Supplemental information for

Emissions of C_9-C_{16} hydrocarbons from kelp species on Vancouver Island: *Alaria marginata* (winged kelp) and *Nereocystis luetkeana* (bull kelp) as an atmospheric source of limonene

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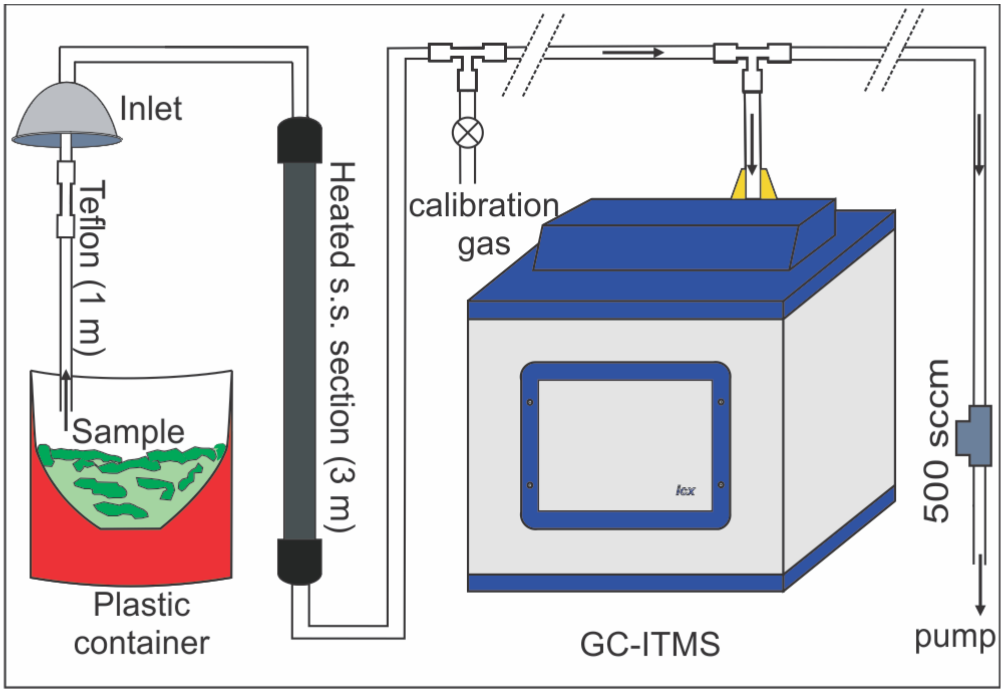

Figure S-1. Setup for head space sampling (not to scale). GC-ITMS = gas chromatograph ion trap mass spectrometer. MFC = mass flow controller. s.s. = stainless steel.

Figure S-2. Photo of *Fucus gardneri* (rock weed) in the container.

Figure S-3. Photo of *Ulva spp.* (sea lettuce).

Figure S-4. Photo of *Callophyllis spp.* (red sea fans)

Figure S-5. Photo of *Alaria marginata* (winged kelp).

Figure S-6. Photo of *Nereocystis luetkeana* (bull kelp).

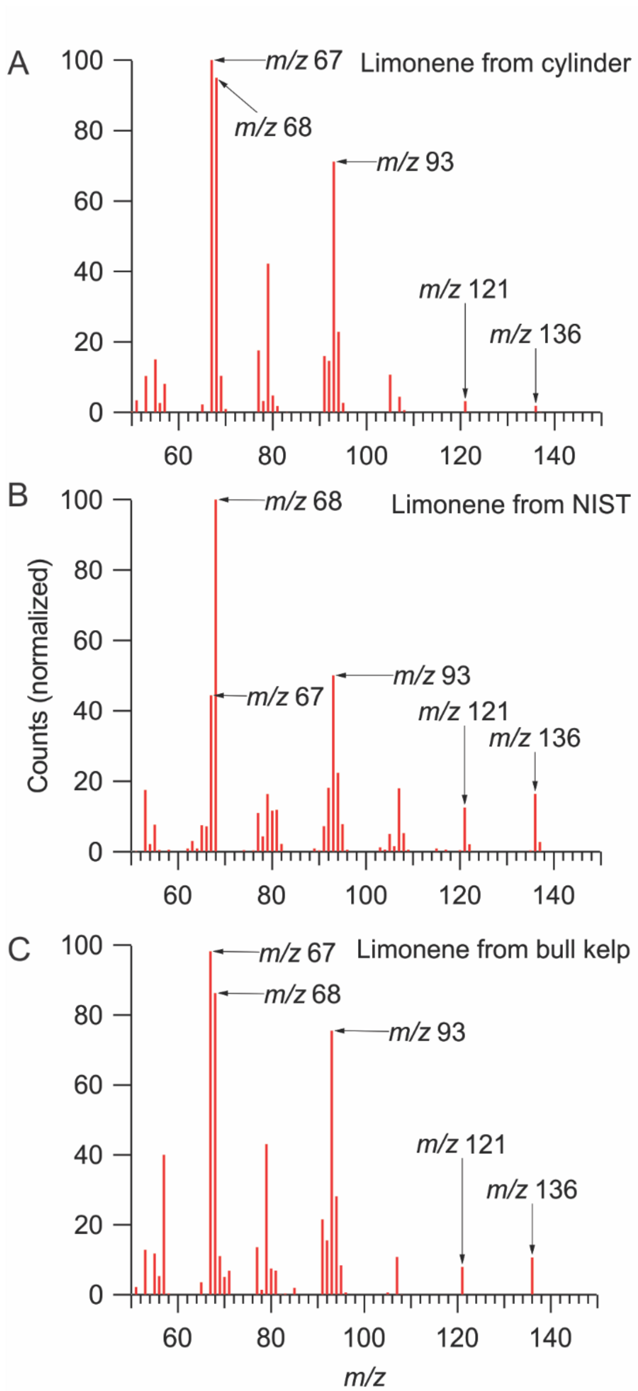

Figure S-7. Comparison of limonene mass spectra from different sources. (**A**) The VOC calibration cylinder used in the field, (**B**) Mass spectrum downloaded from the NIST mass spectrometry data center, and (**C**) the headspace of bull kelp. The observed RI (1033) matches a literature average of 1033 (Table S-1).

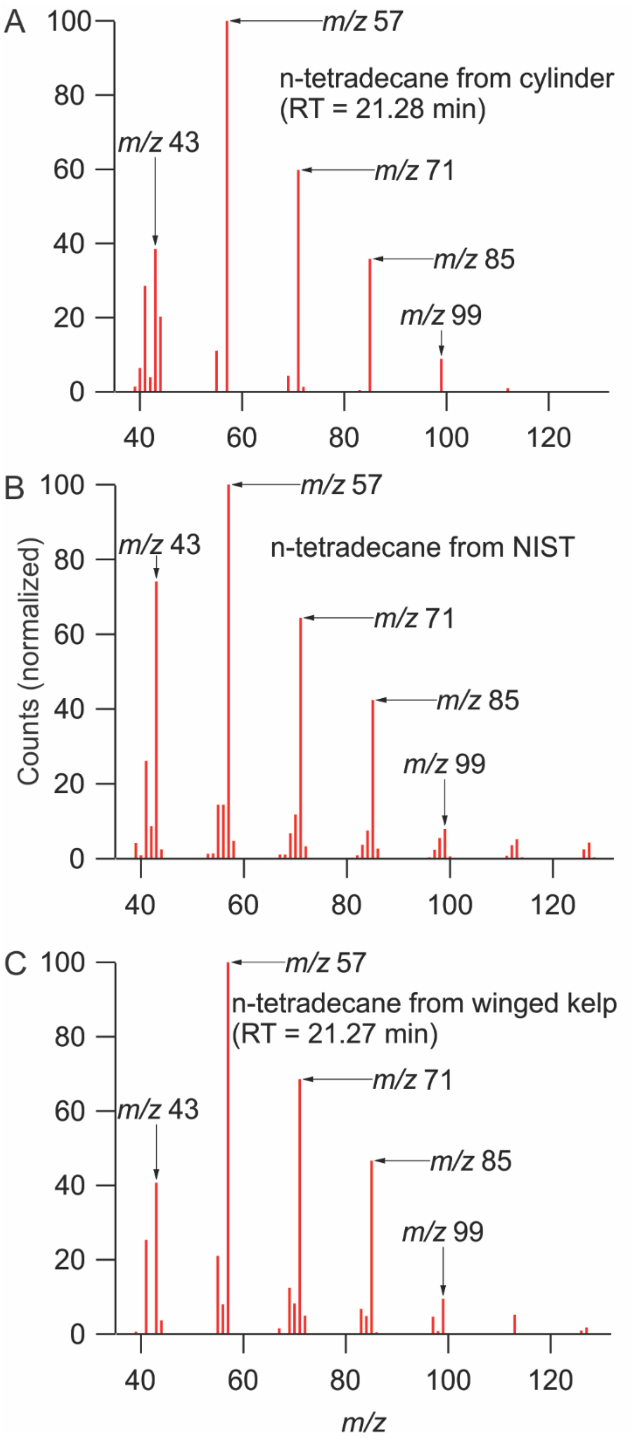

Figure S-8. Normalized mass spectra from A) an analytical standard in a calibration mixture, B) NIST reference, and C) sample taken from the headspace of winged kelp.

Table S-1. Quantification and retention information for observed VOCs. RT = retention time. RI = retention index based on an n-alkane hydrocarbon ladder on a DB-5MS column. For quantification of monoterpenes, counts at *m/z* 92 and 94 were added to those of the dominant fragment at *m/z* 93 ($C_7H_9^+$) because it improved the shape of the chromatographic peaks in some cases. The likely cause is (random) jitter of the electromagnetic fields that control ion selection in the ion trap mass spectrometer (Bell et al., 2015).

RT (min)	VOC	RI (observed)	RI (literature)*	Major ion(s) (*m/z*)
8.33	n-Nonane	900	900	71, 85
9.71	α-Pinene	936	939	93
10.32	Camphene	950	951	93
11.41	β-Pinene	978	979	93
12.51	n-Decane	1000	1000	71, 85
12.76	Carene	1010	1017	80, 91
13.82	Limonene	1033	1033	93
16.34	Terpinolene	1093	1088	121, 136
16.86	n-Undecane	1100	1100	71, 85
16.98	Nonanal	1108	1106	98
18.85	n-Dodecane	1200	1200	71, 85
20.02	n-Tridecane	1300	1300	71, 85
21.28	n-Tetradecane	1400	1400	71, 85
22.22	n-Pentadecane	1500	1500	71, 85

* Averaged value of retention indices reported by (Angioni et al., 2004; Angioni et al., 2006; Lucero et al., 2006; Maia et al., 2005; Mevy et al., 2006; Miyazaki et al., 2011; Sartin et al., 2001; Silva et al., 2010; Slavkovska et al., 2005; Tuberoso et al., 2005; Xu et al., 2003)

Table S-2. Experimental details and VOC mixing ratios in head spaces sampled.

	Empty container		**Seawater**		***F. gardneri***		***Ulva spp.***		***Callophyllis spp.***		***A. marginata***		***N. luetkeana***	
VOC	**Mixing ratio**	**±**	**Mixing ratio**	**±**	**Mixing ratio**	**±**	**Mixing ratio**	**±**	**Mixing ratio**	**±**	**Mixing ratio**	**±**	**Mixing ratio**	**±**
Time (Local)	July 20 12:10		July 20 15:25		July 19 19:16		July 19 14:38		July 20 16:04		July 22 19:22		July 23 12:44	
Air temperature (°C)	15.1		17.9		17.3		16.3		18.0		14.5		17.1	
α-pinene (pptv)	4	0	12	1	1	0	3	0	8	0	65	4	22	1
Camphene (pptv)	0	0	0	0	0	0	0	0	0	0	26	2	10	1
β-pinene (pptv)	5	0	9	1	1	0	3	0	7	0	141	6	65	3
Carene (pptv)	0	0	0	0	0	0	0	0	1	0	0	0	0	0
Limonene (pptv)	12	1	44	3	17	1	25	2	42	3	2248	135	1834	110
Terpinolene (pptv)	0	0	0	0	0	0	0	0	0	0	0	0	11	1
Nonanal (pptv)	9556	1789	11475	2149	5558	1041	9242	1731	10437	1954	7879	582	61125	4517
n-Dodecane (pptv)	31	3	12	1	9	1	6	0	11	1	156	28	247	44
n-Tridecane (pptv)	94	10	50	5	14	2	13	1	45	5	296	24	476	38
n-Tetradecane (pptv)	61	8	37	5	24	3	23	3	36	5	783	29	1304	49
n-Pentadecane (pptv)	127	19	163	24	12	2	27	4	150	22	591	57	2646	256

Table S-3. Ambient air VOC mixing ratios observed prior to each head space analysis.

	Empty container		**Sea water**		***F. gardneri***		***Ulva spp.***		***Callophyllis spp.***		***A. marginata***		***N. luetkeana***	
VOC	**Avg**	**2σ**	**Avg**	**2σ**	**Avg**	**2σ**	**Avg**	**2σ**	**Avg**	**2σ**	**Avg**	**2σ**	**Avg**	**2σ**
α-Pinene (pptv)	9	6	9	6	2	1	4	5	9	6	7	3	56	25
Camphene (pptv)	0	0	0	0	0	0	0	0	0	0	1	1	6	1
β-Pinene (pptv)	8	4	8	4	2	0	2	2	8	4	8	5	34	7
Carene (pptv)	0	0	0	0	0	0	0	0	0	0	0	0	1	1
Limonene (pptv)	24	21	24	21	4	4	8	8	24	21	28	10	55	32
Terpinolene (pptv)	1	0	1	0	0	0	0	0	1	0	1	1	1	1
Nonanal (pptv)	19	12	19	12	23	31	11	6	19	12	113	160	25	7
n-Dodecane (pptv)	0	0	0	0	0	0	0	0	0	0	0	1	1	0
n-Tridecane (pptv)	0	0	0	0	0	0	1	0	0	0	4	3	3	2
n-Tetradecane (pptv)	5	1	5	1	6	0	7	1	5	1	23	10	14	3
n-Pentadecane (pptv)	1	0	1	0	1	1	1	1	1	0	83	161	5	3

Table S-4. VOCs identified (but not quantified) by retention information and major ions. The number for each sample is the logarithm of the peak area for the tabulated major ions for each of the samples analyzed. Cases where peaks were absent are indicated with "-". RT = retention time. RI = retention index based on an n-alkane hydrocarbon ladder on a DB-5MS column.

RT (min)	**VOC**	**RI (observed)**	**RI (literature)***	**Major ions (*m/z*)**	Empty Container	Sea-water	*F. gardneri*	*Ulva spp.*	*Callo-hyllis spp.*	*A. margi-nata*	*N. luetkeana*
4.70	Toluene	765	771	91, 92	4	3	6	5	5	8	7
11.82	2,3 -octanedione	986	991	43, 71, 99	5	5	5	5	5	†	6
11.88	6-methyl-5-hepten-2-one	987	992	55, 69, 93, 108	6	5	5	6	5	6	6
12.68	n-octanal	1006	1008	70, 83, 98	6	5	5	5	5	7	6
13.57	2-ethyl-1-hexanol	1028	1028	93, 121, 136	-	-	-	-	-	6	-
16.38	Terpinolene	1093	1088	70, 82, 95, 112	-	3	-	-	3	-	5
17.39	Limona ketone	1119	1121	67, 95, 123	-	-	-	-	-	-	5
18.95	n-decanal	1205	1204	69, 125, 136, 151	5	5	5	5	5	5	6
21.73	Geranyl Acetone	1450	1450	125,136, 151	5	5	5	5	5	5	5

* Averaged value of retention indices reported by (Angioni et al., 2004; Angioni et al., 2006; Lucero et al., 2006; Maia et al., 2005; Mevy et al., 2006; Miyazaki et al., 2011; Sartin et al., 2001; Silva et al., 2010; Slavkovska et al., 2005; Tuberoso et al., 2005; Xu et al., 2003)

†Peak unresolved

Table S-5. Retention information for unknown compounds that appeared as standalone peaks. RT = retention time. RI = retention index based on an n-alkane hydrocarbon ladder on a DB-5MS column.

RT (min)	**RI (observed)**	**Major ions (*m/z*)**	Empty Container	Sea-water	*F. gardneri*	*Ulva spp.*	*Callo-hyllis spp.*	*A.a marginata*	*N. luetkeana*
7.91	895	69, 84, 111	✓	✓	✓	✓	×	✓	×
9.16	923	81, 105, 123	×	×	×	×	×	✓	×
12.94	1013	69, 111	×	×	×	×	×	✓	×
14.02	1039	57, 71, 85, 111	✓	×	✓	×	×	✓	×
15.06	1063	57, 71, 112	×	×	✓	×	×	✓	×
15.54	1075	57, 71, 152	×	✓	×	×	✓	×	✓
15.68	1078	57, 71, 113	×	×	✓	✓	×	✓	×
16.04	1087	57,71, 85, 99	✓	✓	✓	×	✓	✓	×
16.18	1090	57, 71,85, 112	×	×	✓	×	×	✓	×
16.56	1099	133, 105, 126	×	×	×	×	×	✓	✓
16.79	1104	57, 126, 127	×	×	×	✓	×	✓	×
17.95	1130	79, 91, 105	×	×	×	×	×	×	✓
18.16	1135	57, 71, 85, 112	✓	×	✓	×	×	✓	×
18.30	1148	57, 71, 85, 105	×	×	✓	×	×	✓	×
18.51	1166	105, 133, 162	×	✓	✓	✓	✓	×	✓
18.65	1178	91, 105, 119	×	×	✓	×	×	✓	✓
18.71	1184	83, 105, 119	×	×	✓	×	✓	×	✓
18.83	1194	119, 91	✓	✓	✓	✓	✓	×	✓
19.37	1242	57, 71, 85	×	×	×	×	×	×	✓
19.70	1271	91, 131, 160	×	×	×	×	×	×	✓
19.75	1275	91, 131, 160	×	×	×	×	×	×	✓
20.20	1315	57, 71, 85, 99	✓	✓	✓	✓	✓	✓	×
20.47	1338	83, 97, 131	×	×	✓	×	×	✓	✓
20.56	1346	91, 117, 131	×	✓	✓	✓	×	✓	✓
20.60	1350	117, 131, 145	✓	✓	✓	✓	✓	✓	✓
20.72	1361	57, 71, 85, 99	×	×	✓	✓	×	✓	×

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