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Total OH reactivity over the Amazon rainforest: variability with temperature, wind, rain, altitude, time of day, season, and an overall budget closure

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Supplementary Information

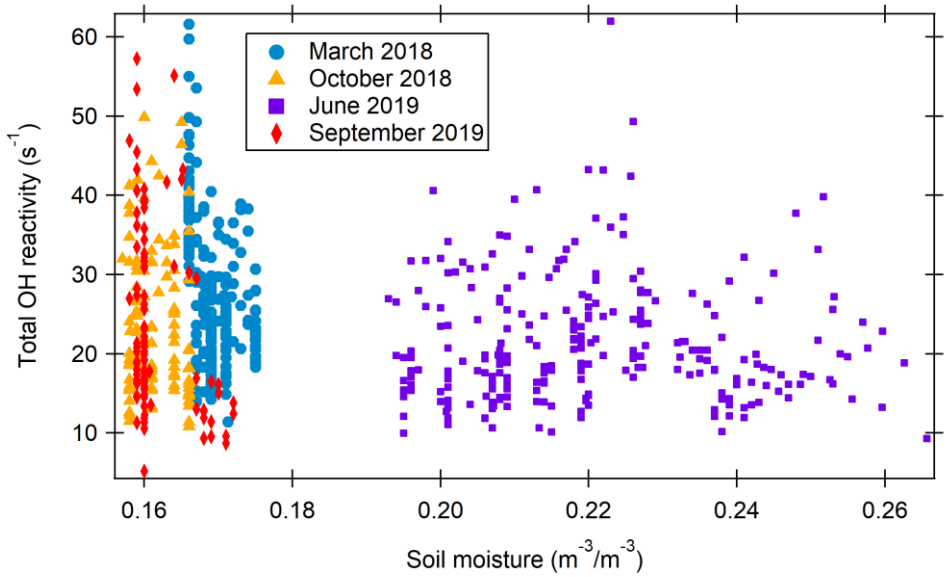

Figure S1. Soil moisture and total OH reactivity in hourly time resolution for the four measurement periods.

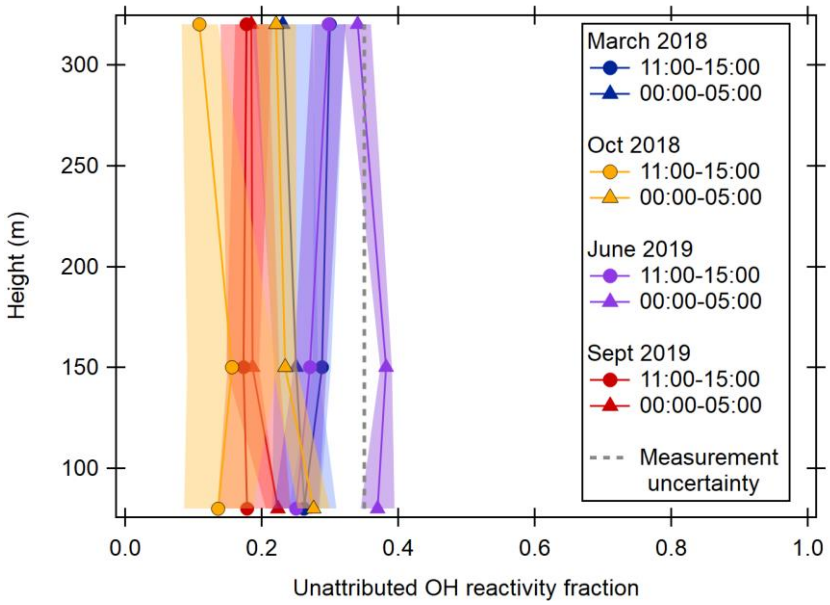

Figure S2. Unattributed OH reactivity fraction profiles for noon- and nighttime in each measurement period. The shaded areas represent the standard deviation. The measurement uncertainty given is the average over all observation periods. Note that the unattributed fraction is usually below the measurement uncertainty.

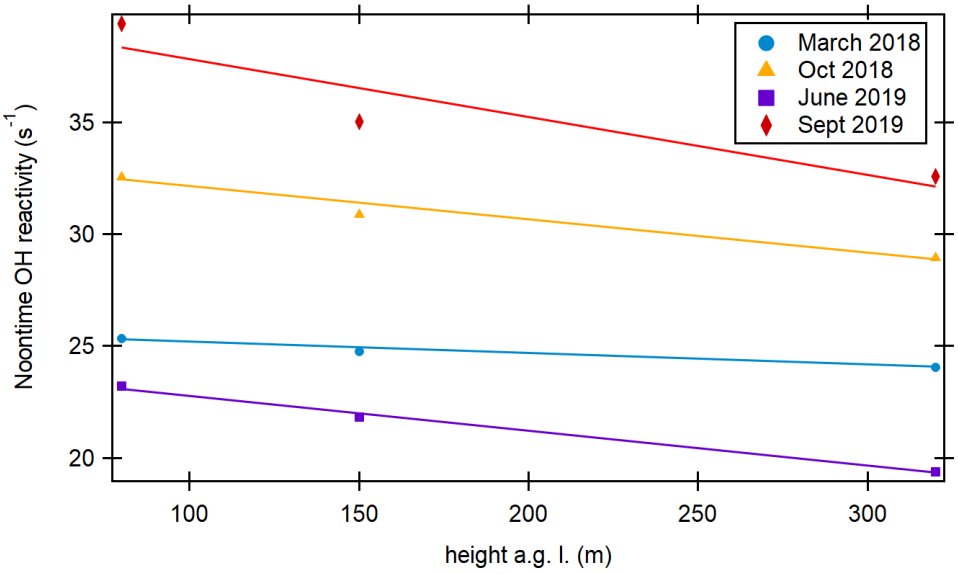

Figure S3. Campaign average noontime total OH reactivities as a function of height with linear regressions for gradient determination. The results of the linear regressions were: March 2018: R = -0.005*h + 25.7; October 2018: R = -0.015*h + 34.0; June 2019: R = -0.016*h + 24.3; September 2019: R = -0.026*h + 40.4.

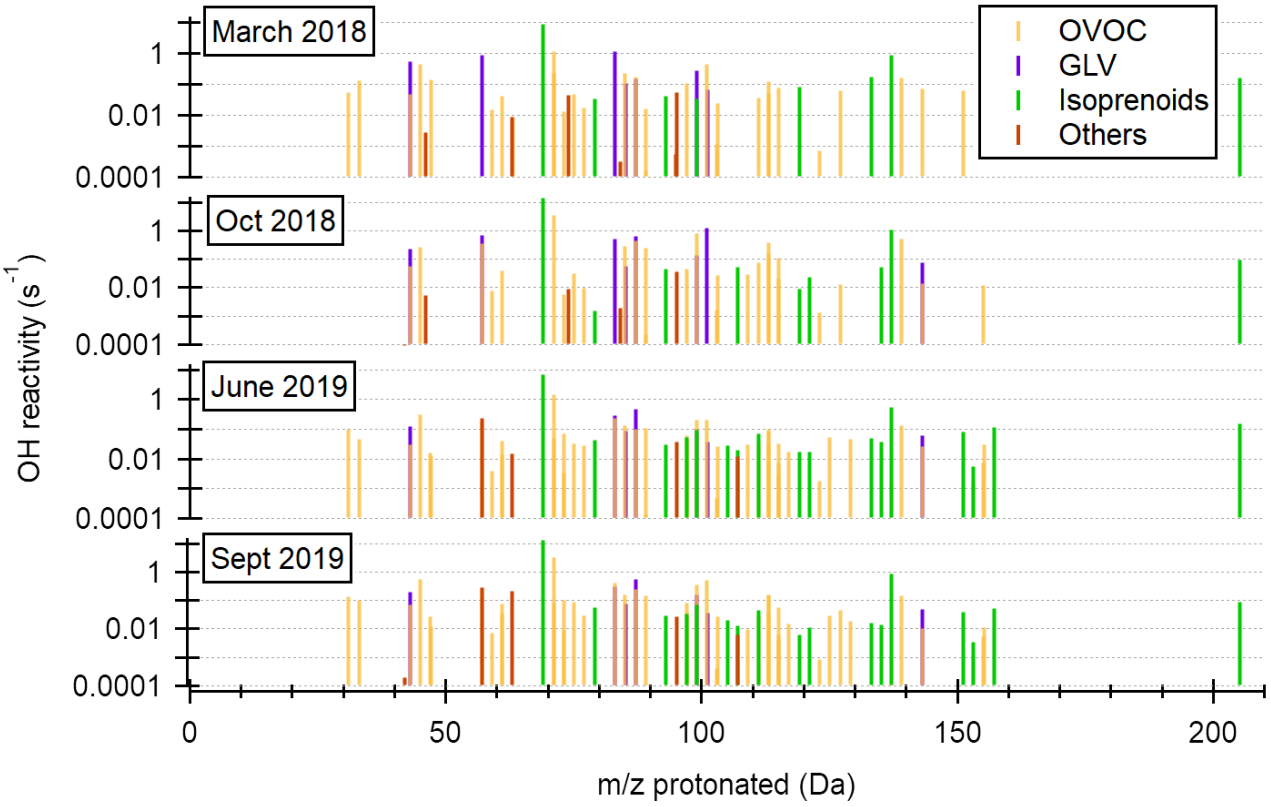

Figure S4. Daytime OH reactivity for each season by protonated mass-to-charge ratio (m/z) of PTR-ToF-MS ions and colored by compound class (see Table S1). Isoprenoids include isoprene, monoterpenes and sesquiterpenes as specified in Table S1 (including primarily emitted oxygenated monoterpenes). Ions colored as isoprenoids or GLVs include fragments as denoted in Table S1. Note that the y axis is in logarithmic scale.

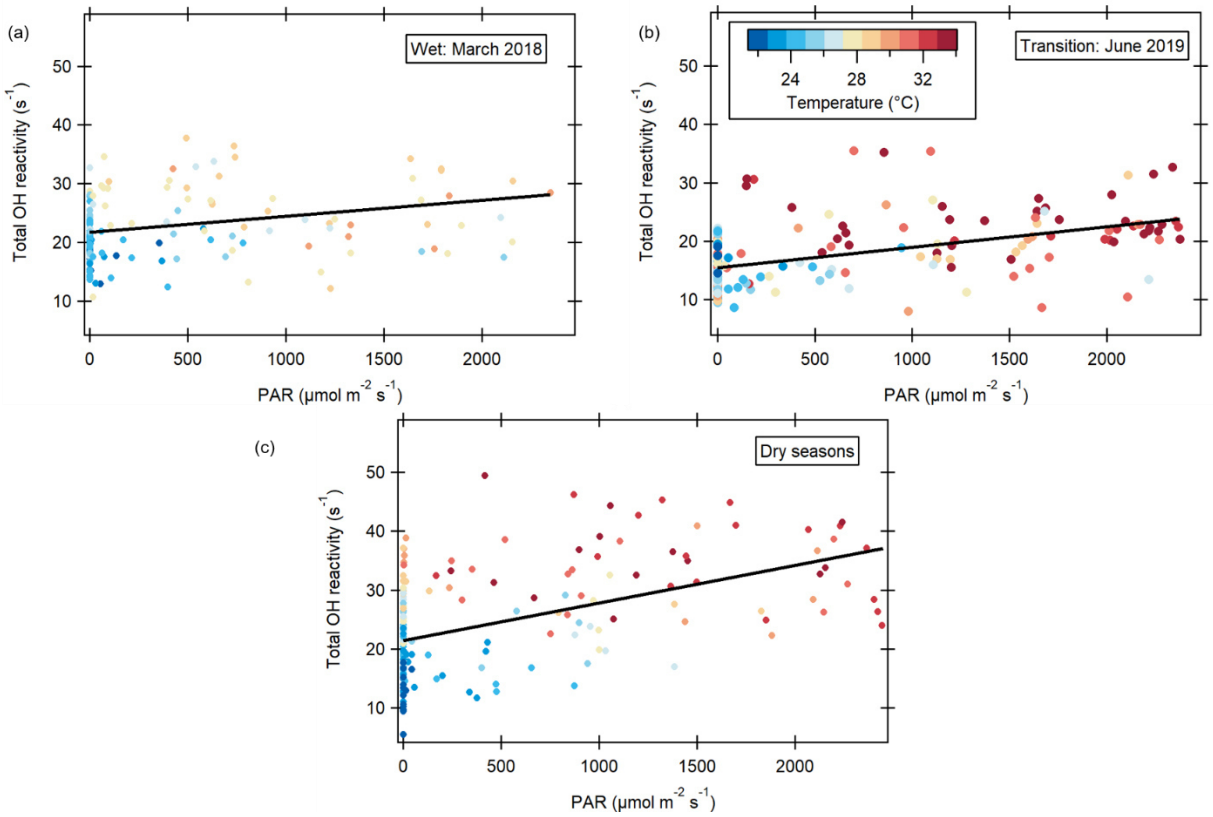

Figure S5. Hourly averages of total OH reactivity at 80 m a. g. l. at the ATTO tower as a function of photosynthetically active radiation (PAR). Temperature color scale shown in (b) for all panels. (a) Wet season (March 2018), fit function: R = 21.7– 0.003*[PAR], r^2 = 0.08 (b) Transition season (June 2019), fit function: R = 15.4– 0.004*[PAR], r^2 = 0.27 (c) Dry seasons (October 2018 and September 2019), fit equation: R = 21.4– 0.006*[PAR], r^2 = 0.27.

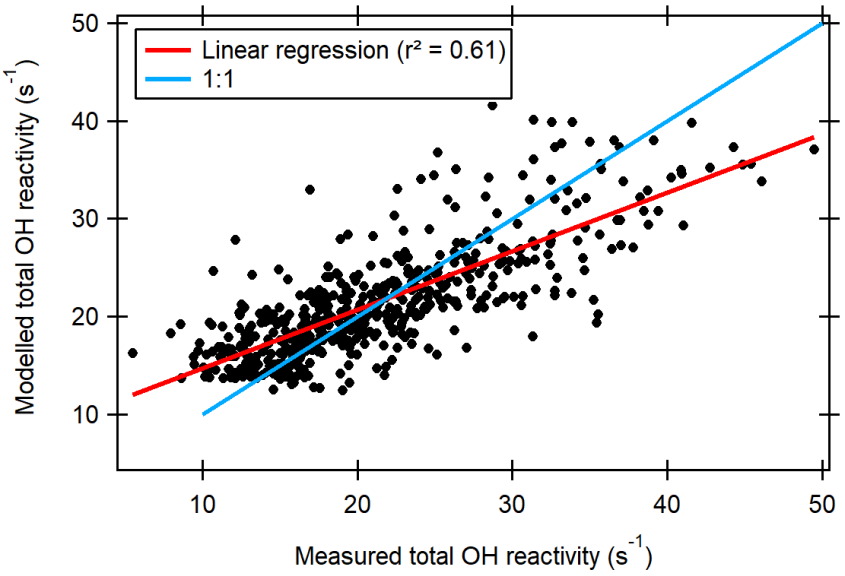

Figure S6. Modelled total OH reactivity from the temperature-dependent parameterization (Sect. 3.3.1) vs. measured total OH reactivity. Linear regression: $y = 8.7 + 0.6x$, $r^2 = 0.61$.

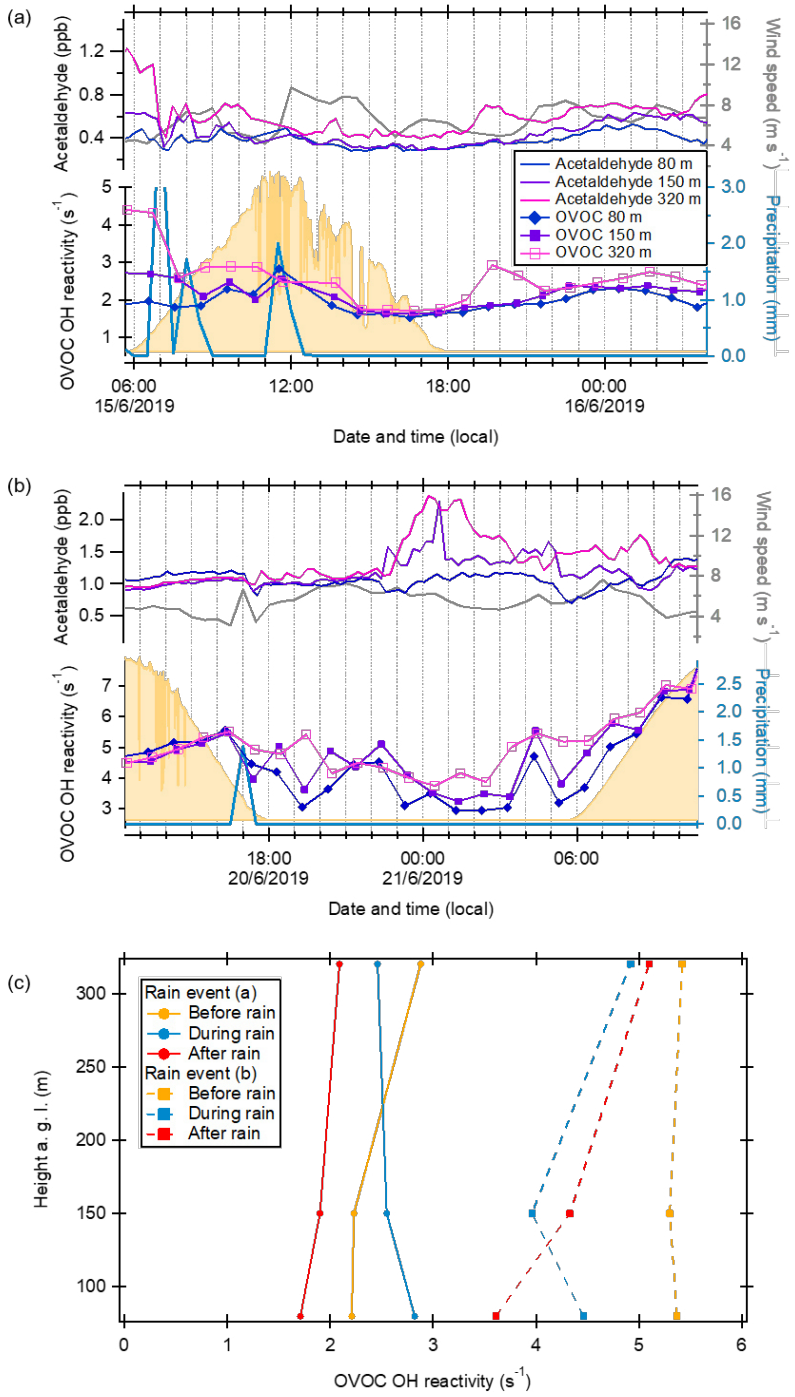

Figure S7. Timeseries of meteorological parameters (wind speed at 320 m, precipitation at 320 m, PAR at 80 m), OVOC OH reactivity and acetaldehyde mixing ratios around (a) a daytime rain event and (b) an evening rain event. (c) Vertical profiles of OVOC-attributed OH reactivity for two rain events.

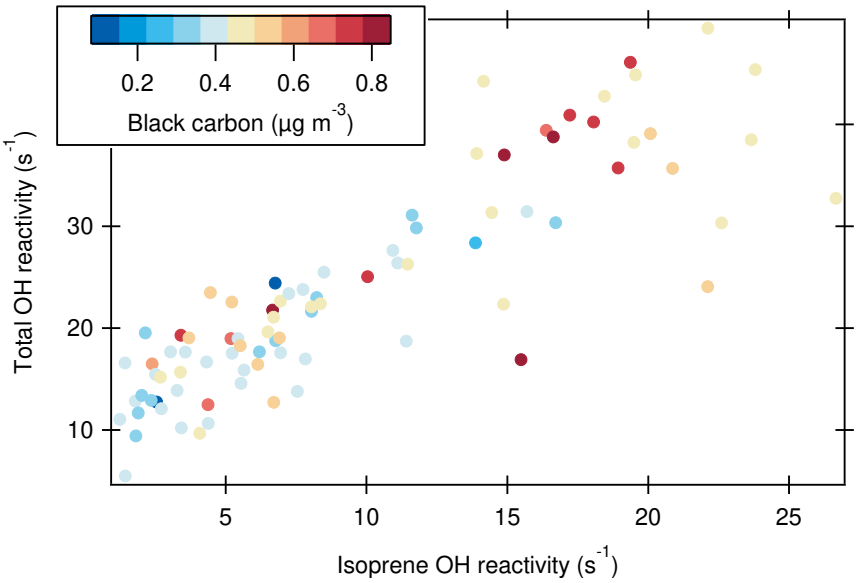

Figure S8. Total OH reactivity as a function of terpenoid reactivity with black carbon mass concentration as a colour scale for September 2019. The Pearson Correlation coefficient for total OH reactivity vs. isoprene OH reactivity is $r^2 = 0.75$, for total OH reactivity vs. black carbon (not shown) it is $r^2 = 0.14$, showing that the dependence of total OH reactivity on plant activity is larger than on biomass burning.

Table S1: Chemical species used for calculating speciated OH reactivity

Compound/ protonated mass (grey shaded compounds are gas standard calibrated with low uncertainty, compounds marked with a * were included in Nölscher et al., 2016)	**Chemical formula**	k_{VOC+OH} [cm³ molecules^{-1} s^{-1}]	**Detected by**	**Compounds attributed to protonated mass**	**If no unambiguous compound identification: reaction rate coefficient derived from…**	**Literature reference for reaction rate coefficent**	**Avg. OH reactivity in Sept 2019 at 80 m [s^{-1}]**	**Compound class /comments**
Methane*	CH_4	6.45E-15	Picarro Cavity ring-down spectroscopy instrument			IUPAC, 2020	0.29	Inorganic
Carbon monoxide*	CO	1.44E-13	Picarro Cavity ring-down spectroscopy instrument			IUPAC, 2020	0.04	Inorganic
Ozone*	O_3	7.30E-14	UV Photometric O_3 Analyzer			IUPAC, 2020	0.02	Inorganic
33.0335*	CH_3OH	9.00E-13	PTR-ToF-MS	Methanol		IUPAC, 2020	0.09	OVOC
42.0338*	C_2H_3N	2.20E-14	PTR-ToF-MS	Acetonitrile		IUPAC, 2020	2.0e-4	Others
45.0335*	C_2H_4O	1.50E-11	PTR-ToF-MS	Acetaldehyde		IUPAC, 2020	0.53	OVOC
59.0491*	C_3H_6O	1.80E-13	PTR-ToF-MS	Acetone		IUPAC, 2020	0.01	OVOC
63.0263	C_2H_6S	4.80E-12	PTR-ToF-MS	Dimethyl sulfide		IUPAC, 2020	0.24	SVOC
69.0699*	C5H8	1.0E-10	PTR-ToF-MS	Isoprene		IUPAC, 2020	9.48	Isoprene
71.0491*	C_4H_6O	5.62E-11	PTR-ToF-MS	Methyl vinyl ketone; methacrolein; (1,2)-isoprene hydroxy hydroperoxide; (4,3)-isoprene hydroxy hydroperoxide	Weighted average (MVK/MACR = 1.5/1 according to Kuhn et al., 2007)	St Clair et al., 2016; IUPAC, 2020	2.86	OVOC
73.0648*	C_4H_8O	4.87E-11	PTR-ToF-MS	2-butanone (MEK)		IUPAC, 2020	0.01	OVOC
79.0543*	C_6H_6	1.20E-12	PTR-ToF-MS	Benzene		IUPAC, 2020	0.05	Others
93.0699*	C_7H_8	1.45E-11	PTR-ToF-MS	Toluene / here: fragment of aromatic monoterpenes (Kari et al., 2018)	p-cymene reaction rate coefficient	IUPAC, 2020	0.03	MT

107.0856	C_8H_{10}	1.45E-11	PTR-ToF-MS	Xylenes / here: fragment of aromatic monoterpenes [identified by correlation with parent mass]	p-cymene reaction rate coefficient	IUPAC, 2020	0.01	MT
121.1012	C_9H_{12}	1.45E-11	PTR-ToF-MS	Trimethylbenzene / here: fragment of aromatic monoterpenes [identified by correlation with parent mass]	p-cymene reaction rate coefficient	IUPAC, 2020	0.01	MT
137.1325*	$C_{10}H_{16}$	7.23E-11	PTR-ToF-MS (sum), speciation by TD-GC-TOF-MS	Monoterpenes	Weighted average according to speciation: 68.1% α-pinene, 14.0% β-pinene, 9.5% limonene, 5.7% camphene, 1.3% β-myrcene, 0.9% sabinene, 0.3% terpinolene, 0.2% γ-terpinene	IUPAC, 2020	0.60	MT
31.0179	HCHO	8.50E-12	PTR-ToF-MS	Formaldehyde		IUPAC, 2020	0.13	OVOC
41.0386	C_3H_4	none	PTR-ToF-MS	Fragment of isoprene and monoterpenes (Pagonis et al., 2019; Kari et al., 2018)	None, because isoprene and MTs are calibrated		none	none
43.0179	C_2H_2O	6.90E-13	PTR-ToF-MS	Fragment of acetic acid (Pagonis et al., 2019)	Acetic acid reaction rate coefficient	IUPAC, 2020	0.06	OVOC
43.0543	C_3H_6	1.50E-11	PTR-ToF-MS	Fragment of 1-hexanol (Pagonis et al., 2019) [propene was excluded by NO+ PTR-MS measurements]		IUPAC, 2020	0.18	GLV
46.0288	CH_3NO	1.50E-12	PTR-ToF-MS	Formamide		Nizamov and Dagdigian, 2003	0.005	Others. Isotope of acetaldehyde on m/z 46 was subtracted
47.0128	HCOOH	4.50E-13	PTR-ToF-MS	Formic acid		IUPAC, 2020	0.02	OVOC
47.0492	C_2H_6O	3.2E-12	PTR-ToF-MS	Ethanol		IUPAC, 2020	0.01	OVOC
57.0335	C_3H_4O	1.96E-11	PTR-ToF-MS	Acrolein		Atkinson and Arey, 2003	0.24	OVOC
57.0699	C_4H_8	3.78E-11	PTR-ToF-MS	Butenes [identified by NO+ chemistry]; or fragment of hexanol, hexenyl acetate [identified by correlation with parent mass] (Pagonis et al., 2019)	Average of butenes or hexanol/hexenyl acetate reaction rate coefficients according to identification	Atkinson and Arey, 2003; Atkinson et al., 1995	0.28	Others/GLV
61.0285	$C_2H_4O_2$	6.90E-13	PTR-ToF-MS	Acetic acid		IUPAC, 2020	0.03	OVOC
63.0441	$C_2H_6O_2$	1.45E-11	PTR-ToF-MS	1,2-ethanediol		IUPAC, 2020	0.00	OVOC

71.0856	C_5H_{10}	1.30E-11	PTR-ToF-MS	Fragment of 2-pentanol, octanol, nonanol (Pagonis et al., 2019)	average	IUPAC, 2020	0.07	OVOC
73.0284	$C_3H_4O_2$	3.30E-11	PTR-ToF-MS	Methyl glyoxal		IUPAC, 2020	0.09	OVOC
74.0601	C_3H_7NO	1.25E-11	PTR-ToF-MS	N,N-dimethyl formamide, N-methyl acetamide	average	Solignac et al., 2005; Barnes et al., 2010	0.00	Others
75.0441	$C_3H_6O_2$	2.85E-12	PTR-ToF-MS	Hydroxyacetone		IUPAC, 2020	0.08	OVOC
77.0598	$C_3H_8O_2$	1.62E-11	PTR-ToF-MS	2-methoxyethanol; 1,2-propanediol	average	Porter et al., 1997; IUPAC, 2020	0.03	OVOC
83.0492	C_5H_6O	9.30E-11	PTR-ToF-MS	3-methylfuran (isoprene oxidation product)		IUPAC, 2020	0.37	OVOC
83.0856	C_6H_{10}	6.26E-11	PTR-ToF-MS	Fragment of hexenol and hexanal (Pagonis et al., 2019) [identified by correlation with parent mass]	Average	Atkinson and Arey, 2003; Atkinson et al., 1995	0.29	GLV
84.0808	C_5H_9N	2.56E-13	PTR-ToF-MS	Pentanenitrile	rate coefficient of propanenitrile	Sun et al., 2008	0.00	Others; isotope of C_6H_{10} on m/z 84 was subtracted
85.0648	C_5H_8O	4.43E-11	PTR-ToF-MS	E-2-pentenal; 3-methyl-3-buten-2-one; E-2-methyl-2-butenal; 3-penten-2-one; 1-penten-3-one	average	Grosjean and Williams, 1992; Jiménez et al., 2009; Davis et al., 2007	0.14	OVOC
85.1012	C_6H_{12}	1.50E-11	PTR-ToF-MS	Fragment of hexanol (Pagonis et al., 2019) [identified by correlation with other GLVs]		Atkinson and Arey, 2003	0.07	GLV
87.0441	$C_4H_6O_2$	2.38E-11	PTR-ToF-MS	2,3-Butanedione; acetic acid ethenyl ester; 2-propenoic acid methyl ester; 4-hydroxy-2-butenal	average	Baker et al., 2005; Teruel et al., 2006; Blanco et al., 2009; Dagaut et al., 1988	0.23	OVOC
87.0805	$C_5H_{10}O$	6.27E-11	PTR-ToF-MS	Pentanal; Z-2-penten-1-ol; 2-Methyl-3-buten-2-ol; 3-methyl-3-buten-1-ol	average	Atkinson and Arey, 2003; IUPAC, 2020; Cometto et al., 2008; Orlando et al., 2001	0.51	GLV
89.0234	$C_3H_4O_3$	1.20E-13	PTR-ToF-MS	Pyruvic acid		IUPAC, 2020	1.1e-4	OVOC
89.0598	$C_4H_8O_2$	6.47E-12	PTR-ToF-MS	1,4-dioxane; formic acid 1-methylethyl ester; ethyl acetate; butyric acid; acetoin; 1-hydroxy-3-butanone	average	Picquet et al., 1998; IUPAC, 2020; Pimentel et al., 2010; Aschmann et al., 2000; Moriarty et al., 2003	0.13	OVOC

95.0161	$C_2H_6O_2S$	3.00E-13	PTR-ToF-MS	Dimethylsulfone		IUPAC, 2020	0.00	Others
95.0492	C_6H_6O	2.80E-11	PTR-ToF-MS	Phenol		IUPAC, 2020	0.03	Others
97.0284	$C_5H_4O_2$	3.51E-11	PTR-ToF-MS	Furfural		Bierbach et al., 1995	0.03	OVOC
97.0648	C_6H_8O	6.78E-11	PTR-ToF-MS	Hexadienal		Colmenar et al., 2014	0.07	
97.1012	C_7H_{12}	2.96E-11	PTR-ToF-MS	Fragment of heptanal (plant odorant)	Heptanal reaction rate coefficient	Atkinson and Arey, 2003	0.03	OVOC
99.0441	$C_5H_6O_2$	4.04E-11	PTR-ToF-MS	Furfuryl alcohol	Furan reaction rate coefficient	Atkinson, 1986	0.33	OVOC
99.0805	$C_6H_{10}O$	4.76E-11	PTR-ToF-MS	*E*-2-hexenal, *Z*-3-hexenal	average	Atkinson et al., 1995; Xing et al., 2012	0.14	GLV
99.1169	C_7H_{14}	4.60E-11	PTR-ToF-MS	Fragment of decene	1-decene reaction rate coefficient	Aschmann and Atkinson, 2008	0.07	MT
101.0598	$C_5H_8O_2$	6.83E-11	PTR-ToF-MS	C5-hydroxycarbonyl (ISOPOOH conversion product on metal surfaces (Mentler, 2018)); oxopentanal	average	Aschmann et al., 2013; St Clair et al., 2016	0.45	OVOC
101.0961	$C_6H_{12}O$	2.70E-11	PTR-ToF-MS	n-hexanal		Atkinson et al., 1995	0.03	GLV
103.0390	$C_4H_6O_3$	6.90E-13	PTR-ToF-MS	Acetic anhydride	Reaction rate coefficient of acetic acid	IUPAC, 2020	3.5e-4	OVOC
103.0754	$C_5H_{10}O_2$	2.66E-11	PTR-ToF-MS	Butanoic acid methyl ester; acetic acid methylethyl ester, 2-methyl-propanoic acid methylester, n-propyl acetate; 1-hydroxy-2-methyl-3-butanone; 1-hydroxy-3-methyl-2-butanone; 5-hydroxy-2-pentanone; pentanoic acid; C5-diol (ISOPOOH conversion product on metal surfaces (Mentler, 2018))	average	Schütze et al., 2010; Ferrari et al., 1996; Aschmann et al., 2000; NCBI, 2006; St Clair et al., 2016	0.02	OVOC
105.0547	$C_4H_8O_3$	4.66E-12	PTR-ToF-MS	Methoxy methylacetate; methoxy ethylformate; ethoxy methylformate	average	O'Donnel et al., 2004	0.00	OVOC
105.0699	C_8H_8	1.45E-11	PTR-ToF-MS	MT fragment (p-cymene)	p-cymene reaction rate coefficient	IUPAC, 2020	0.02	MT
107.0492	C_7H_6O	1.26E-11	PTR-ToF-MS	Benzaldehyde		IUPAC, 2020	0.01	Others
109.0648	C_7H_8O	3.27E-11	PTR-ToF-MS	Anisol, p-cresol, benzylalcohol	average	IUPAC, 2020; Coeur-Tourneur et al., 2010	0.01	MT

109.1012	C_8H_{12}	none	PTR-ToF-MS	Fragment of sesquiterpenes	none		None	none
111.0805	$C_7H_{10}O$	3.83E-11	PTR-ToF-MS	Heptadienal (ox. product of myrcene, ocimene, terpinolene)		Baker et al., 2004	0.03	OVOC
111.1169	C_8H_{14}	3.60E-11	PTR-ToF-MS	Fragment of octanal	Reaction rate of nonanal	Bowman et al., 2003	0.05	OVOC
113.0233	$C_5H_4O_3$	4.04E-11	PTR-ToF-MS	Furoic acid	Reaction rate coefficient of furan	Atkinson, 1986	0.14	OVOC
113.0598	$C_6H_8O_2$	5.80E-11	PTR-ToF-MS	*E*-hexendione; *Z*-hexendione	average	Tuazon et al., 1985	0.13	OVOC
113.0961	$C_7H_{12}O$	4.39E-11	PTR-ToF-MS	*E*-2-Hepten-1-al		Davis et al., 2007	0.03	OVOC
115.0390	$C_5H_6O_3$	3.35E-12	PTR-ToF-MS	Pentanetrione	Reaction rate coefficient of pentanone	Jiménez et al., 2005	0.00	OVOC
115.0754	$C_6H_{10}O_2$	2.82E-11	PTR-ToF-MS	2,5-hexanedione; ethyl-2-butenoate	average	Dagaut et al., 1988; Teruel et al., 2012	0.05	OVOC
115.1118	$C_7H_{14}O$	7.10E-12	PTR-ToF-MS	2-heptanone; 5-methyl-2-hexanone; 2-,4-dimethyl-3-pentanone; heptanal	average	Atkinson and Arey, 2003	0.01	OVOC
117.0546	$C_5H_8O_3$	9.05E-12	PTR-ToF-MS	1-acetyloxy-2-propanone	Reaction rate coefficient as 119.0703	O'Donnel et al., 2004	0.01	OVOC
119.0703	$C_5H_{10}O_3$	7.10E-12	PTR-ToF-MS	Ethoxy ethylformate; ethoxy methylacetate	average	O'Donnel et al., 2004	0.01	OVOC
119.0856	C_9H_{10}	1.45E-11	PTR-ToF-MS	Fragment of p-cymene	Reaction rate coefficient of p-cymene	Atkinson and Arey, 2003	0.01	MT
123.0441	$C_7H_6O_2$	1.20E-12	PTR-ToF-MS	Benzoic acid	Rate coefficient of benzene	IUPAC preferred value	0.00	Others
125.0598	$C_7H_8O_2$	7.35E-11	PTR-ToF-MS	Guaiacol		Coeur-Tourneur et al., 2010	0.03	OVOC
127.1118	$C_8H_{14}O$	4.05E-11	PTR-ToF-MS	*E*-2-octenal		Gao et al., 2009	0.04	OVOC
129.1274	$C_8H_{16}O$	1.08E-10	PTR-ToF-MS	Octenol	Reaction rate coefficient of hexenol	Atkinson et al., 1995	0.02	OVOC
133.1012	$C_{10}H_{12}$	5.08E-11	PTR-ToF-MS	Cymenene (dimethyl styrene)	Reaction rate coefficient of styrene	IUPAC, 2020	0.02	MT
135.1169	$C_{10}H_{14}$	1.45E-11	PTR-ToF-MS	p-cymene		Atkinson and Arey, 2003	0.01	MT
139.1118	$C_9H_{14}O$	5.49E-11	PTR-ToF-MS	Monoterpene oxidation products (4-acetyl-2-cyclohexene; nopinone; camphenilone; sabinaketone)	average	Atkinson and Aschmann, 1993	0.14	OVOC
143.1067	$C_8H_{14}O_2$	7.84E-11	PTR-ToF-MS	*Z*-3-hexenyl acetate		Atkinson et al., 1995	0.05	GLV
143.1431	$C_9H_{18}O$	3.60E-11	PTR-ToF-MS	Nonanal		Bowman et al., 2003	0.01	OVOC

149.1325	$C_{11}H_{16}$	none	PTR-ToF-MS	Sesquiterpene fragmentation product		none	none	none
151.0995	$C_{10}H_{14}O$	4.90E-11	PTR-ToF-MS	Thymol, carvol	Reaction rate coefficient of cresol	IUPAC, 2020	0.04	MT
153.0547	$C_8H_8O_3$	1.20E-12	PTR-ToF-MS	Methyl salicylate	Reaction rate coefficient of benzene	IUPAC, 2020	0.00	OVOC
153.1274	$C_{10}H_{16}O$	4.30E-12	PTR-ToF-MS	Camphor		Atkinson and Arey, 2003	0.00	MT
155.1067	$C_9H_{14}O_2$	1.24E-11	PTR-ToF-MS	Arbusculone, C9 unsaturated esters	Average of tetrahydrofuran and methoxy ethylformate reaction rate coefficients	O'Donnel et al., 2004; Moriarty et al., 2003	0.01	OVOC
155.1425	$C_{10}H_{18}O$	2.72E-11	PTR-ToF-MS (sum), speciation by TD-GC-TOF-MS	Eucalyptol (1,8-cineole), linalool	Weighted average according to speciation: 89% eucalyptol, 11% linalool	Atkinson et al., 1995; Ceacero-Vega et al., 2011	0.01	MT
157.1586	$C_{10}H_{20}O$	9.24E-11	PTR-ToF-MS	Menthol, citronellol	Average	Ham et al., 2006; Ceacero-Vega et al., 2012	0.05	MT
205.1951	$C_{15}H_{24}$	*Dry season:* 7.12E-11 (80 m), 6.77E-11 (150 m), 6.48E-11 (320 m) *Wet season:* 7.06E-11 (80 m), 6.37E-11 (150 m), 6.11E-11 (320 m)	PTR-ToF-MS (sum), speciation by TD-GC-TOF-MS	Sesquiterpenes	Weighted average according to time-dependent speciation. *Dry season average:* α-copaene : cyperene : longifolene : cyclosativene = 44:26:3:27 (80 m), 37:24:14:25 (150 m), 35:13:40:12 (320 m) *Wet season average:* α-copaene : cyperene : longifolene : cyclosativene = 46:19:19:16 (80 m), 29:22:32:17 (150 m). For cyperene, the reaction rate coefficient of α-cedrene was used, and for cyclosativene, the one of longifolene.	IUPAC, 2020	0.08	SQT

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Table S2. Contributions of different classes of compounds during daytime rain events compared to dry daytime periods (calculated from hourly OH reactivity averages).

OH reactivity contributed by	**Rain (daytime, n= 18, ± standard deviation)**	**Dry (daytime, n=81, ± standard deviation)**
Isoprene	32 ± 18 %	36 ± 19 %
Monoterpenes	3 ± 1 %	6 ± 4 %
OVOC	16 ± 6 %	22 ± 10 %
GLV	6 ± 2 %	9 ± 4 %
SQT	1 ± 0.3 %	1 ± 0.9%
Inorganics	3 ± 0.1 %	3 ± 0.1 %
Others	0 %	0 %
Unattributed fraction	39 ± 19 %	23 ± 25 %