

1 Short communication

2 Emissions of C₉ – C₁₆ hydrocarbons from kelp species on Vancouver Island: *Alaria marginata*
3 (winged kelp) and *Nereocystis luetkeana* (bull kelp) as an atmospheric source of limonene
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18 **Abstract**

19 In this paper, measurements of C₉ – C₁₆ biogenic volatile organic compounds (BVOCs) in the
20 headspaces above near-shore marine vegetation samples of *Fucus gardneri* (rock weed), *Ulva*
21 *spp.* (sea lettuce), *Callophyllis spp.* (red sea fans), *Alaria marginata* (winged kelp), and
22 *Nereocystis luetkeana* (bull kelp) collected on the west coast of Vancouver Island, British
23 Columbia, Canada, are presented. Numerous BVOCs were observed in the headspace samples,
24 including n-alkanes (e.g., n-dodecane, n-tridecane, n-tetradecane and n-pentadecane) and
25 oxygenated hydrocarbons (e.g., octanal, nonanal, geranyl acetone, and 6-methyl-hepten-2-one),
26 though the majority of VOCs emitted was not identified. The emissions from *Ulva spp.*,
27 *Callophyllis spp.* and *F. gardneri* samples contained a similar assortment of n-alkanes and
28 oxygenated BVOCs (e.g., n-aldehydes) as observed at Mace Head, Ireland, whereas the
29 headspaces above *N. luetkeana* and *A. marginata* contained monoterpenes, foremost limonene,
30 and toluene. Further studies are needed to constrain emissions of BVOCs from near-coastal
31 vegetation as they have the potential to substantially impact coastal O₃ budgets and the organic
32 content of marine derived aerosol.

33

34 **Keywords**

35 BVOC emissions; kelp; seaweed; monoterpenes; limonene; hydrocarbons

36 **1. Introduction**

37 Oceanic emissions of hydrocarbons are important components of global biogeochemical element
38 cycles (Carpenter et al., 2012; Lovelock et al., 1972). Large quantities of organic carbon and
39 molecular oxygen are produced by phytoplankton, microscopic organisms invisible to the
40 unaided eye (Falkowski et al., 1998). Their biological activity yields biogenic volatile organic
41 compounds (BVOCs), including isoprene (C_5H_8) (Bonsang et al., 2010; Broadgate et al., 1997)
42 and, to a lesser extent, monoterpenes ($C_{10}H_{16}$) (Meskhidze et al., 2015; Yassaa et al., 2008) that
43 partition to the marine boundary layer and, upon oxidation, contribute to the organic content of
44 marine aerosol (Booge et al., 2018; Luo and Yu, 2010). In addition, macroalgae, broadly defined
45 as algae visible to the naked eye, and sea grasses produce BVOCs in the marine environment
46 (Broadgate et al., 2004; Garcia-Jimenez et al., 2013; Giese et al., 1999; Laturus, 1996; Leedham
47 et al., 2013). Generally, these are of regional importance, for example in coastal marine
48 ecosystems and 'hot spots' in the tropics (Exton et al., 2015). However, BVOC emissions from
49 macroalgae are poorly constrained by observations. Broadgate et al. (2004) showed that
50 macroalgae emit isoprene and other $C_{\leq 5}$ non-methane hydrocarbons, and Sartin et al. (2001;
51 2002) showed that seaweeds in the inter-tidal zone emit C_8 - C_{15} n-alkanes and C_8 - C_{10} aldehydes;
52 emissions of the latter are associated with stress factors such as temperature changes, plant life
53 cycle and age, and emersion at low tide (Goullitquer et al., 2009).

54 In July 2015, we operated a gas chromatograph equipped with a cylindrical ion trap mass
55 spectrometer (GC-ITMS) for quantification of C_9 - C_{16} hydrocarbons at the Amphitrite Point
56 Observatory (APO) on the west coast of Vancouver Island near Ucluelet, British Columbia, and
57 found that ambient air sampled during on-shore flow was enriched in limonene relative to α - and
58 β -pinene (Tokarek et al., 2017). A similar enhancement was observed when headspace vapors

59 above *Nereocystis luetkeana* (bull kelp) were analyzed, suggesting that near-shore vegetation is a
60 source of monoterpenes (Tokarek et al., 2017). On the west coast of North America, large kelp
61 "forests" are located from the California coast to the Aleutian Islands due to a favorable balance
62 of available nutrients (from the upwelling of ocean currents), sunlight, and oceanic temperature
63 (Steneck et al., 2002). Genera found in these forests include *Laminaria* (Devil's apron, sea
64 colander), *Ecklonia* (brown algae), *Macrocystis* (giant kelp), *Nereocystis*, and *Pterygophora*
65 (stalked kelp) (Reed and Brzezinski, 2009).

66 In this paper, measurements of C₉-C₁₆ hydrocarbons in the headspaces of several macroalgae
67 species collected near the APO, *Fucus gardneri* (rock weed), *Ulva spp.* (sea lettuce),
68 *Callophyllis spp.* (red sea fans), *Alaria marginata* (winged kelp), and *N. luetkeana*, are presented
69 to elucidate potential BVOC sources in the region.

70 **2. Methods**

71 The APO is located at 48.92° N and 125.54° W less than 100 m from the high tide line of the
72 Pacific Ocean. Figure 1 of Tokarek et al. (2017) shows a map of the study region.

73 Measurements were performed using a FLIR 450 GC-ITMS as described earlier (Tokarek et al.,
74 2017). Briefly, this instrument was equipped with an electron impact ionization source and a
75 Tenax TA and Carboxen 1017 dual sorbent pre-concentration cartridge, was operated in scan
76 mode from m/z 35 to 450 at a rate of 3 Hz, and sampled from a stainless-steel inlet (Figure S-1).

77 A 3.0 m long section of this inlet was heated to 125 °C to scrub ozone and to minimize oxidation
78 of hydrocarbons during pre-concentration (Hellén et al., 2012). Air was sampled at a by-pass
79 flow rate of 500 standard mL min⁻¹ and an instrument flow rate of 213 mL min⁻¹ for 8 min onto
80 the sorbent trap held at 40 °C. After pre-concentration, the sorbent trap was heated to 240 °C for

81 5 min while it was flushed with helium carrier gas (Praxair, ECD grade) onto a 30 m long,
82 0.25 mm inner diameter and 0.25 μm film thickness DB-5MS analytical column (20% split). The
83 column was initially at 40 $^{\circ}\text{C}$ for 3 min, then heated to 70 $^{\circ}\text{C}$ at a rate of 3 $^{\circ}\text{C min}^{-1}$ and held for
84 2 min, and then heated to 200 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C min}^{-1}$ and held for 2 min, for a total runtime of
85 25.7 min.

86 Samples of marine organisms were collected in the intertidal and shallow subtidal zones near the
87 APO. The species sampled were attached to the sea floor via frail roots and were pulled up with
88 minimal effort and damage to the plant, with exception of the bull kelp sample which floated on
89 the surface. Figures S2-S6 show photographs of the species collected.

90 The samples were placed in a 12 L polypropylene container filled with seawater to a constant
91 height (~ 10 cm from the top). The container was covered with polyethylene wrap to allow for
92 gases to collect in the headspace for a period of ~ 1 hour in the shade and analyzed within two
93 hours of collection. A ~ 1 m long, 0.635 cm outer and 0.476 cm inner diameter FEP TeflonTM
94 tube was attached to the inlet, and one end was placed inside the headspace for ~ 5 min prior to
95 the sample cycle. Chromatograms were collected for the empty container (rinsed with tap water)
96 and the container filled with seawater, or with seawater and a macroalgae sample. Peaks were
97 identified using authentic standards, via their retention indices (RIs), and/or National Institute of
98 Standards (NIST) mass spectra library searches. Retention times (RTs), RIs and quantification
99 ions are summarized in Table S-1.

100 Ambient air VOC mixing ratios were measured by averaging results from four consecutive
101 chromatograms taken prior to each headspace analysis (Table S-3); these backgrounds (which
102 initially filled the headspaces) were subtracted from the observed concentrations (Table S-2).

103 3. Results

104 3.1. Overview

105 Total ion chromatograms of the headspace vapors above *N. luetkeana* and above seawater void
106 of visible organisms are shown in Figure 1A. The total ion counts (TICs; blue trace) of the kelp
107 sample were elevated by a factor of $\sim 10^2$ to $\sim 10^3$ compared to the seawater sample (black trace)
108 over a range of retention times, indicating that the kelp outgassed a number of hydrocarbons,
109 many of which were not resolved. Selected ion chromatograms were used to resolve, identify
110 and, when possible, quantify the compounds emitted (section 3.2). An example showing counts
111 at m/z 93 \pm 1, an ion ($C_7H_9^+$) associated with monoterpenes, is superimposed in Figure 1A (right-
112 hand axis). It shows baseline resolved peaks, notably of β -pinene and limonene.

113 Shown in Figure 1B are analogous plots for the head space above *A. marginata*. These
114 chromatograms are qualitatively similar in that peaks were enhanced over the range of retention
115 times shown, although in different relative proportions.

116 Shown in Figures 2A, 2B and 2C are the results for headspace vapors above samples of *F.*
117 *gardneri*, *Ulva spp.*, and *Callophyllis spp.*, respectively. In contrast to the data shown in Figure
118 1, these chromatograms show little to no hydrocarbon enhancements relative to the seawater
119 sample.

120 3.2. Identification and quantification of BVOCs

121 The observed BVOCs broadly fell into three categories.

122 The first set of BVOCs included compounds for which authentic standards, i.e., reference mass
123 spectra and instrument response factors were available such as n-alkanes, nonanal, and

124 monoterpenes. These were identified in nearly all samples, though only the *A. marginata* and *N.*
125 *luetkeana* samples showed enhancements of up to factors of 50 compared to the headspace above
126 seawater (Table 1). Cylinder and headspace mass spectra for limonene (RT 13.82 min) and n-
127 tetradecane (RT 21.28 min) are shown in Figures S-7 and S-8, respectively, to illustrate the
128 quality of the quantification.

129 The second category included compounds that were identified on the basis of RI and from a
130 match of major ions with NIST mass spectra library entries but were not quantified (Table S-4).
131 Some of these compounds were identified only because we looked for them, either because of
132 chemical similarity to compounds listed in Table 1 (e.g., decanal) and/or because their presence
133 had been reported in previous headspace analyses of kelp species e.g., octanal, 2-ethyl-1-
134 hexanol, geranyl acetone, or 6-methyl-5-hepten-2-one (Goulitquer et al., 2009; Sartin et al.,
135 2001; Sartin et al., 2002). Other molecules of note in this category are toluene and limona
136 ketone.

137 The third category included BVOC that did not resolve on the chromatographic column and/or
138 were not identified (Table S-5).

139 What follows is a closer examination of the monoterpene (section 3.2.1), n-alkane (section
140 3.2.2), oxygenated (section 3.2.3), and aromatic hydrocarbon data (section 3.2.4).

141 **3.2.1. Monoterpenes**

142 The *A. marginata* and *N. luetkeana* headspace samples were enriched in monoterpenes, foremost
143 in limonene, which accumulated to mixing ratios of ~2.1 ppbv and 1.8 ppbv, respectively. In
144 contrast, emissions of α - and β -pinene and camphene were lower than those of limonene (Table

145 1). The headspace samples of *F. gardneri*, *Ulva spp.*, and *Callophyllis spp.* showed no
146 enhancements of monoterpenes other than a marginal enrichment in limonene.

147 **3.2.2 n-Alkanes**

148 All analyzed samples were enhanced in C₁₂-C₁₅ n-alkane concentration (Table 1). Mixing ratios
149 of n-pentadecane were enhanced the most, followed by n-tetradecane and n-tridecane. The
150 highest mixing ratios were observed for the *N. luetkeana* and *A. marginata* samples.

151 Surprisingly large mixing ratios were observed for the seawater sample and the empty container
152 which had been rinsed with tap water (Table 1). This suggests that the n-alkanes outgassed from
153 the inner walls of the container and/or the water itself, possibly due to in-field contamination
154 followed by temperature- and/or light-driven volatilization. While similar mixing ratios were
155 observed for *Callophyllis spp.*, lower concentrations were measured for *F. gardneri* and *Ulva*
156 *spp.* (Table 1) for reasons that are unclear, though it suggests that the plants absorbed some of
157 the VOCs.

158 **3.2.3. Oxygenated Volatile Organic Compounds (OVOCs)**

159 An assortment of OVOCs similar to what was reported by Sartin et al. (2001; 2002) was
160 observed in two seaweed samples, those of *A. marginata* and *N. luetkeana*, including octanal,
161 nonanal, decanal, 6-methyl-5-hepten-2-one, geranyl acetone, 2-ethyl-1-hexanol (Table S-4), with
162 the exception of di-tert-butyl-p-benzoquinone, which was not detected. Nonanal was present in
163 all samples in unreasonably high abundance, including the seawater and container blanks, which
164 suggests that its abundance was affected by emissions from the container walls and/or the plastic
165 wrap.

166 Limona ketone, an oxidation product of limonene (Rossignol et al., 2012), was tentatively
167 identified in the headspace of *N. luetkeana* on the basis of its RI and mass fragmentation pattern
168 (Table S-4) but was not observed in the other chromatograms.

169 **3.2.4. Aromatic hydrocarbons**

170 Toluene was the only aromatic compound detected and was present in all samples. It eluted at
171 ~4.6 min; its dominant electron impact mass fragments are m/z 91 and 92, with a minor
172 isotopomeric contribution at m/z 93 (Figures 1A and 1B). Its concentration was enhanced by
173 orders of magnitudes in the headspaces above all of the seaweed samples.

174

175 **4. Discussion**

176 Our results are the first to indicate that near-shore marine macroalgae (*N. luetkeana* and *A.*
177 *marginata*) emit monoterpenes, though little to no evidence for terpene emissions was found for
178 *Ulva* spp., *Callophyllis* spp. or *F. gardneri* (Table 1). The only other study that has probed
179 monoterpene emissions from marine algae, of *F. spiralis* at Mace Head, had found no evidence
180 for terpene emissions (Sartin et al., 2001; 2002).

181 Marine algae produce monoterpenes as secondary metabolites (Wise, 2003), possibly as a
182 defense against herbivores or as a response to wounding. Extracts have shown that monoterpenes
183 and chemically modified monoterpenes, including halogenated variants, are present within
184 macroalgae (Naylor et al., 1983; Shaw et al., 2010; Wise, 2003). Relevant to this study, limonene
185 has been detected in *Laminaria* sp. (Naylor et al., 1983), which belongs to the same family as *N.*

186 *luetkeana*. Further, Wise et al. (2003) reported limonene production from neryl diphosphate in
187 *Ochtodes secundiramea*. Hence, the observed terpene emissions are plausible.

188 The observations of enhanced C₁₂ to C₁₅ n-alkane concentrations (Table 1) are consistent with
189 those of Sartin et al. (2001; 2002), who observed C₈-C₁₅ n-alkanes in their analyses and reported
190 biochemical, photosynthetically active radiation (PAR) controlled emissions of n-pentadecane
191 from *F. spiralis* as well as temperature-driven volatilization of n-alkanes in the absence of
192 seaweed (i.e., when the headspace above a combination of sand and seawater was examined).
193 Emissions of n-alkane in the empty container was likely an artifact, since it was rinsed only with
194 water, which would not adequately remove any residual alkanes. Interestingly, mixing ratios of
195 n-alkanes were greatly enhanced in the presence of *A. marginata* or *N. luetkeana*, suggesting that
196 these species have biochemical routes for n-alkane synthesis.

197 The observations of aldehydes (Table S-4) are also consistent with literature (Bravo-Linares et
198 al., 2010; Goulitquer et al., 2009; Sartin et al., 2001; Sartin et al., 2002). The only exception was
199 nonanal, which was present in all samples and was likely an artifact.

200 Toluene out-gassed from all seaweed species examined (Table S-4). We found no indications for
201 the presence of toluene in, or emissions from, seaweed in the literature, including recent
202 comprehensive studies (López-Pérez et al., 2017). Toluene emissions are known for terrestrial
203 vegetation (Graus et al., 2013; White et al., 2009), such that emissions from marine organisms
204 are not far-fetched. We considered that the source of toluene may have been of anthropogenic
205 origin (e.g., leaked fuel from a watercraft). However, this is inconsistent with the absence of
206 other aromatic species (e.g., o-xylene, ethylbenzene, etc.) that are present in fuel and that the
207 GC-ITMS is sensitive to. Biogenic emissions of toluene would likely be small compared to

208 anthropogenic sources and therefore may have gone unnoticed in other studies. If a small oceanic
209 toluene source were to exist, its oxidation would yield glyoxal, whose budget in the marine
210 boundary layer is currently not reconciled (Mahajan et al., 2014).

211 The chromatograms contained numerous species that could not be identified (Table S-5) let
212 alone resolved on the chromatographic column. Their mass spectra were dominated by m/z 57,
213 71, and 85, ions typical of branched alkanes or highly alkylated species of which there are many
214 structural isomers. Such compounds have been observed in seaweed extracts (López-Pérez et al.,
215 2017). The unresolved fraction may have also included oxygenated molecules such as the
216 aldehydes identified by Goullitquer et al. (2009), i.e., (E)-hex-2-enal, (E)-non-2-enal,
217 dodecadienal, (E)-4-hydroxyhex-2-enal, and (E)-4-hydroxynon-2-enal, whose retention times
218 and mass spectra are not known. These compounds likely generate $C_2H_5CO^+$ (m/z 57.0335),
219 which appears at the same m/z as $C_4H_9^+$ (m/z 57.0699) in the GC-ITMS. Furthermore, we would
220 have expected to observe halogenated terpenes, whose mass spectra and retention times are also
221 not known. Clearly, studies with more advanced analytical instrumentation than used here are
222 needed to resolve, identify and quantify all of the hydrocarbons emitted by kelp.

223 Environmental factors and mechanical stresses such as our harvesting method and tissue damage
224 (and potential microbial decomposition) due to the nature of the intertidal region (i.e., battering,
225 herbivory, exposure to heat and PAR, changes to water salinity) may have been factors in the
226 observed emissions. As these stresses occur naturally, we believe that our observations are
227 nevertheless atmospherically relevant.

228 The current study is limited by its small sample size (each species was analyzed only once) and
229 by the experimental design, which did not allow for rigorous control of environmental variables

230 (e.g., air and water temperature and PAR exposure). The next steps are to determine emission
231 factors as a function of biomass and environmental factors, such as temperature, PAR, plant life
232 cycle and age, season, and stress factors such as emersion at low tide. It would be particularly
233 useful to measure hydrocarbon fluxes directly over kelp fields, for example using a fast response
234 instrument such as a proton-transfer mass spectrometer. It may turn out that some of the
235 differences in emission profiles observed here are more a reflection of the biological activity of
236 individual plants than a property of each species. Emissions from the seawater itself and artifacts
237 arising from container walls should also receive further scrutiny, perhaps through use of more
238 inert materials (such as Teflon™) to minimize container emissions.

239 The literature on ocean-atmosphere trace gas exchange has to date focused on small, highly
240 volatile molecules such as the methyl halides. Larger molecules such as the monoterpenes or n-
241 alkanes observed in this work are comparatively understudied. BVOC emissions from seaweed
242 or kelp species are not currently included in chemical transport model simulations investigating
243 O₃ or aerosol budgets or climate, such that their impact is currently not known. However, this
244 impact may be significant considering that the majority of the world's population lives in the
245 proximity of an ocean, and sea grasses and kelp forests are increasing in size due to fertilizer run-
246 off. The emissions of limonene from *N. luetkeana* and *A. marginata* are potentially important
247 because both are prominent kelp species on the northern west coast of North America (Antrim et
248 al., 1995; Paine, 2002). It is hence likely that these species emit BVOCs along the entire northern
249 Pacific coastline. BVOC emissions from kelp will affect OH reactivity and hence the rates of
250 photochemical O₃ production in coastal regions. Furthermore, much of this material will
251 ultimately add to the organic content of marine derived aerosol, potentially affecting
252 concentrations of cloud condensation and ice nuclei, believed to impact the atmosphere as a

253 whole (Wilson et al., 2015). Emission of limonene is of particular interest since it has a greater
254 aerosol formation potential in the presence of O₃ than any of the other common monoterpenes
255 (Draper et al., 2015).

256

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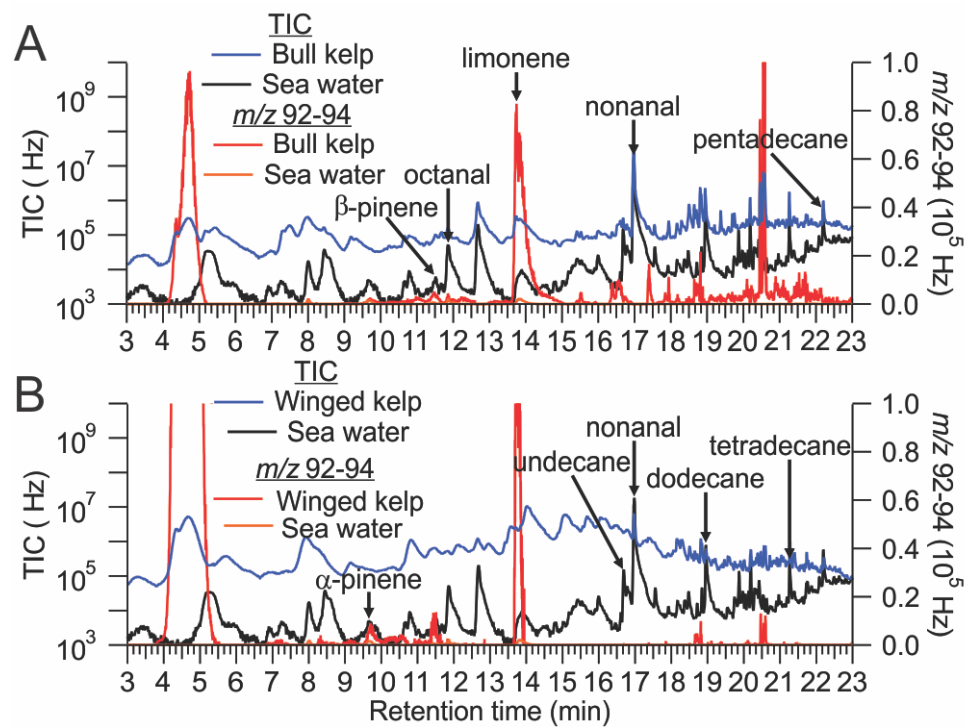
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374

375 **Table 1.** Enhancement of VOC mixing ratios in the sampled headspaces. Ambient air mixing ratios observed immediately prior to
 376 headspace analysis (Table S-3) were subtracted from observed mixing ratios (Table S-2). The uncertainty is measurement precision
 377 ($\pm 2\sigma$) of the mixing ratios of four consecutive ambient air chromatograms taken prior to the headspace analysis. n/d = not detected.
 378 Enhancement deemed significant ($>2\sigma$) are bolded.

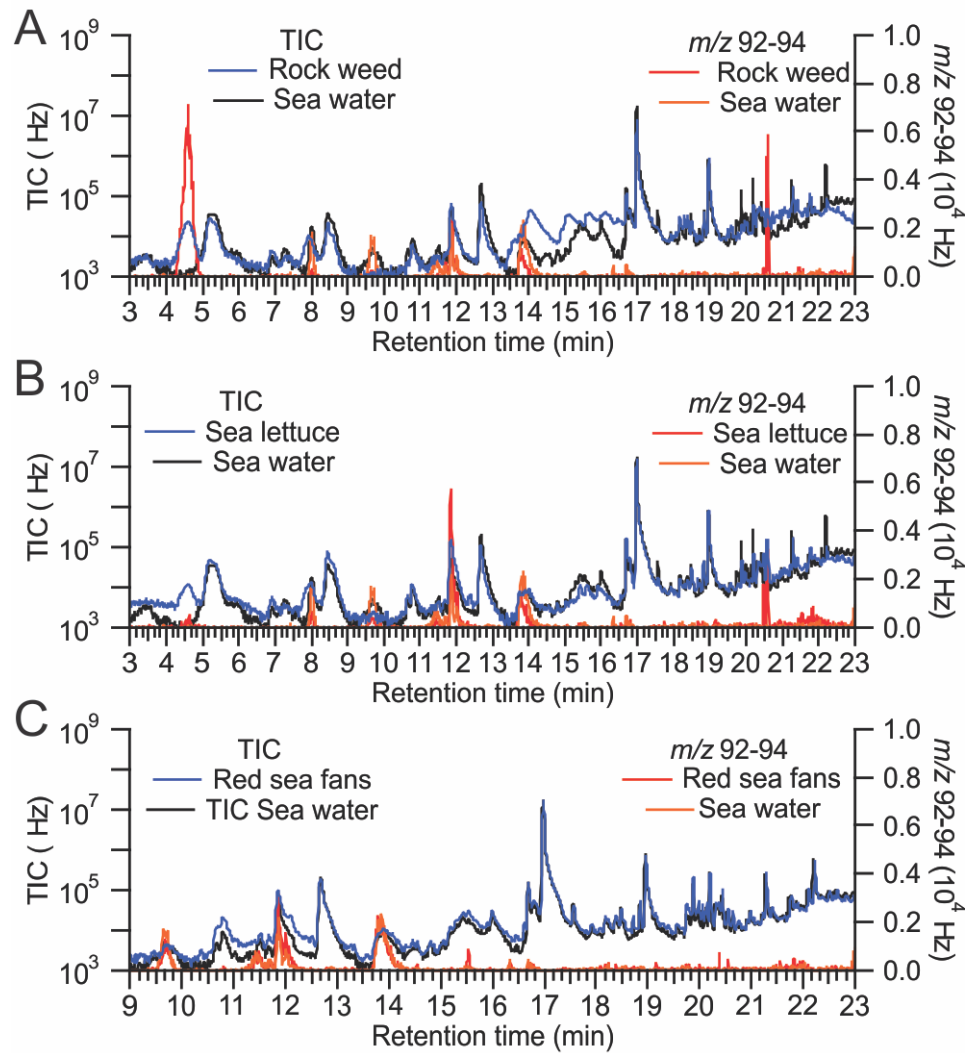
	Empty Container	Seawater	<i>F. gardneri</i>	<i>Ulva spp.</i>	<i>Callophyllis spp.</i>	<i>A. marginata</i>	<i>N. luetkeana</i>
α -pinene (pptv)	-5 \pm 6	3 \pm 6	0 \pm 1	-1 \pm 5	-1 \pm 6	58\pm5	-34 \pm 25
Camphene (pptv)	n/d	n/d	n/d	n/d	n/d	25\pm2	4 \pm 1
β -pinene (pptv)	-2 \pm 4	2 \pm 4	-1 \pm 1	1 \pm 2	0 \pm 4	133\pm8	31\pm7
Carene (pptv)	n/d	n/d	n/d	n/d	n/d	n/d	0 \pm 1
Limonene (pptv)	-12 \pm 21	21 \pm 21	13\pm4	17\pm9	19 \pm 21	2220\pm135	1779\pm115
Terpinolene (pptv)	n/d	n/d	n/d	n/d	n/d	n/d	10\pm2
Nonanal (ppbv)*	9.5\pm1.8	11.4\pm2.1	5.5\pm1.0	9.2\pm1.7	10.4\pm2.0	7.8\pm0.6	61.1\pm4.5
n-Dodecane (pptv)	31\pm3	12\pm1	9 \pm 1	6 \pm 1	11\pm1	156\pm28	247\pm44
n-Tridecane (pptv)	94\pm10	49\pm5	14\pm2	13\pm2	45\pm5	293\pm24	473\pm38
n-Tetradecane (pptv)	56\pm8	32\pm5	18\pm3	16\pm3	31\pm5	760\pm31	1289\pm49
n-Pentadecane (pptv)	126\pm19	162\pm24	11\pm2	26\pm4	149\pm22	507\pm171	2641\pm256

379 * **artifact**



380

381 **Figure 1.** Total ion chromatograms (left axis, blue and black) and selective ion chromatograms
 382 of m/z 93 \pm 1 which is a fragment associated with monoterpenes (right axis, red and orange) of
 383 headspaces above kelp species (**A**) *Nereocystis luetkeana* (bull kelp) and (**B**) *Alaria marginata*
 384 (winged kelp). The chromatograms obtained for a sample of seawater are superimposed TIC =
 385 total ion count.



387

388 **Figure 2.** Total ion chromatograms (left axis, blue and black) and residual ion chromatograms of
 389 m/z 93 \pm 1 (right axis, red and orange) of headspaces above seaweed species (A) *Fucus gardneri*
 390 (rock weed), (B) *Ulva* spp. (sea lettuce), and (C) *Callophyllis* spp. (red sea fans). The
 391 chromatograms obtained for a sample of seawater are superimposed.

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