.61	58.27	61.92	51.61	61.92
ND7 (olive + pine)	44.71	46.84	44.71	39.68	46.84	39.68
ND8 (olive + pine)	41.07	48.68	41.07	51.60	48.68	51.60
Sample size	$n_2 = 8$	$n_1 = 8$	$n_2 = 8$	$n_1 = 8$	$n_2 = 8$	$n_1 = 8$

Mean value	$\bar{\mu}_2 = 37.81$	$\bar{\mu}_1 = 54.43$	$\bar{\mu}_2 = 37.81$	$\bar{\mu}_1 = 62.92$	$\bar{\mu}_2 = 54.43$	$\bar{\mu}_1 = 62.92$
SD	$\sigma_2^2 = 111.02$	$\sigma_1^2 = 185.44$	$\sigma_2^2 = 111.02$	$\sigma_1^2 = 415.8$	$\sigma_2^2 = 185.44$	$\sigma_1^2 = 415.8$
$\sqrt{SD}$	$\sigma_2 = 10.54$	$\sigma_1 = 13.62$	$\sigma_2 = 10.54$	$\sigma_1 = 20.39$	$\sigma_2 = 13.62$	$\sigma_1 = 20.39$
t_0	2.730		3.094		0.979	
Degrees of freedom	14		14		14	
F(ct)	0.95		0.95		0.95	
α	0.05		0.05		0.05	
ct	1.761		1.761		1.761	
Check	$t_0 > ct$		$t_0 > ct$		$t_0 < ct$	
Hypothesis accepted	H_1		H_1		H_0	

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