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Supplement of

Speciated measurements of semivolatile and intermediate volatility organic compounds (S/IVOCs) in a pine forest during BEACHON-RoMBAS 2011

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Table S1. Full list of tentatively identified compounds measured by SV-TAG

System Name	Actual Name	Formula	CAS	Assigned Internal Std	Quant Ions	Assigned External Std	Alkane RI	Lee RI	Reference Alkane RI	Reference Lee RI	RI Reference	10th percentile concentration (ng/m3)	90th percentile concentration (ng/m3)	Median concentration (ng/m3)
Alkanes														
C14	n-Tetradecane	C14H30	629-59-4	C16D	57;71	C14	1401	240.00				0.44	1.28	0.69
ALKANE1	Branched alkane isomer	n/a	629-62-9	C16D	57;71	C15	1463	250.31				0.28	0.65	0.42
C15	n-Pentadecane	C15H32	629-62-9	C16D	57;71	C15	1500	256.24				0.63	1.28	0.90
C16	n-Hexadecane	C16H34	544-76-3	C16D	57;71	C16	1600	272.12				0.68	1.33	0.90
C17	n-Heptadecane	C17H36	629-78-7	C16D	57;71	C17	1700	287.57				0.26	0.88	0.47
PRISTANE	Pristane	C19H40	1921-70-6	C16D	57;71	PRISTANE	1706	288.58				0.21	0.45	0.29
C18	n-Octadecane	C18H38	593-45-3	C20D	57;71	C18	1800	302.67				0.22	0.71	0.38
PHYTANE	Phytane	C20H42	638-36-8	C20D	57;71;43	PHYTANE	1810	304.19				0.12	0.33	0.19
C19	n-Nonadecane	C19H40	629-92-5	C20D	57;71	C19	1900	317.54				0.29	1.03	0.59
C20	n-Eicosane	C20H42	112-95-8	C20D	57;71	C20	2000	332.10				0.30	0.73	0.47
C21	n-Heneicosane	C21H44	629-94-7	C20D	57;71	C21	2101	346.43				0.62	1.41	1.00
C22	n-Docosane	C22H46	629-97-0	C24D	57;71	C22	2200	360.51				0.64	1.45	0.92
C23	n-Tricosane	C23H48	638-67-5	C24D	57;71	C23	2300	374.37				0.98	1.77	1.34
C24	n-Tetracosane	C24H50	646-31-1	C24D	57;71	C24	2400	388.09				0.70	1.25	0.97
C25	n-Pentacosane	C25H52	629-99-2	C24D	57;71	C25	2500	401.66				0.39	0.66	0.49
PAHs														
BIPHENYL	Biphenyl	C12H10	92-52-4	PHEND	154;152	ACENAPHTHENE	1378	236.14			236.59 Rostad	0.30	0.68	0.42
DIMETHYLNAPHTHALENE	Naphthalene, 1,6-dimethyl-	C12H12	575-43-9	PHEND	156;141	FLUORENE	1421	243.42			244.06 Rostad	0.09	0.39	0.21
ACENAPHTHYLENE	Acenaphthylene	C12H8	208-96-8	PHEND	152;151	ACENAPHTHYLENE	1448	247.89			248.75 Rostad	0.06	0.39	0.12
METHYLBIPHENYL	Biphenyl, 3-methyl	C13H12	643-93-6	PHEND	168;153	FLUORENE	1484	253.67			254.33 Rostad	0.10	0.43	0.17
ISOP_NAPHTHALENE	1-Isopropenyl-naphthalene or isomer	C13H12	1855-47-6	PHEND	153;126;168	FLUORENE	1494	255.25				0.12	0.49	0.20
TETRAMETHYLTETRALIN	Naphthalene, 1,2,3,4-tetrahydro-5,6,7,8-tetramethyl-	C14H20	19063-11-7	C16D	173;188	FLUORENE	1522	259.90				0.44	1.24	0.74
FLUORENE	Fluorene	C13H10	86-73-7	PHEND	166;165	FLUORENE	1583	269.52			270.77 Rostad	0.15	1.06	0.33
DIMETHYLBIPHENYL1	3,3'-Dimethylbiphenyl	C14H14	612-75-9	PHEND	182	FLUORENE	1589	270.44			271.27 Rostad	0.04	0.13	0.06
DIMETHYLBIPHENYL2	Dimethylbiphenyl isomer	C14H14	620-47-3	PHEND	182;167	FLUORENE	1602	272.40				0.06	0.13	0.09
DIMETHYLBIPHENYL3	4,4'-Dimethylbiphenyl	C14H14	620-47-3	PHEND	182;167	FLUORENE	1609	273.64			274.08 Rostad	0.04	0.07	0.05
ISOPROPYLBIPHENYL	1,1'-Biphenyl, 3-(1-methylethyl)-	C15H16	20282-30-8	PHEND	196;181	PHENANTHRENE	1692	286.39				0.02	0.05	0.03
TRIMETHYLPHENYLINDENE	1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	C17H17	3910-35-8	PHEND	221;143;91	PHENANTHRENE	1722	290.94				0.04	0.12	0.06
PHENANTHRENE	Phenanthrene	C14H10	85-01-8	PHEND	178;152	PHENANTHRENE	1782	300.07			300 Rostad	0.42	2.41	0.88
ANTHRACENE	Anthracene	C14H10	120-12-7	PHEND	178;152	ANTHRACENE	1793	301.63			301.75 Rostad	0.24	0.53	0.38
PHENYLNAPHTHALENE	2-Phenyl-naphthalene	C16H12	35465-71-5	PHEND	203;204	PHENANTHRENE	1860	311.62			312.74 Rostad	0.03	0.09	0.05
METHYLPHENANTHRENE	Methylphenanthrene isomer	C15H12	832-69-9	PHEND	192;191	PHENANTHRENE	1902	317.76				0.03	0.14	0.06
METHYLANTHRACENE	Methylanthracene isomer	C15H12	613-12-7	PHEND	192;191	ANTHRACENE	1926	321.26			321.47 Rostad	0.08	0.21	0.13
FLUORANTHENE	Fluoranthene	C16H10	206-44-0	PYRD	202	FLUORANTHENE	2066	341.54			344.68 Knobloch	0.21	0.86	0.36
PYRENE	Pyrene	C16H10	129-00-0	PYRD	202	PYRENE	2119	348.99			352.9 Knobloch	0.18	0.44	0.30
CHRYSENE	Chrysene	C18H12	218-01-9	CHRYSD	228;226	CHRYSENE	2470	397.64			400	0.55	0.87	0.67
Oxygen- and Sulfur-Containing PACs														
DIMETHYLINDANONE	1H-Inden-1-one, 2,3-dihydro-3,3-dimethyl-	C11H12O	26465-81-6	ANTHQD	160;145;115	BENZOPHENONE	1366	234.26				0.00	0.01	0.00
NAPHTHOQUINONE	Naphthoquinone	C10H6O2	130-15-4	ANTHQD	158;76	BENZOPHENONE	1408	241.30			241.6 NIST Webbook	0.01	0.09	0.01
DIMETHOXYBENZALDEHYDE	Dimethoxybenzaldehyde isomer	C9H10O3	613-45-6	ANTHQD	166;160;159	BENZOPHENONE	1435	245.64				0.31	1.83	0.69
METHYLBENZOFURANONE	1(3H)-Isobenzofuranone, 5-methyl-	C9H8O2	54120-64-8	ANTHQD	119;148	BENZOPHENONE	1475					0.02	0.11	0.06
DIBENZOFURAN	Dibenzofuran	C12H8O	132-64-9	ANTHQD	168;139	BENZOPHENONE	1516	258.90			259.75 Rostad	0.45	4.69	1.20
DIETHYLPHTHALATE	Diethyl Phthalate	C12H14O4	84-66-2	ANTHQD	149;177	BENZOPHENONE	1593	271.13			269.9 NIST Webbook	0.01	0.03	0.02
METHYLDIBENZOFURAN	Dibenzofuran, 4-methyl-	C13H10O	7320-53-8	ANTHQD	182;181;152	BENZOPHENONE	1622	275.56				0.04	0.42	0.09
BENZOPHENONE	Benzophenone	C13H10O	119-61-9	ANTHQD	182;105;77	BENZOPHENONE	1630	276.77	1626		Adams	0.15	0.28	0.21
XANTHENE	9H-Xanthene	C13H10O	92-83-1	ANTHQD	181;182;152	XANTHONE	1636	277.82			281.04 Rostad	0.11	0.65	0.23
DIBENZOPYRAN	6H-Dibenzo[b,d]-pyran	C13H10O	229-95-8	ANTHQD	182;181	BENZOPHENONE	1647	279.43				0.01	0.07	0.02
FLUORENONE	9H-Fluoren-9-one	C13H8O	486-25-9	ANTHQD	180;152	9HFLUORENONE	1739	293.55			293.88 Rostad	0.42	3.34	1.02

System Name	Actual Name	Formula	CAS	Assigned Internal Std	Quant Ions	Assigned External Std	Alkane RI	Lee RI	Reference	Reference	RI Reference	10th percentile	90th percentile	Median	
									Alkane RI	Lee RI		concentration (ng/m3)	concentration (ng/m3)	concentration (ng/m3)	
DIBENZOTHIOPHENE	Dibenzothiophene	C12H8S	132-65-0	PHEND	184;139	PHENANTHRENE	1755	295.95			296.03	Rostad	0.07	0.49	0.15
BENZOICACIDPHENYLETHYLESTER	Benzoic acid, 2-phenylethyl ester	C15H14O2	94-47-3	ANTHQD	77;104	ANTHRAQUINONE	1857	311.19					0.06	0.33	0.14
METHYLDIBENZOTHIOPHENE	Dibenzothiophene, 4-methyl-	C13H10S	7372-88-5	PHEND	198	PHENANTHRENE	1859	311.49			311.95	NIST	0.02	0.06	0.04
ANTHRAQUINONE	Anthraquinone	C14H8O2	84-65-1	ANTHQD	208;180;152	ANTHRAQUINONE	1973	328.19			330.5	Knobloch	0.52	1.95	0.85
NAPHTHALICANHYDRIDE	1,8-Naphthalic anhydride	C12H6O3	81-84-5	ANTHQD	198;154;126	ANTHRAQUINONE	2040	337.84			340.8	Knobloch	0.01	0.11	0.03
CYCLOPENTAPHENANTHRENONE	Cyclopenta(def)phenanthrenone	C15H8O	5737-13-3	ANTHQD	204;176	ANTHRAQUINONE	2050	339.26			342.9	Knobloch	0.01	0.09	0.03
Sesquiterpenoids and Diterpenoids															
LONGIFOLENE	Longifolene	C15H24	475-20-7	C16D	161;189;204	LONGIFOLENE	1392	238.60	1400			Adams	0.14	1.12	0.45
BCARYOPHYLLENE	β-caryophyllene	C15H24	87-44-5	C16D	161;189;204	BCARYOPHYLLENE	1412	241.85	1408			Adams	0.32	2.63	1.07
AROMADENDRENE	Aromadendrene	C15H24	489-39-4	C16D	204;189	SQT avg	1430	244.85	1439			Adams	below quantification limits		
HUMULENE	Humulene	C15H24	6753-98-6	C16D	204;189	SQT avg	1457	249.38	1452			Adams	below quantification limits		
ALLOAROMADENDRENE	Alloaromadendrene	C15H24	25246-27-9	C16D	161;189;204	ALLOAROMADENDRENE	1470	251.36	1458			Adams	0.42	1.65	0.77
SQT202_1	β-vatirenene isomer	C15H22	19419-67-1	C16D	202;187;145	SQT avg	1471	251.57					0.20	0.94	0.36
SQT204	C15H24 isomer	C15H24	489-39-4	C16D	204;189	SQT avg	1481	253.28					0.43	0.84	0.61
SQT202_2	β-vatirenene isomer	C15H22	19419-67-1	C16D	202;187;145	SQT avg	1501	256.51					0.21	1.55	0.67
MUUROLENE	α-Muurolene	C15H24	31983-22-9	C16D	204	SQT avg	1504	256.94	1500			Adams	0.15	0.62	0.28
CUPARENE	Cuparene	C15H22	16982-00-6	C16D	202;132	SQT avg	1511	258.12	1504			Adams	0.52	1.94	1.02
CALAMENENE	Calamenene	C15H22	483-77-2	C16D	159	SQT avg	1528	260.73	1528			Adams	1.19	7.96	3.02
SQT202_3	β-vatirenene isomer	C15H22	19419-67-1	C16D	202;187;145	SQT avg	1543	263.16					0.15	0.74	0.35
CADINATRIENE	Cadina-1(10),6,8-triene	C15H22	1460-96-4	C16D	202;187;159	SQT avg	1593	271.06					0.09	0.58	0.26
CADALENE	Cadalene	C15H18	483-78-3	C16D	198;183;168	SQT avg	1680	284.51	1675			Adams	1.05	4.97	2.15
CADALENE2	Cadalene isomer	C15H18	483-78-3	C16D	198;183;168	SQT avg	1706	288.58					0.12	0.34	0.19
DITERPENE1	19-norabieta-8,11,13-triene	C19H28	n/a	PYRD	241;185;159	RETENE	1988	330.31	1969			Bleton	0.11	0.31	0.18
DITERPENE2	18-norabieta-8,11,13-triene	C19H28	n/a	PYRD	241;159	RETENE	2026	335.73	2007			Bleton	0.21	0.65	0.36
DITERPENE3	Abietatriene	C20H30	19407-28-4	PHEND	270;255;159	RETENE	2066						0.10	0.17	0.13
RETENE	Retene	C18H18	483-65-8	PYRD	219;234;204	RETENE	2224	363.75			355.93	Bastow	0.06	0.18	0.10
METHYLRETENE1	9-methylretene	C19H20	n/a	PYRD	248;233;218	RETENE	2352	381.52			367.36	Bastow	0.03	0.21	0.07
METHYLRETENE2	2-methylretene	C19H20	n/a	PYRD	248;233;218	RETENE	2389	386.54			376.91	Bastow	0.01	0.18	0.05
Other Oxygen-Containing Compounds															
COUMARIN	Coumarin	C9H6O2	583-17-5	ANTHQD	146;119;90;63	BENZOPHENONE	1436	245.89	1432			Adams	0.58	1.46	0.86
DODECENOICACID	Dodecenoic acid or isomer	C12H24O2	2430-94-6	ANTHQD	41;55	C16FAME	1536	262.03					1.44	6.59	3.02
LONGICAMPHENYLONE	(+)-Longicamphenylone	C14H22O	58560-59-1	ANTHQD	107;41;93	BENZOPHENONE	1569	267.37	1562			Adams	0.37	3.25	1.30
TETRADECENOICACID	Myristoleic acid or isomer	C14H28O2	544-64-9	ANTHQD	55;41;83	C16FAME	1737	293.21					1.34	6.59	3.08
TRIMETHYLPENTADECANONE	2-Pentadecanone, 6,10,14-trimethyl-	C18H36O	502-69-2	ANTHQD	43;57;58	C16FAME	1844	309.27					1.24	2.37	1.64
HEXADECENOICACID	Palmitoleic acid	C16H32O2	n/a	ANTHQD	55;41	C16FAME	1941	323.50					0.93	4.26	1.70
MANOYLOXIDE	Manoyl Oxide	C20H34O	596-84-9	ANTHQD	275;257;192	C16FAME	2004	332.66	1987			Adams	0.30	0.64	0.48
DEHYDROABIETICACIDMETHYLESTER	Dehydroabietic acid, methyl ester	C21H30O2	1235-74-1	ANTHQD	239	C18FAME	2346	380.75	2336			Isidorov	0.34	0.88	0.56

Table S2. List of external standards

System Name	Actual Name	Quant Ions	CAS
C14	n-Tetradecane	57;71	629-59-4
C15	n-Pentadecane	57;71	629-62-9
C16	n-Hexadecane	57;71	544-76-3
C17	n-Heptadecane	57;71	629-78-7
PRISTANE	Pristane	57;71	1921-70-6
C18	n-Octadecane	57;71	593-45-3
PHYTANE	Phytane	57;71	638-36-8
C19	n-Nonadecane	57;71	629-92-5
C20	n-Eicosane	57;71	112-95-8
C21	n-Heneicosane	57;71	629-94-7
C22	n-Docosane	57;71	629-97-0
C23	n-Tricosane	57;71	638-67-5
C24	n-Tetracosane	57;71	646-31-1
C25	n-Pentacosane	57;71	629-99-2
C26	n-Hexacosane	57;71	630-01-3
C27	n-Heptacosane	57;71	593-49-7
BENZOPHENONE	Benzophenone	182;105;77	119-61-9
9HFLUOREN9ONE	9H-Fluoren-9-one	180;152	486-25-9
ANTHRAQUINONE	Anthraquinone	208;180;152	84-65-1
XANTHONE	Xanthone	196;168;139	90-47-1
ACENAPHTHENE	Acenaphthene	153;152;154	83-32-9
ACENAPHTHYLENE	Acenaphthylene	152;76	208-96-8
FLUORENE	Fluorene	166;165	86-73-7
PHENANTHRENE	Phenanthrene	178	85-01-8
ANTHRACENE	Anthracene	178	120-12-7
FLUORANTHENE	Fluoranthene	202	206-44-0
PYRENE	Pyrene	202	129-00-0
BENZANTHRACENE	Benz[a]anthracene	228;226	56-55-3
CHRYSENE	Chrysene	228;226	218-01-9
RETENE	Retene	219;234;204	483-65-8
LONGIFOLENE	Longifolene	161;189;204	475-20-7
BCARYOPHYLLENE	β -caryophyllene	161;189;204	87-44-5
ALLOAROMADENDRENE	Alloaromadendrene	161;189;204	489-39-4
C16FAME	Methyl palmitate	74;87	112-39-0
C18FAME	Methyl stearate	74;87	112-61-8

Table S3. List of deuterated internal standards

System Name	Actual Name	Quant Ions
MTHXYBENZALD_D	4-methoxy-d3-benzaldehyde	138;139
PHTHANHYRD	Phthalic acid-d4	108;80
C16D	Hexadecane-d34	66;82
PHEND	Phenathrene-d10	188
ANTHRAQD	Anthraquinone-d8	160;188;216
C20D	Eicosane-d42	66;82
PYRENED	Pyrene-d10	212
C24D	Tetracosane-d50	66;82
CHYRSENE	Chrysene-d12	240
C28D	Octacosane-d58	66;82

Table S4. Correlation coefficients (r) of compounds measured by SV-TAG with PMF factors

	Factor 1	Factor 2	Factor 3		Factor 1	Factor 2	Factor 3
C14	0.07	0.30	-0.14	DIMETHYLINDANONE	-0.37	0.73	0.25
ALKANE1	0.67	-0.07	-0.07	NAPHTHOQUINONE	-0.48	0.75	0.30
C15	0.19	0.29	0.31	DIMETHOXYBENZALDEHYDE	0.49	-0.20	0.11
C16	-0.08	0.56	0.16	METHYLBENZOFURANONE	0.62	-0.43	0.18
C17	-0.34	0.67	0.55	DIBENZOFURAN	-0.31	0.92	-0.09
PRISTANE	-0.33	0.79	0.23	DIETHYLPHTHALATE	-0.08	-0.05	0.25
C18	-0.40	0.75	0.49	METHYLDIBENZOFURAN	-0.39	0.96	0.09
PHYTANE	-0.35	0.78	0.27	BENZOPHENONE	0.13	0.18	0.01
C19	-0.37	0.59	0.61	XANTHENE	-0.32	0.96	0.03
C20	-0.21	0.35	0.67	DIBENZOPYRAN	-0.38	0.95	0.09
C21	-0.01	0.24	0.58	FLUORENONE	-0.43	0.95	0.13
C22	0.25	0.10	0.38	DIBENZOTHIOPHENE	-0.46	0.98	0.09
C23	0.45	0.04	-0.03	BENZOICACIDPHENYLETHYLESTER	-0.03	0.11	0.71
C24	0.56	-0.21	-0.12	METHYLDIBENZOTHIOPHENE	-0.21	0.73	0.28
C25	0.56	-0.10	-0.33	ANTHRAQUINONE	-0.53	0.64	0.59
				NAPHTHALICANHYDRIDE	-0.39	0.49	0.61
BIPHENYL	-0.48	0.78	0.31	CYCLOPENTAPHENANTHRENONE	-0.49	0.87	0.29
DIMETHYLNAPHTHALENE	-0.02	0.63	-0.10				
ACENAPHTHYLENE	-0.37	0.93	-0.02	LONGIFOLENE	0.53	0.13	0.18
METHYLBIPHENYL	-0.29	0.89	0.02	BCARYOPHYLLENE	0.56	0.18	0.15
ISOP_NAPHTHALENE	-0.38	0.93	0.11	ALLOAROMADENDRENE	0.84	-0.22	-0.33
TETRAMETHYLTETRALIN	0.60	-0.01	0.15	SQT202_1	0.76	-0.25	-0.29
FLUORENE	-0.25	0.91	-0.11	SQT204	0.80	-0.17	-0.33
DIMETHYLBIPHENYL1	-0.27	0.91	0.01	SQT202_2	0.89	-0.49	-0.26
DIMETHYLBIPHENYL2	0.47	0.42	-0.22	MUUROLENE	0.73	-0.18	-0.24
DIMETHYLBIPHENYL3	0.13	0.61	-0.06	CUPARENE	0.73	-0.25	-0.35
ISOPROPYLBIPHENYL	-0.13	0.80	-0.06	CALAMENENE	0.89	-0.21	-0.40
TRIMETHYLPHENYLINDENE	-0.33	0.87	0.00	SQT202_3	0.94	-0.37	-0.31
PHENANTHRENE	-0.36	0.91	-0.03	CADINATRIENE	0.93	-0.38	-0.34
ANTHRACENE	0.10	0.23	-0.02	CADALENE	0.85	-0.27	-0.20
PHENYLNAPHTHALENE	-0.31	0.83	0.19	CADALENE2	0.60	0.04	-0.16
METHYLPHENANTHRENE	-0.45	0.80	0.44	DITERPENE1	0.60	-0.16	-0.16
METHYLANTHRACENE	-0.25	0.66	0.40	DITERPENE2	0.61	-0.23	-0.20
FLUORANTHENE	-0.47	0.63	0.61	DITERPENE3	0.52	0.09	0.10
PYRENE	-0.25	0.63	0.42	RETENE	0.34	-0.07	-0.07
CHRYSENE	0.34	0.26	-0.21	METHYLRETENE1	0.45	-0.14	-0.24
				METHYLRETENE2	0.50	-0.09	-0.37
				COUMARIN	0.54	0.01	-0.04
				DODECENOICACID	0.15	0.30	0.05
				LONGICAMPHENYLONE	0.78	-0.43	-0.13
				TETRADECENOICACID	-0.29	0.42	0.60
				TRIMETHYLPENTADECANONE	-0.15	0.47	0.58
				HEXADECENOICACID	-0.39	0.48	0.64
				MANOYLOXIDE	0.27	0.27	0.17
				DEHYDROABIETICACIDMETHYLESTER	0.28	-0.03	0.23

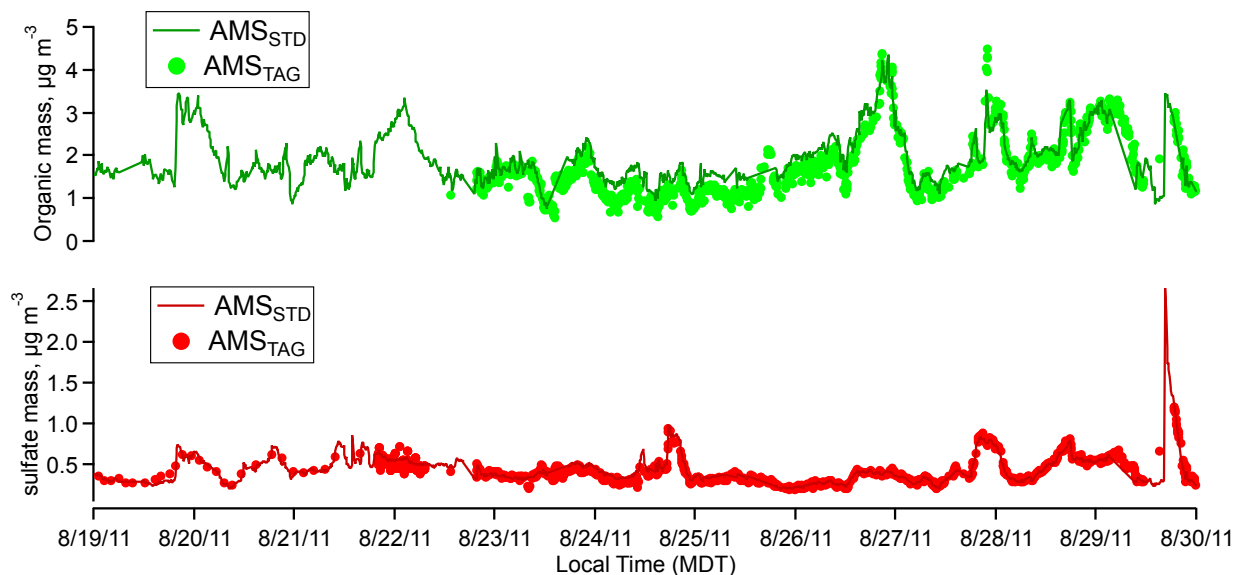


Figure S5. Time series of organic (green) and sulfate (red) mass concentrations. The markers denote measurements by the HR-ToF-AMS in the combined SV-TAG-AMS instrument (AMS_{TAG}). The line denote measurements by a colocated standalone HR-ToF-AMS (AMS_{STD}).

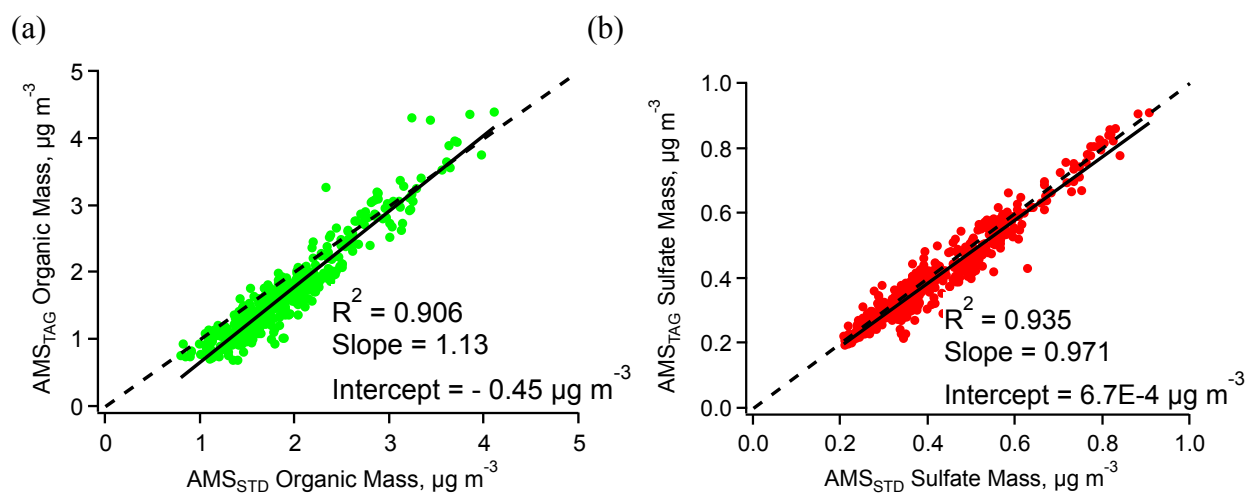


Figure S6. Scatter plot of (a) organic and (b) sulfate mass concentrations as measured by the AMS in combined TAG-AMS instrument (AMS_{TAG}) and colocated standalone AMS (AMS_{STD}). The solid line is the best-fit line for the data, and the dashed line denotes 1:1 relationship.

Text S7. Error in integrating chromatographic peaks

In this work, we assume that major source of imprecision is the error in drawing the baseline for peak integrations. Here we determine the error for each compound from the sample giving the median peak area for that compound. Different integration baselines were drawn for the same peak, and the precision was determined to be the range in peak areas from integrating using different baselines. Examples of error calculations are shown below. The beginning of a peak is usually well defined, with an obvious rise in signal from the baseline. On the contrary, the end of the peak is often more difficult to define, as the signal can drop very slowly to its baseline. Such occurrences, known as peak tailing, can be caused by finite mixing volumes in the GC flow path, or by condensation of analytes onto surfaces or active sites downstream of the column. Compounds that have wider peaks or lower signal/noise are expected to have greater errors.

Example 1: Compounds with high S/N ratio (Anthraquinone)

In our samples, anthraquinone is highly abundant, and has a high S/N ratio (the peak height/baseline ratio is consistently >100). In the below figure, we draw two integration baselines: The first integration baseline was drawn from the beginning of the peak to where the signal returns to twice the signal baseline. The second integration baseline was drawn from the start of the peak to where the signal returns to the signal baseline. As the peak height of anthraquinone is much greater than the signal baseline, there is only a small difference (less than 5%) in peak areas calculated from these two baselines.

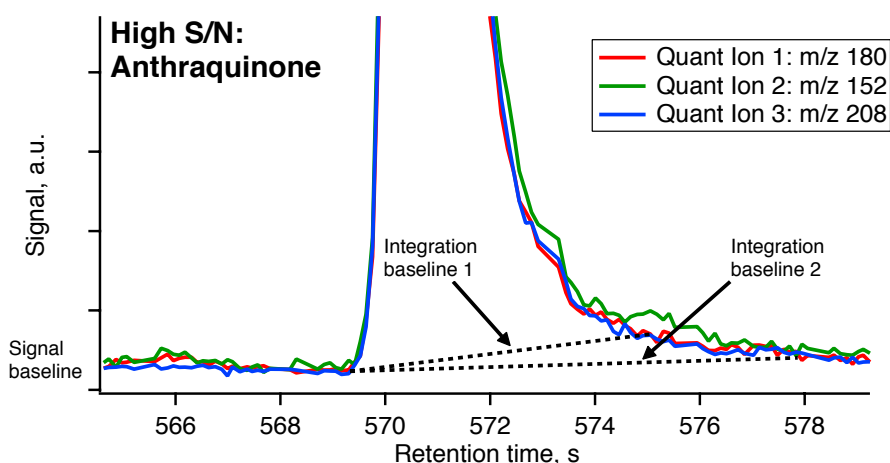


Figure S8. Estimating error in calculating peak area for anthraquinone.

Example 2: Compounds with low S/N ratio (Naphthalic Anhydride)

Naphthalic anhydride is one of the least abundant compounds detected (see Table S1 for range of concentrations). Two baselines are drawn similar to example 1, and they give very different peak areas (difference of 23%). Therefore, the precision in integrating naphthalic anhydride peaks is expected to be greater than compounds that have higher S/N. Therefore, for naphthalic anhydride, we estimate the integration error to be $\pm 12\%$.

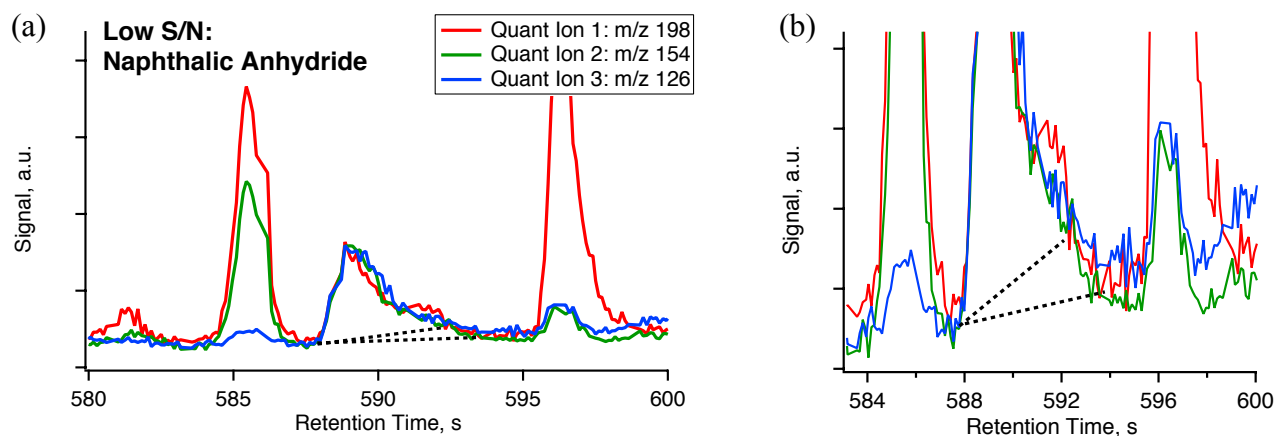


Figure S9. (a) Estimating error in calculating peak area for naphthalic anhydride. Panel (b) presents a zoomed-in view of the naphthalic anhydride peak and the integration baselines.

This process was performed manually for each compound and each day, using the measurement with the median value of the day. These errors are used in the PMF model.

Table S10. Correlation coefficients (r) of PMF factors with other measurements. Aerosol species were measured by the AMS, and the volatile organic compounds are measured by PTR-TOF-MS. All positive correlations greater than 0.4 or negative correlations less than -0.4 are highlighted. Correlation coefficients of PMF factors with TAG compounds are shown in Table S4.

Measurement	Correlation with Factor 1	Correlation with Factor 2	Correlation with Factor 3	Measurement	Correlation with Factor 1	Correlation with Factor 2	Correlation with Factor 3
Aerosol species (AMS):				Meteorological parameters:			
Ammonium	-0.07	0.19	-0.03	Precipitation	-0.22	0.03	0.21
Chloride	-0.11	0.02	0.05	Pressure	0.08	-0.42	0.27
Nitrate	0.14	-0.03	-0.18	Relative Humidity	0.56	-0.62	-0.23
Organic	0.32	-0.04	-0.20	Temperature	-0.61	0.65	0.28
Sulfate	-0.18	0.29	0.12	Wind Direction	0.37	-0.41	-0.04
f ₄₃	0.51	-0.47	-0.23	Wind Speed	-0.53	0.50	0.18
f ₄₄	-0.40	0.24	0.01				
f ₅₇	-0.06	0.06	-0.06	Volatile organic compounds (PTR-TOF-MS):			
f ₆₀	-0.09	0.03	-0.01	acetaldehyde	0.12	0.01	0.23
f _{60,sub} *	-0.35	0.05	0.21	acetone + propanal	0.03	0.15	0.06
H/C	0.24	-0.19	-0.01	acetonitrile	-0.10	0.48	-0.28
O/C	-0.28	0.12	0.06	benzene	0.11	0.05	-0.22
				MBO + isoprene	-0.18	0.33	0.15
Trace gases:				methyl ethyl ketone	-0.01	0.13	-0.12
SO ₂	-0.20	0.44	0.17	methanol	0.36	-0.05	0.03
CO ₂	0.65	-0.54	-0.21	methyl vinyl ketone + methacrolein	-0.06	0.44	0.02
CO	0.02	0.47	0.18	total monoterpenes	0.41	-0.32	0.10
H ₂ O	0.23	-0.37	-0.04	total sesquiterpenes	0.51	-0.19	0.17
NO ₂	0.29	0.00	-0.25	toluene	0.38	-0.24	-0.09
NO _x	0.32	-0.02	-0.27				
NO	0.48	-0.23	-0.37	Correlation between factors:			
O ₃	-0.76	0.59	0.41	Factor 1	n/a	-0.52	-0.40
				Factor 2	-0.52	n/a	0.10
				Factor 3	-0.40	0.10	n/a

* Fraction of *m/z* 60 after subtraction of background SOA (0.3% of AMS organic concentration)

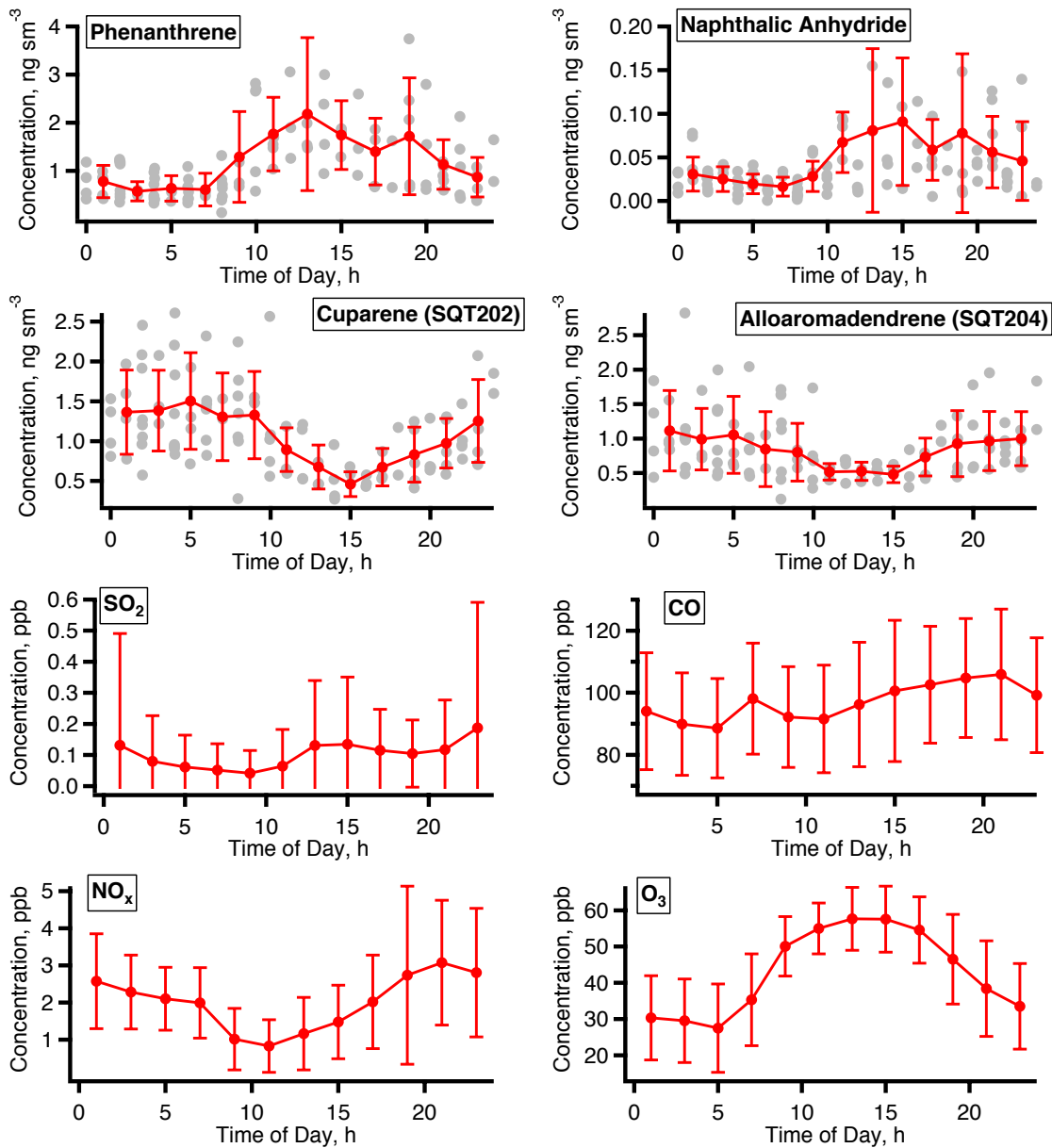


Figure S11. Diurnal trends of selected compounds and trace gases. The grey markers represent the concentrations of the different species Aug 19 and Aug 31 grouped by hour of day. The red markers represent the diel averages and the error bars are the standard deviation for each hour of the day.

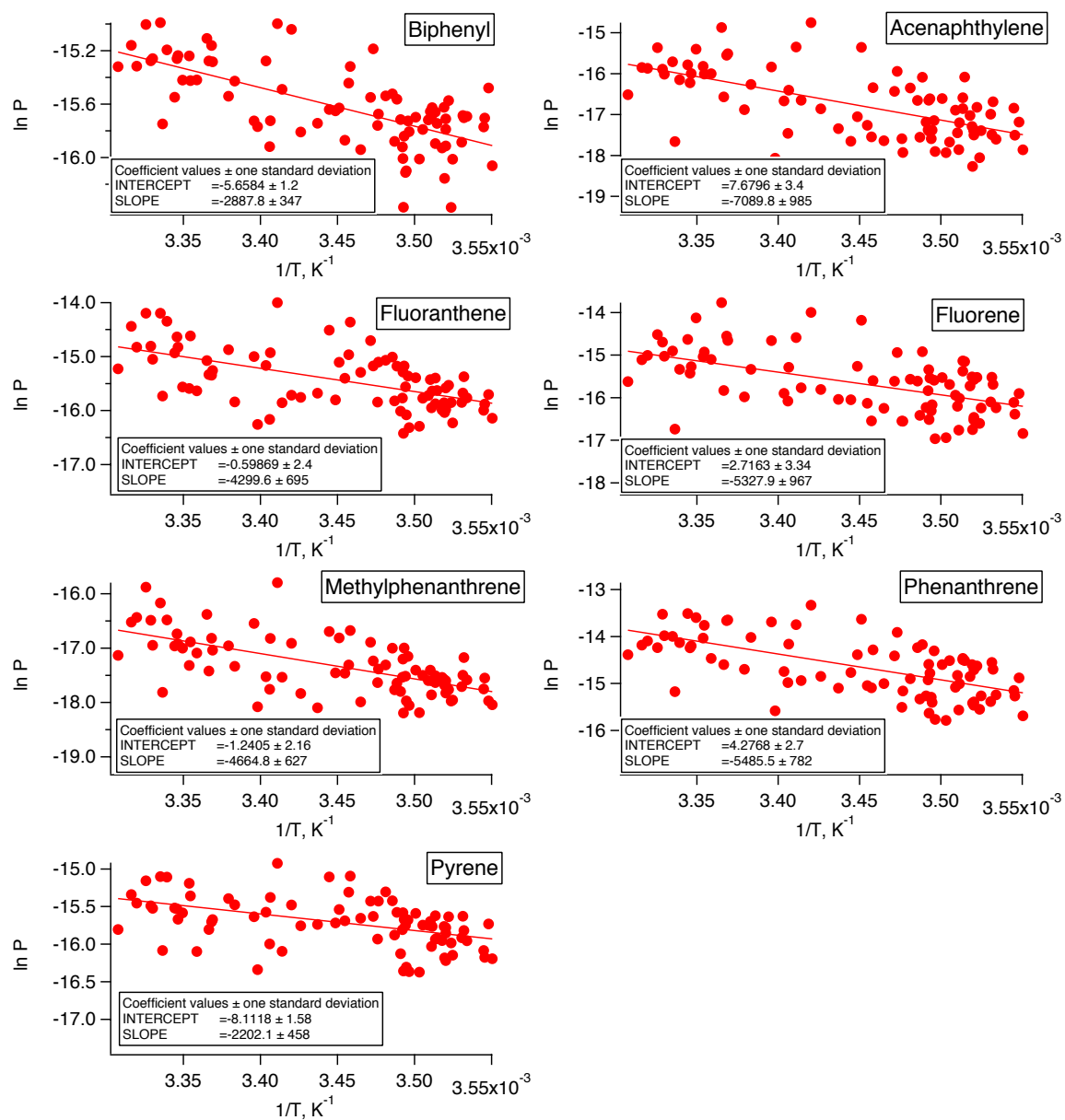


Figure S12. Clausius-Clapeyron plot of select PAHs. The enthalpy for volatilization (ΔH^*) of each compound is derived from the slope.

Table S13. Summary of field and experimental ΔH values. ΔH^* are enthalpies of volatilization derived in this work. ΔH_H are experimental Henry's Law enthalpies from Bamford et al. (1999). ΔH_{vap} are enthalpies of vaporization from a critical review by Roux et al. (2008) and Chickos and Hanshaw (2004). ΔH_{OS} are enthalpies of volatilization from field measures in the Athabasca oil sands region (Hsu et al., 2015).

Compound	ΔH^* , kJ/mol	ΔH_H , kJ/mol	ΔH_{vap} , kJ/mol	ΔH_{OS} , kJ/mol
<i>n</i> -Hexadecane	14.7 ± 3.4	–	82	–
<i>n</i> -Heptadecane	30.1 ± 4.8	–	86.3	–
Pristane	22.1 ± 3.2	–	–	–
<i>n</i> -Octadecane	33.6 ± 4.6	–	91.1	–
Phytane	27.6 ± 4.1	–	–	–
Biphenyl	24.0 ± 2.9	–	62.5 – 65.6	–
Dimethylnaphthalene	18.7 ± 7.3	–	–	–
Acenaphthylene	58.9 ± 8.2	52.2 ± 1.3	64.6 – 69.1	52.3
Methylbiphenyl	34.0 ± 6.1	–	–	–
Isoprenyl naphthalene	34.0 ± 5.5	–	–	–
Fluorene	44.3 ± 8.0	48.8 ± 0.8	66.9 – 74.4	43.0
Dimethylbiphenyl	27.3 ± 5.1	–	–	–
Isopropylbiphenyl	18.0 ± 4.1	–	–	–
Trimethylphenylindene	24.2 ± 4.1	–	–	–
Phenanthrene	45.6 ± 6.5	47.3 ± 1.2	72.2 – 80.4	44.1
Phenylnaphthalene	29.3 ± 4.8	–	88.6	–
Methylphenanthrene	38.8 ± 5.2	35.4 ± 1.9	–	–
Methylanthracene	20.5 ± 3.7	–	–	–
Fluoranthene	35.7 ± 5.8	38.7 ± 2.5	79.3 – 97.6	45.9
Pyrene	18.3 ± 3.8	42.9 ± 2.3	79.4 – 104.2	42.2
Dimethylindanone	50.2 ± 9.8	–	–	–
Naphthoquinone	81.1 ± 10.7	–	–	–
Dibenzofuran	67.9 ± 9.8	–	–	–
Methyldibenzofuran	72.6 ± 9.8	–	–	–
Xanthene	47.6 ± 7.7	–	–	–
Dibenzopyran	52.6 ± 7.7	–	–	–
Fluorenone	60.1 ± 8.1	–	–	–
Dibenzothiophene	55.1 ± 6.9	–	–	–
Methyldibenzothiophene	18.8 ± 3.6	–	–	–
Anthraquinone	43.7 ± 5.7	–	–	–
Cyclopentaphenanthrenone	72.2 ± 9.1	–	–	–

Text S14. OH and Ozone Reactivities of Sesquiterpenes

Since many of SQT204 and SQT202 were measured in the forest atmosphere for the first time, here we estimate their contributions to atmospheric chemistry to assess their significance. It should be noted that the temporal and spatial variabilities in sesquiterpenes are often significant owing to their short lifetimes, and have been demonstrated at other sites. Also, we take the SV-TAG measurements to be lower limits for SQT204 concentrations. Another source of uncertainty in reactivity calculations lies in the value of rate constants. To the authors' knowledge, the rate constants of SQT202 have not been measured in laboratory experiments, but they are structurally similar to SQT204, whose atmospheric chemistry is relatively well studied. Since they may contain an additional double bond, SQT202 could be more reactive than SQT204 and thus the estimates here are likely to represent lower limits. To estimate the impacts of these newly observed SQT202, we calculate the OH and ozone reactivities of all measured sesquiterpenes. The rate constants are taken from literature where available (Atkinson and Arey, 2003). For SQT202, α -muurolene and unspciated SQT204, the rate constants are assumed to be the average rate constant of all known SQT204. For some SQT202, such as cuparene and calamenene, this assumption could lead to overestimated ozone reactivities, since they are aromatic and are likely to be less reactive towards ozone than other non-aromatic sesquiterpenes. We stress that Further laboratory measurements are needed to constrain these rate constants.

The time series of the ozone reactivities of all sesquiterpenes are shown in Fig. S15a. The contribution of these sesquiterpenes to overall ozone reactivity (also termed ozone-olefin loss) is significant and is comparable to that of monoterpenes, also shown. The ozone reactivity of monoterpenes is calculated as the product of monoterpene concentrations (measured by PTR-TOF-MS) and the average ozone rate constant of α -pinene, β -pinene and 3-carene, the three most abundant monoterpenes at this field site (Ortega et al., 2014). Despite their lower concentrations, sesquiterpenes contribute disproportionately to ozone reactivities owing to their high ozone rate constants. For example, β -caryophyllene, the commonly most abundant SQT204, has an ozone rate constant more than two orders of magnitude higher that of α -pinene, and a lifetime against this reaction of ~ 2 min at 30 ppb of O_3 . This highlights the need for highly sensitive measurements of these reactive sesquiterpenes because even at low concentrations, they can strongly affect the oxidant chemistry in the forest atmosphere.

At BEARPEX 2007, a study in a pine forest, monoterpenes contributed to 60% of the ozone reactivity while sesquiterpenes contributed a smaller fraction at 7.6% (Bouvier-Brown et al., 2009). This difference between BEARPEX 2007 and BEACHON-RoMBAS is likely due to a difference in sesquiterpene composition between the two sets of measurements. At BEARPEX 2007, sesquiterpenes were dominated by α -bergamotene and α -farnesene, while at BEACHON-RoMBAS, β -caryophyllene was the most dominant SQT204. Bouvier-Brown et al. (2009a) estimated the ozone rate constant of α -bergamotene to be $8.6 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, based on structure-reactivity relationships. Meanwhile, the ozone rate constant of β -caryophyllene was taken to be $1.16 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ in this work based on laboratory measurements (Atkinson and Arey, 2003). Since the reactivities of different sesquiterpenes can span orders of magnitude, it is essential that measurements of sesquiterpenes be speciated to accurately assess the total reactivities. Future work should also focus on laboratory measurements of rate constants of SQT202 with OH, ozone and NO_3 , as they are currently not available from literature. Other

compounds measured by SV-TAG, such as alkanes and PAHs are not included in these calculations, as they react much more slowly with all of these oxidants than the SQTs.

The measured concentrations are also used to estimate OH reactivities at this site, shown in Fig. 9b. The combined OH reactivities of sesquiterpenes are less than 0.02 s^{-1} . This is not a significant contribution as the overall OH reactivity at this site is around $6\text{--}10 \text{ s}^{-1}$ (Kim et al., 2013). Although OH radicals react more rapidly with sesquiterpenes than with monoterpenes and MBO, the difference in rate constants is within one order of magnitude. Since MBO and monoterpene concentrations exceed those of sesquiterpenes by more than a factor of 100, the measured OH reactivity at this site is dominated by MBO and monoterpenes. In order for sesquiterpenes to contribute to 1 s^{-1} of OH reactivity (roughly 20% of total OH reactivity), the concentrations of sesquiterpenes would need to be 100 times those measured by our instrument. The newly observed compounds are unlikely to account for a substantial portion of the “missing” OH reactivity reported by other field studies (Di Carlo et al., 2004; Nölscher et al., 2012). We stress that the rate constants for SQT in the literature span a wide range (1 to 2 orders of magnitude). Since it was difficult to decide which rate constant to use, we opt to use an intermediate value for the calculations here. Based on these assumptions, we can conclude that OH reactivities are still dominated by monoterpenes in the forest (even with an upper limit of SQT + OH of $1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, the collision limit), while O_3 reactivities are likely comparable between monoterpenes and SQT.

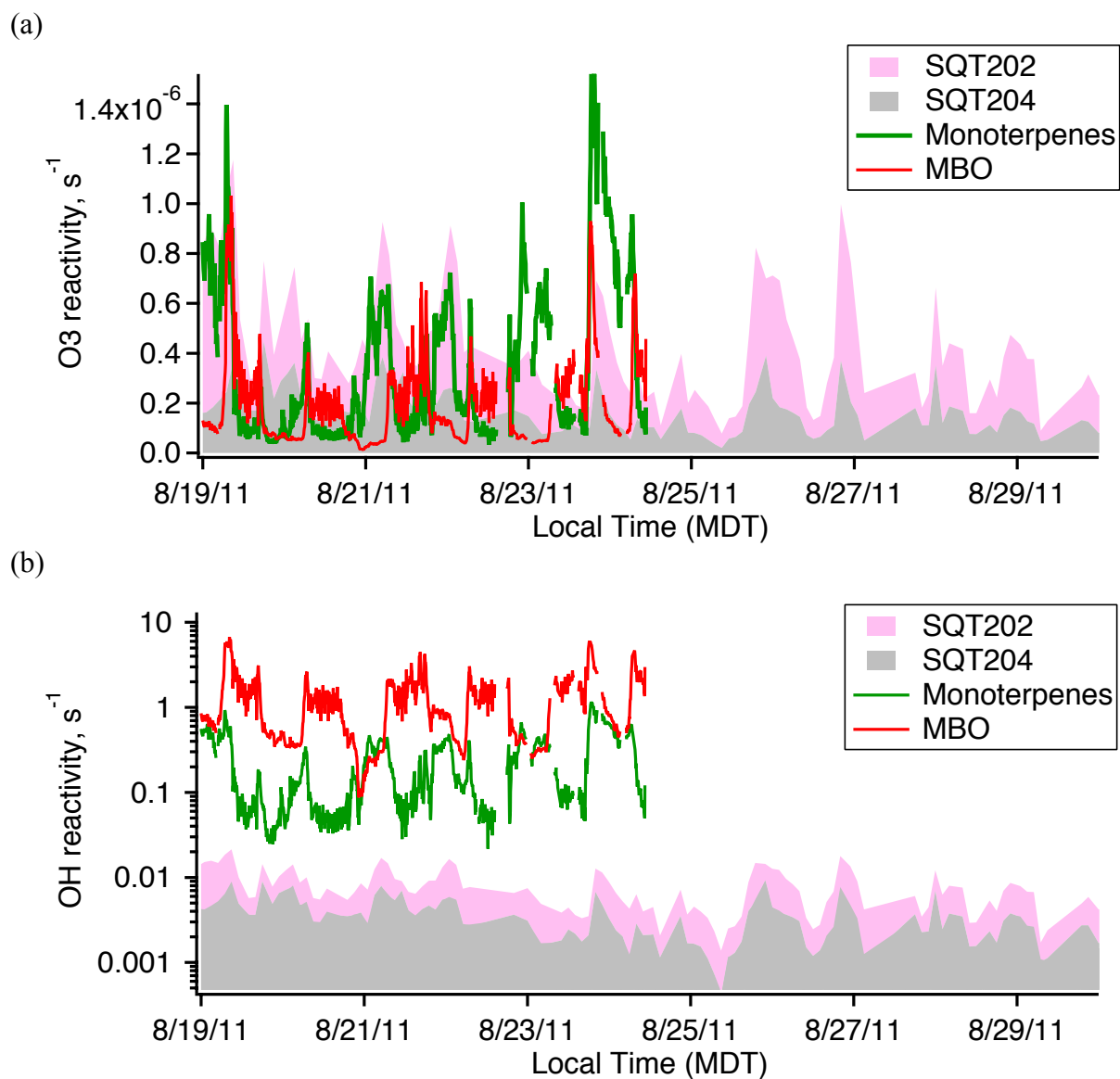


Figure S15. Contributions of different biogenic VOCs to (a) O₃ reactivity and (b) OH reactivity.

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