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Seasonal monitoring of lipid degradation processes in the western English Channel links bacterial 10S-DOX enzyme activity to free fatty acid production by phytoplankton

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27 **Abstract.** In a few recent studies, the action of a bacterial dioxygenase (10S-DOX) on
28 palmitoleic acid was observed within some polar and estuarine settings. To add further
29 mechanistic information regarding the action of this enzyme in marine settings, we measured a
30 range of lipids (sterols, fatty acids and the chlorophyll phytyl side chain) and their biotic and
31 abiotic degradation products in water samples collected in 2018 from two depths (5 m and 25
32 m) at the temperate oceanographic time series site L4, located in the western English Channel.
33 Lipid distributions indicated a dominance of diatoms and copepods during the spring bloom,
34 while a peak in dinoflagellate activity was evident in samples collected from late
35 summer/autumn, both outcomes being consistent with taxonomic data reported previously for
36 the same sampling site and interval. Monitoring of lipid oxidation products characteristic of
37 different degradation pathways showed a relatively weak effect of photo- and autoxidation
38 processes, with these acting mainly on the more reactive lipids (i.e. chlorophyll and
39 polyunsaturated fatty acids). In contrast, monitoring of biotic degradation processes revealed
40 significant quantities of 10S-hydroxyhexadec-8(*E*)-enoic acid in samples collected at the end
41 of April (reaching 40% of the residual parent palmitoleic acid), attributed to the involvement of
42 bacterial 10-dioxygenase (10S-DOX) activity during the spring bloom. We propose that this
43 enzyme could be utilised by bacteria to detoxify free fatty acids released by wounded diatoms
44 in the presence of copepods

45

46 **Keywords:** Biotic and abiotic degradation; 10S-DOX enzymatic activity; Bacteria; Wounded
47 diatoms.

48

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51 **1. Introduction**

52 Suspended particles sink very slowly through the water column and constitute most of the
53 standing stock of particulate matter in the oceans (Bacon et al., 1985; Wakeham and Lee, 1989).
54 These particles are composed of a heterogeneous mixture of biogenic, lithogenic, and
55 authigenic components, with their relative proportions dependent on location and depth.
56 However, biogenic (mainly phytoplanktonic) material normally dominates particle composition
57 in the upper 100 m (Honjo et al., 1982). Suspended particles are also generally considered to
58 contain more highly degraded organic matter (OM) than sinking particles due to their longer
59 residence times in the water column (Tanoue and Handa 1980). However, several previous
60 field-based studies have shown high abundances of relatively undegraded labile material in
61 suspended particles (Lee et al., 1983; Wakeham et al., 1985; Wakeham and Canuel, 1988;
62 Sheridan et al., 2002). It is thus important to understand: (i) the mechanisms by which such
63 organic matter is degraded in the water column, and (ii) the relative importance of biotic vs.
64 abiotic processes responsible for this degradation.

65 Biotic degradation of algal material in the water column depends not only on zooplankton
66 grazing (Harvey et al., 1987), but also on the remineralization activity of the associated bacteria.
67 Indeed, particles are rapidly colonized by prokaryotes, and particle-attached communities are
68 often more metabolically active (Grossart et al., 2003; 2007) and phylogenetically diverse
69 (Ortega-Retueta et al., 2013; Ganesh et al., 2014) than free-living assemblages.

70 Although less widely studied than its biologically mediated (heterotrophic) counterpart,
71 abiotic degradation by processes such as photooxidation and autoxidation (spontaneous free
72 radical reaction of organic compounds with oxygen) is now understood to play a role in the fate
73 of phytoplankton in the ocean (for a recent review, see Rontani and Belt, 2020). While, due to
74 the presence of chlorophyll *a*, a very efficient photosensitizer (Foote, 1976), visible-light-
75 induced photosensitization involves mainly reaction with singlet oxygen ($^1\text{O}_2$) and acts on the

76 unsaturated lipid components of algae, the mechanism by which autoxidation is initiated in
77 phytodetritus appears to be homolytic cleavage of photochemically-produced hydroperoxides
78 (Girotti, 1998; Rontani et al., 2003). Consequently, both photooxidation and autoxidation can
79 significantly affect the composition of lipids in suspended particles (Rontani and Belt, 2020).

80 Lipids, which constitute one of the three main classes of organic matter in algal material
81 (Sun et al., 2002), are less labile than carbohydrates and proteins and are thus often used as
82 biomarkers to determine the sources (Volkman, 1986, 2003) and the alteration state of specific
83 organisms (Rontani et al, 2012; 2016).

84 In the present work, we monitored the biotic and abiotic degradation of lipids in
85 suspended particle material (SPM) collected in 2018 from the Western Channel Observatory
86 (WCO, <https://www.westernchannelobservatory.org.uk/>) marine station L4, which is a highly
87 seasonal temperate shelf site (Widdicombe et al 2010, Atkinson et al 2015, Cornwell et al 2020).
88 A focus of the study was the action of a particular bacterial enzyme (10S-DOX), which was
89 previously observed in Arctic sea ice and sinking particles (Amiriaux et al., 2017; Rontani et al.,
90 2018), and in estuaries of diverse latitudes (Galeron et al., 2018); however, the role of this
91 enzyme in the environment has hitherto remained unclear. Here, we hypothesised that this
92 enzyme could be employed by bacteria to detoxify free fatty acids released by wounded
93 diatoms, perhaps as a result of increased copepod activity (i.e. grazing).

94

95

96 **2. Experimental**

97

98 *2.1. Site description*

99 The oceanographic time-series and marine biodiversity reference site L4 (50° 15'N, 4° 13'W,
100 ca. 53 m water depth), is located in the Western English Channel, 13 km south southwest of

101 Plymouth, UK (Fig. 1). L4 is one of Europe's principal coastal time series sites and the
102 Plymouth Marine Laboratory has sampled its natural phytoplankton community since 1992.
103 The seasonal phytoplankton community at L4 has been well documented over many years (e.g.
104 Widdicombe et al. 2010, Atkinson et al. 2015, Tarran and Bruun 2015, Cornwell et al. 2020).
105 Specifically, phytoplankton biomass at L4 typically comprises a background population of
106 flagellates, which increase steadily into summer (Atkinson et al 2015). A diatom bloom often
107 begins in April, with a bloom of *Phaeocystis* spp. (Prymnesiophyte) in some years
108 (Widdicombe et al 2010, Atkinson et al 2015). With the onset of summer stratification and
109 nutrient limitation, Chl *a* levels often diminish around June as the diatom bloom is succeeded
110 by a peak of autotrophic dinoflagellates (Atkinson et al 2015). Coccolithophores increase in the
111 autumn of some years, but their contribution to biomass overall is relatively minor (Atkinson
112 et al. 2015).

113 The microzooplankton protist assemblages are dominated by ciliates and colourless
114 dinoflagellates (defined here as heterotrophic). Ciliates typically peak at around the same time
115 as the spring diatom bloom (Widdicombe et al 2010, Atkinson et al 2015, Cornwell et al 2020),
116 whereas the stronger peak of dinoflagellates appears later (Atkinson et al 2015). The non-
117 carnivorous holoplankton, which also includes copepods, starts to increase before the spring
118 bloom and is often sustained until October (Atkinson et al 2015). In contrast, the carnivorous
119 zooplankton typically peak during the autumn (Atkinson et al., 2015).

120

121 2.2 SPM sampling

122 Water samples from 5 m and 25 m water depth were collected from the L4 station throughout
123 2018 (and some in 2019) on board the *R/V Plymouth Quest* (approximately monthly) using 10
124 L Niskin bottles mounted on to a conductivity, temperature and depth (CTD) rosette sampler.
125 The particulate fractions were collected under subdued light conditions from 2-4 L of water by

126 means of vacuum filtration on 47 mm glass microfibre filters (Whatman, GF/F, as supplied).
127 Water samples were processed immediately after collection and filtered materials kept frozen
128 (-20°C) until further analysis.

129

130 *2.3. Lipid extraction*

131 Filtered water samples (GF/F filters) were reduced at room temperature with excess NaBH₄ (70
132 mg) after adding MeOH (25 mL, 30 min) to reduce labile hydroperoxides (resulting from photo-
133 or autoxidation) to alcohols, which are more amenable to analysis by gas chromatography (GC).
134 Water (25 mL) and KOH (2.8 g) were then added and the resulting mixture saponified by
135 refluxing (2 h). After cooling, the mixture was acidified (HCl, 2 N) to pH 1 and extracted with
136 dichloromethane (DCM; 3 × 20 mL). The combined DCM extracts were dried over anhydrous
137 Na₂SO₄, filtered and concentrated by rotary evaporation at 40°C to give total lipid extracts
138 (TLEs). TLEs were then silylated and analyzed by gas chromatography-electron impact
139 quadrupole time-of-flight mass spectrometry (GC-QTOF). Analysis of blank filters showed the
140 presence of small amounts (< 10% of the values obtained from water samples) of cholesterol
141 and saturated fatty acids, which were subtracted.

142 A different treatment was used to determine the proportion of free fatty acids (FFAs). The
143 samples were extracted three times with chloroform-MeOH-H₂O (1:2:0.8, v:v:v) using
144 ultrasonication. The supernatant was separated by centrifugation at 3500G for 9 min. To initiate
145 phase separation, purified H₂O was added to the combined extracts to give a final volume ratio
146 of 1:1 (v:v). The upper aqueous phase was extracted three times with DCM and the combined
147 DCM extracts were filtered and the solvent removed via rotary evaporation. The residue
148 obtained after extraction was dissolved in 4 mL of DCM and separated into two equal
149 subsamples. After evaporation of the solvent, fatty acids were directly quantified by GC-QTOF
150 in the first subsample after silylation, while the second subsample was saponified and treated

151 as described above. Comparison of the amounts of fatty acids present before and after
152 saponification enabled estimation of the percentage of FFAs. All the solvents (pesticide/glass
153 distilled grade) and reagents (Puriss grade) were obtained from Rathburn and Sigma-Aldrich,
154 respectively.

155

156 *2.4. Silylation*

157 Dry TLEs and standards were derivatized by dissolving them in 300 μ L pyridine/bis-
158 (trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v/v) and silylated in a heating block
159 (50 °C, 1 h). After evaporation to dryness under a stream of N₂, the derivatized residue was
160 dissolved in ethyl acetate/BSTFA (2:1, v/v) (to avoid desilylation) and analysed by GC-QTOF.

161

162 *2.5. Gas chromatography-EI quadrupole time-of-flight mass spectrometry*

163 Accurate mass measurements were made in full scan mode using an Agilent 7890B/7200
164 GC/QTOF system (Agilent Technologies, Parc Technopolis – ZA Courtaboeuf, Les Ulis,
165 France). A cross-linked 5% phenyl-methylpolysiloxane (Macherey-Nagel; OPTIMA-5MS
166 Accent, 30 m \times 0.25 mm, 0.25 μ m film thickness) capillary column was used. Analyses were
167 performed with an injector operating in pulsed splitless mode set at 270°C. Oven temperature
168 was ramped from 70°C to 130°C at 20°C min⁻¹ and then to 300°C at 5°C min⁻¹. The pressure
169 of the carrier gas (He) was maintained at 0.69×10^5 Pa until the end of the temperature program.
170 Instrument temperatures were 300°C for transfer line and 230°C for the ion source. Nitrogen
171 (1.5 mL min⁻¹) was used as collision gas. Accurate mass spectra were recorded across the range
172 m/z 50–700 at 4 GHz with the collision gas opened. The QTOF-MS instrument provided a
173 typical resolution ranging from 8009 to 12252 from m/z 68.9955 to 501.9706.
174 Perfluorotributylamine (PFTBA) was used for daily MS calibration. Compounds were

175 identified by comparing their TOF mass spectra, accurate masses and retention times with those
176 of standards. Quantification of each compound involved extraction of specific accurate
177 fragment ions, peak integration and determination of individual response factors using external
178 standards and Mass Hunter (Agilent Technologies, Parc Technopolis – ZA Courtaboeuf, Les
179 Ulis, France) software.

180

181 2.6. Standard compounds

182 Phytol (**12**), fatty acids, most of the sterols and 2,6,10,14-tetramethylpentadecanoic acid
183 (pristanic acid) (**15**) were purchased from Sigma-Aldrich (St. Quentin Fallavier, France). 3,6-
184 Dihydroxycholest-4-ene (**10**) (employed for sterol photooxidation estimates) was obtained from
185 Maybridge Ltd. The synthesis of 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol
186 (phytyldiol) (**13**) was described by Rontani and Aubert (2005). 4,8,12-Trimethyltridecanoic
187 acid (4,8,12-TMTD acid) (**16**) was synthesized from isophytol (**19**) (Interchim, Montluçon,
188 France) by a previously described procedure (Rontani et al., 1991). 3,7,11,15-
189 Tetramethylhexadecanoic acid (phytanic acid) (**14**) was produced in three steps from phytol
190 (**12**) as described previously (Rontani et al., 2003). Cholestane-3 β ,5 α ,6 β -triol (**11**) (employed
191 for sterol autoxidation estimates) was produced by oxidation of cholesterol (**2**) with
192 H₂O₂/KI/H₂SO₄ (Li and Li, 2013). (8-11)-Hydroperoxyhexadec-(8-10)-enoic acids (*Z* and *E*)
193 (**30-35**) were produced by Fe²⁺/ascorbate-induced autoxidation (Loidl-Stahlhofen and Spiteller,
194 1994) of palmitoleic acid (**23**). Subsequent reduction of these different hydroperoxides in
195 methanol with excess NaBH₄ afforded the corresponding hydroxyacids. A standard of *threo*
196 7,10-dihydroxyoctadec-8(*E*)-enoic acid containing 10% of *threo* 7,10-dihydroxyhexadec-8(*E*)-
197 enoic acid (**42**) previously produced by *Pseudomonas aeruginosa* PR3 (Suh et al., 2011) was
198 obtained from Dr. H.R. Kim (School of Food Science and Biotechnology, Kyungpook National
199 University, Daegu, Korea).

200

201 *2.7. Estimation of autoxidative, photooxidative and 10S-DOX degradation*

202 The role played by autoxidation, photooxidation and 10S-DOX oxidation in the degradation of
203 palmitoleic acid was estimated based on the profiles of isomeric allylic hydroxyacids obtained
204 after NaBH₄-reduction as described previously by Rontani et al. (2018).

205

206 **3. Results**

207

208 *3.1. Trophic environment at station L4 in 2018*

209 The main sterols in the filtered water samples: 24-norcholesta-5,22*E*-dien-3β-ol (24-norsterol)
210 (**1**), cholest-5-en-3β-ol (cholesterol) (**2**), cholesta-5,22*E*-dien-3β-ol (22-dehydrocholesterol)
211 (**3**), cholest-5,24-dien-3β-ol (desmosterol) (**4**), 24-methylcholesta-5,22*E*-dien-3β-ol (*epi*-
212 brassicasterol) (**5**), 24-methylcholesta-5,24(28)-dien-3β-ol (24-methylenecholesterol) (**6**), 24-
213 ethylcholest-5-en-3β-ol (sitosterol) (**7**), 24-ethylcholesta-5,22*E*-dien-3β-ol (fucosterol) (**8**) and
214 4α,23,24-trimethyl-5α-cholest-22*E*-en-3-ol (dinosterol) (**9**), were quantified to estimate the
215 nature and the amount of the algal material present in SPM samples across the 2018 time series.
216 At 5 m, sterol concentrations showed the occurrence of two peaks of phytoplanktonic biomass
217 at the end of April and in September (Table 1, Fig. 2A). In April, the sterol profile was
218 characterized by the presence of high percentages of cholesterol (**2**) and 24-norsterol (**1**), while
219 in September, cholesterol (**2**), brassicasterol (**5**), 24-methylenecholesterol (**6**) and dinosterol (**9**)
220 were the most abundant. At 25 m, two peaks of phytoplanktonic biomass could be observed at
221 the end of April and May (Table 2, Fig. 2B) with the percentages of cholesterol (**2**) and 24-
222 norsterol (**1**) again relatively abundant during these two events. A relatively high abundance of
223 brassicasterol (**5**) was also observed at 25 m in May.

224 At 25 m, the concentration of phytol (chlorophyll phytyl side-chain) (**12**) followed
225 logically the same trend as that of the sterols (Table 2). In contrast, we observed a small lag
226 between the date of the highest concentration of phytol (**12**) (08/13/18) and total sterols
227 (09/17/18) at 5 m (Table 1). Concerning isoprenoid acids, a peak in phytanic acid (**14**)
228 concentration was detected on 04/30/18 at both depths, while highest 4,8,12-TMTD acid (**16**)
229 concentrations were observed in February and March at 5 m (Tables 1 and 2, Fig. 3).

230 We also quantified the main saturated (SFAs), monounsaturated (MUFAs) and
231 polyunsaturated (PUFAs) fatty acids (Tables 3 and 4). While SFAs appeared to be dominant
232 and the percentage of MUFAs relatively constant at both depths across the 2018 time series,
233 PUFAs were highly variable at both depths. SFAs were dominated by C_{16:0} (**21**) and C_{14:0} (**20**),
234 MUFAs by C_{16:1 ω 9} (palmitoleic acid) (**22**) and C_{18:1 ω 9} (oleic acid) (**24**), and PUFAs by C_{20:5} (**26**)
235 and C_{22:6} (**27**). The bacterially-derived C_{18:1 ω 7} (*cis*-vaccenic acid) (**25**) and branched (*iso* and
236 *anteiso*) C_{15:0} acids (BrC_{15:0}) (**28** and **29**) were also detected.

237

238 3.2. Biotic and abiotic degradation of lipid components of phytoplankton at station L4 in 2018

239

240 3.2.1. Photooxidation

241 Due to the higher solar irradiance available, it is perhaps not surprising that photooxidation
242 processes acted more intensively at 5 m than at 25 m, although only the most reactive lipids
243 (e.g. chlorophyll) appeared to be strongly affected by this process (Tables 1 and 2, Fig. 4). Thus,
244 chlorophyll photooxidation estimates were highly variable at 5 m (ranging from 8% to 100%)
245 (Table 1, Fig. 4) yet relatively consistent and low at 25 m (10%–26%) (Table 2). The
246 photooxidation of MUFAs (reaching 2.4% and 2.0% at 5 m and 25 m, respectively) was very
247 limited at both depths (Fig. 5), while Δ^5 -sterols appeared to be essentially unaffected.

248

249 3.2.2. Autoxidation

250 3,7,11,15-tetramethylhexadec-3(*cis/trans*)-ene-1,2-diols (**17**) and 3,7,11,15-tetramethyl-
251 hexadec-2(*cis/trans*)-ene-1,4-diols (**18**) resulting from autoxidation of the chlorophyll phytyl
252 side-chain could be identified in the different samples investigated, but were not quantified.
253 Similarly, the detection of *cis*-hydroxyhexadecenoic acids (**40** and **41**, see appendix) provides
254 evidence for autoxidation of palmitoleic acid (**22**), although this was relatively minor, reaching
255 only a maximum of 14% and 16% in January at 5 and 25 m, respectively (Fig. 5). In contrast,
256 autoxidation products of Δ^5 -sterols (i.e. 3 β ,5 α ,6 β -steratriols; Rontani, 2012) were not detected
257 in any of the samples.

258

259 3.2.3. Biotic degradation

260 A clear dominance of 10-hydroxyhexadec-8(*E*)-enoic acid (**36**) was observed within the
261 palmitoleic acid oxidation products in the sample collected on 04/30/18 at 25 m (Fig. 6B), and
262 attributed to the involvement of a bacterial 10-dioxygenase enzyme (10S-DOX). Similar
263 evidence for the involvement of this enzyme was also observed in the corresponding sample
264 collected at 5 m, but in this case 8-hydroxyhexadec-9(*E*)-enoic acid (**38**) was also dominant
265 (Fig. 6A). 10S-DOX degradation of palmitoleic acid (**22**) in these samples was estimated to be
266 27% and 25% at 5 m and 25 m, respectively (Fig. 5A and 5B). Analysis of samples collected
267 in 2019, albeit from 25 m water depth only, provides further indication of the seasonal nature
268 of this bacterial activity at the L4 station (10S-DOX degradation of palmitoleic acid reaching
269 6% in April; Rontani et al., unpublished data), although multi-annual studies are needed to
270 confirm this.

271 Quantification of the free fatty acid (FFA) content in the sample collected on 04/30/18 at
272 5 m showed a very high proportion of free palmitoleic (**22**) and C_{20:5} (**26**) acids (76% and 74%,
273 respectively). Interestingly, *threo* 7,10-dihydroxyhexadec-8(*E*)-enoic acid (**42**) could also be

274 identified in these samples by comparison of its accurate mass spectrum and retention time with
275 those of a reference compound (Fig. S1). A slightly later eluting compound (Fig. S1), exhibiting
276 the same mass spectrum as *threo* 7,10-dihydroxyhexadec-8(*E*)-enoic acid (**42**), was identified
277 as a mixture of the *erythro* diastereoisomers of this diol (**43**). Such an elution order is in good
278 agreement with the results of Hansel and Evershed (2009).

279

280 **4. Discussion**

281 *4.1. Trophic environment at station L4 in 2018*

282 Sterols possess structural characteristics, such as double bond positions, nuclear methylation
283 and patterns of side-chain alkylation, which are restricted to a few groups of organisms (for
284 reviews see Volkman, 1986; 2003; Rampen et al., 2010). These lipids are thus often used to
285 estimate phytoplanktonic diversity (e.g. Veron et al., 1998; Taipale et al., 2016). For example,
286 24-norsterol (**1**) has previously been identified as a characteristic sterol in diatoms, both in
287 culture of the centric diatom *Thalassiosira antarctica* (Rampen et al., 2007) and in the
288 environment (e.g. Suzuki et al., 2005). The relatively high proportions of 24-norsterol (**1**)
289 observed in our SPM samples collected on 04/30/18 at 5 m and 25 m (30% and 20% of total
290 sterols, respectively) (Tables 1 and 2), along with relatively high values of the diatom fatty acid
291 ratio $((C_{14:0} + C_{16:1\omega7} + \Sigma C_{16} \text{ PUFAs})/C_{16:0})$ (Léveillé et al., 1997) and the diatom-specific $C_{20:5}$
292 FA (Tables 3 and 4), thus suggest a strong contribution from diatoms during this period. Indeed,
293 our lipid data are consistent with previous taxonomic results of Cornwell et al. (2020), who
294 showed that diatom biomass increased strongly (more than fourfold) between weeks 16 and 18
295 of 2018 (corresponding to our 04/19/18 and 04/30/18 samples, respectively). In particulate
296 matter, the $(\text{MUFAs} + \text{PUFAs})/\text{SFAs}$ ratio varies generally from 0.6 during the initial and lag
297 phases of phytoplankton blooms to greater than 1.0 at high rates of organic production (Marty

298 et al., 1988; Mayzaud et al., 1989). The high values observed on 04/30/18 and 05/30/18 at 25
299 m (1.7 and 1.2, respectively), accompanied by elevated values of C_{20:5} FA (Table 4), are thus
300 also consistent with the occurrence of diatom blooms on these dates (Cornwell et al., 2020).
301 Interestingly, Widdicombe et al. (2010) previously observed a shift in phytoplankton
302 composition at the L4 station between late March and early May from a winter community
303 (dominated by centric and benthic diatoms) towards a community dominated by *Chaetoceros*
304 spp., *Thalassiosira* spp. (potential sources of 24-norsterol, Rampen et al., 2007) and
305 *Skeletonema costatum*.

306 On the basis of the relatively high abundance of brassicasterol (**5**) in the 25 m sample
307 collected in May (Table 2, Fig. 2), a significant contribution of *Phaeocystis* could be inferred
308 (Nichols et al., 1991), as is frequently the case at the L4 station during April/May (Widdicombe
309 et al., 2010).

310 Dinoflagellates are important primary producers in the oceans (Kokke et al., 1982),
311 differing from other classes of marine algae with respect to the dominance of 4 α -methylsterols
312 among their sterols. Dinosterol (**9**), for example, which is the major sterol in several
313 dinoflagellates (Shimizu et al., 1976; Kokke et al., 1982), is often employed as tracer for the
314 contribution of these organisms in the marine environment (Robinson et al., 1984). The
315 significant proportion of this sterol in the 09/17/18 sample at 5 m (Fig. 2), along with relatively
316 elevated concentrations of the C_{22:6} FA (produced in high proportion by several dinoflagellates,
317 Peltomaa et al., 2019) (Table 3), thus suggests an important contribution of dinoflagellates to
318 this bloom event, consistent with the results of Cornwell et al. (2020), who identified a peak in
319 ellipsoid-shaped dinoflagellates between weeks 36 and 38 (Sept 2018) at 10 m water depth.

320 The lag between the highest concentrations of phytol (**12**) (08/13/18) and sterols
321 (09/17/18) at 5 m (Table 1), can be attributed to the presence of a bloom of cyanobacteria (well-
322 known to contain very low proportions of sterols; Volkman, 2003) at the end of August, as also

323 supported by the observations of Cornwell et al. (2020), who showed the presence of a single
324 biomass maximum of *Synechococcus* at the L4 station during the same period.

325 Pelagic crustaceans assimilate the chlorophyll phytyl chain when feeding herbivorously
326 (for a review see Rontani and Volkman, 2003). Phytanic acid (**14**), which arises from
327 hydrogenation and terminal oxidation of phytol (**12**), is an important lipid in species of *Calanus*
328 (Blumer and Cooper, 1967; Avigan and Blumer, 1968; Prahl et al., 1984). Classical oxidative
329 metabolism of this isoprenoid acid (Mize et al., 1969) affords pristanic (**15**) and 4,8,12-TMTD
330 (**16**) acids, which have also been detected in different *Calanus* species (Avigan and Blumer,
331 1968; Prahl et al., 1984). These three isoprenoid acids may also be produced during the
332 biodegradation of phytol (**12**) by marine bacteria (Rontani et al., 1999). The high concentrations
333 of phytanic acid (**14**) observed at the end of April at 5 m and 25 m (Fig. 3) therefore strongly
334 suggests the presence of a high proportion of copepods, evident also from a high proportion of
335 cholesterol (**2**) in these samples (Fig. 2). Indeed, herbivorous crustaceans use common dietary
336 algal sterols such as *epi*-brassicasterol (**5**) or 24-methylenecholesterol (**6**) to synthesize
337 cholesterol (**2**) via dealkylation and reduction (Grieneisen, 1994; Behmer and Nes, 2003). The
338 weak proportion of desmosterol (**4**) (an intermediate in the conversion of dietary phytosterols
339 to cholesterol (**2**) by copepods; Goad 1978) observed in the April samples likely reflects the
340 highly efficient conversion of phytosterols to cholesterol (**2**) by copepods, with little
341 accumulation of desmosterol (**4**) (Cass et al., 2011). The presence of a high proportion of
342 copepods inferred from the sterol composition in April further aligns with the results of
343 Cornwell et al. (2020) who conducted a 1-year intensive study of the copepod *Oithona similis*
344 at the L4 station over the 2017–2018 season. Thus, increasing abundances of *O. similis* were
345 identified during the same period as the elevated cholesterol levels in our SPM samples (i.e.
346 between weeks 15 and 19 of 2018) (Cornwell et al., 2020), together with an increase in fecal
347 pellets in the phytoplankton community (phytoplankton net, 20 µm mesh size) (Widdicombe,

348 personal communication). Indeed, increased copepod grazing and feeding on diatoms are
349 common occurrences during the spring bloom at L4 (e.g. Bautista and Harris (1992), Harris et
350 al. (2000)).

351 In summary, biomarker analysis of the SPM samples provide valuable background
352 information about the trophic environment at L4 during 2018. Specifically, elevated
353 contributions from diatoms and *Phaeocystis* could be identified during the spring, along with
354 copepods. On the other hand, the late summer/autumn biomarker pool provides evidence for an
355 environment dominated by dinoflagellates, with some contribution from cyanobacteria. These
356 lipid data are also in very good agreement with recent and long-term studies of trophic
357 environments at L4 (e.g. Cornwell et al 2020, Atkinson et al 2015, Widdicombe et al 2010,
358 Eloire et al 2010).

359

360 *4.2. Biotic and abiotic degradation of lipid components of phytoplankton at station L4 in 2018*

361

362 *4.2.1. Photooxidation*

363 Due to the presence of chlorophylls, which are very efficient photosensitizers (Foote, 1976;
364 Knox and Dodge, 1985), unsaturated lipid components of phytoplankton are susceptible to Type
365 II photosensitized oxidation (i.e. involving singlet oxygen ($^1\text{O}_2$)) processes (Rontani and Belt,
366 2020). The efficiency of these processes is strongly dependent on: (i) the residence time of cells
367 within the euphotic layer (Zafiriou et al., 1984; Mayer et al., 2009), and (ii) the physiological
368 state of phytoplanktonic cells (Merzlyak and Hendry, 1994; Nelson, 1993). Indeed, $^1\text{O}_2$
369 production can exceed the quenching capacities of the photoprotective system (and thus induce
370 cell damage) only when the photosynthetic pathways are not operative as is the case of
371 senescent or highly stressed cells (Nelson, 1993).

372 Based on its high specificity and widespread occurrence in the environment (Cuny and
373 Rontani, 1999), 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol) (**13**)
374 produced during Type II photosensitized oxidation of the chlorophyll phytyl side-chain
375 (Rontani et al., 1994), was proposed previously as a specific and stable tracer of chlorophyll
376 photodegradation (Cuny et al., 2002). The molar ratio phytyldiol (**13**)/phytol (**12**) is often
377 referred to as the Chlorophyll Phytyl side-chain Photodegradation Index (CPPI) and provides a
378 useful semi-quantitative estimate for photodegradation of all chlorophylls with a phytyl side-
379 chain in the marine environment (Cuny et al., 2002). Interestingly, in our SPM samples, the
380 highest chlorophyll photo-oxidation estimates at 5 m mirror the two bloom events and are
381 strongly anti-correlated to the concentration of phytol (**12**) (and therefore of chlorophyll) (Fig.
382 4) ($R^2 = 0.81$, $n = 14$), indicating that photooxidation processes act before and after the blooms
383 on old or senescent cells, but not on healthy cells during the blooms.

384 Unsaturated fatty acids, which generally predominate in the photosynthetic membranes
385 of algae (Woods, 1974), may also be strongly affected by Type II photosensitized oxidation
386 processes in senescent phytoplanktonic cells (Rontani and Belt, 2020). The photodegradation
387 rates of these compounds logically increase with their degree of unsaturation (Rontani et al.,
388 1998), rendering PUFAs, in particular, very reactive towards these processes (Frankel, 1998;
389 Rontani et al., 1998). Based on the correspondence between the lowest proportions of PUFAs
390 and the highest chlorophyll photooxidation estimates at 5 m (Fig. 4), the involvement of Type
391 II photosensitized oxidation processes in PUFA degradation would be expected, yet no PUFA
392 photooxidation products were detected. This is possibly due to: (i) the instability of the
393 polyunsaturated hydroperoxides formed, or (ii) the involvement of intermolecular cross-linking
394 reactions leading to the formation of compounds with macromolecular structures (Neff et al.,
395 1988), which are not readily analyzed by gas chromatography. Exceptionally, for the sample
396 collected on 01/22/18 at 5 m, where chlorophyll photooxidation % and the proportion of PUFAs

397 were both low (Fig. 4), PUFA degradation seems to result from autoxidation processes (see
398 section 4.2.2).

399 Type II photosensitized oxidation of Δ^9 MUFAs produces similar proportions of 9- and
400 10-hydroperoxides with an allylic *trans*-double bond (Frankel et al. 1979; Frankel, 1998),
401 which can subsequently undergo stereoselective radical allylic rearrangement to 11-*trans* and
402 8-*trans* hydroperoxides, respectively (Porter et al. 1995). In contrast, MUFA autoxidation
403 results mainly in the formation of 9-*trans*, 10-*trans*, 11-*trans*, 11-*cis*, 8-*trans* and 8-*cis*
404 hydroperoxides (Frankel, 1998). Autoxidative processes can be readily characterised after
405 NaBH₄-reduction due to the formation of *cis* allylic hydroxyacids, which are specific products
406 of these degradation processes (Porter et al., 1995; Frankel, 1998). The contribution of
407 hydroxyacids resulting from autoxidative processes may be distinguished from that arising from
408 photooxidative processes according to the proportions of *cis*-hydroxyacids detected and the
409 water temperature (Frankel, 1998; Marchand and Rontani, 2001). The results obtained here
410 showed only a very weak photooxidation of palmitoleic acid (**22**) (the main MUFA present in
411 the samples) at both depths (Fig. 5).

412 Finally, as important unsaturated components of biological membranes, Δ^5 -sterols are
413 also susceptible to photooxidative degradation during the senescence of phytoplankton
414 (Rontani and Belt, 2020). However, their photodegradation is generally slower than that of
415 MUFAs due to steric hindrance between the sterol Δ^5 double bond and ¹O₂ (Beutner et al.,
416 2000). The failure to detect photooxidation products of Δ^5 -sterols is therefore consistent with
417 the very weak photodegradation of MUFAs (Tables 3 and 4). During the time series
418 investigated, Type II photosensitized oxidation thus seems to have acted most intensively only
419 on the more reactive lipids (i.e. chlorophyll and PUFAs).

420

421 *4.2.2. Autoxidation*

422 3,7,11,15-tetramethylhexadec-3(*cis/trans*)-ene-1,2-diols (**17**) and 3,7,11,15-tetramethyl-
423 hexadec-2(*cis/trans*)-ene-1,4-diols (**18**) were previously proposed as indicators of radical-
424 mediated oxidative degradation of the chlorophyll phytyl side-chain in the environment
425 (Rontani and Aubert, 2005), and were indeed detected in the current water column samples.
426 Unfortunately, despite the high specificity and widespread occurrence of these diols in the
427 environment, the formation of several additional labile oxidation products during the
428 autoxidation of the phytyl side-chain (Rontani et al., 2003) prevented semi-quantitative
429 estimation of chlorophyll autoxidation.

430 Although more intense than photooxidation, autoxidation of palmitoleic acid (**22**) was
431 relatively low during the time series (Fig. 5). It may be noted that the autoxidation percentages
432 (ranging from 0 to 16%) are clearly in the low range previously observed in polar, tropical and
433 temperate regions (for a review see Rontani and Belt, 2020). Highest autoxidation (14.2 and
434 16.2% at 5 and 25 m, respectively) was observed in January (Fig. 5), suggesting that
435 autoxidative processes also likely played an important role in the degradation of PUFAs at that
436 time (Fig. 4). Indeed, PUFAs such as C_{20:5} (**26**) are autoxidized at a rate more than one order of
437 magnitude faster than MUFAs in senescent diatom cells (Rontani et al., 2014). It was proposed
438 previously that the induction of autoxidative processes in phytodetritus derives likely from the
439 cleavage of photooxidative hydroperoxides (Girotti, 1998; Rontani et al., 2003) so it might be
440 expected that high rates of autoxidation would correspond to high rates of photooxidation. This
441 is clearly not the case in January, when the autoxidation state of MUFAs was the highest (Fig.
442 5) and chlorophyll photooxidation (%) was the lowest (Fig. 4), probably because the intensity
443 of autoxidative processes depends not only on the quantity of photochemically-produced
444 hydroperoxides present in the cells, but also on conditions favouring their homolytic cleavage
445 (e.g. the presence of LOXs or redox-active metal ions, heat or light; Sheldon and Kochi, 1976;
446 Schaich, 2005).

447 Autoxidation of Δ^5 -sterols is generally slower than that of MUFAs in senescent diatom
448 cells (Rontani et al., 2014). Since the extent of MUFA autoxidation was relatively low in the
449 SPM samples (Fig. 5), the very weak autoxidation of sterols was as expected. Therefore, as
450 seen for Type II photosensitized oxidation, autoxidation seems to have acted mainly on the
451 most reactive lipids (i.e. chlorophyll and PUFAs).

452

453 4.2.3. Biotic degradation

454 Type II photosensitized oxidation and free-radical induced oxidation of Δ^9 MUFAs such as
455 palmitoleic acid (**22**) produce (after NaBH₄-reduction of hydroperoxyacids) equal proportions
456 of the major 9-*E* and 10-*E* isomeric allylic hydroxyacids (**36** and **37**) (Frankel, 1998). The strong
457 predominance of 10-hydroxyhexadec-8(*E*)-enoic acid (**36**) observed in the SPM samples
458 collected on 04/30/18 (Fig. 6) can thus be attributed to the involvement of a specific biotic
459 oxidation process. A similar dominance of this isomer among palmitoleic acid (**22**) oxidation
460 products was observed previously in sea ice and in sinking particles in the Canadian Arctic
461 (Amiriaux et al., 2017; Rontani et al., 2018), and also in estuaries of diverse latitudes (Galeron
462 et al., 2018). Its occurrence has previously been attributed to the involvement of specific
463 bacterial dioxygenase activity and to a 10*S*-DOX enzyme, in particular. Indeed, a 10*S*-DOX
464 enzyme capable of converting palmitoleic acid (**22**) to 10(*S*)-hydroperoxyhexadec-8(*E*)-enoic
465 acid (**30**) (reduced to the corresponding hydroxyacid during NaBH₄-reduction) was previously
466 isolated from the bacteria *Pseudomonas aeruginosa* 42A2 (Guerrero et al., 1997; Busquets et
467 al., 2004) and, more recently, found in other genera of marine bacteria, namely
468 *Pseudoalteromonas*, *Shewanella* and *Aeromonas* (Shoja Chaghervand, 2019). The involvement
469 of 10*S*-DOX enzymatic activity in these SPM samples is further supported by detection of *threo*
470 7,10-dihydroxyhexadec-8(*E*)-enoic acid (**42**) (Fig. S1), formed from the specific action of
471 7*S*,10*S*-hydroperoxide diol synthase (linked to the 10*S*-DOX enzymatic activity) (Estupiñán et

472 al., 2014; 2015) on 10(*S*)-hydroperoxyhexadec-8(*E*)-enoic acid (**30**) (Fig. 7). It may be noted
473 that isomerization of the latter by hydroperoxide isomerases (Fig. 7), which are well known to
474 produce *erythro* allylic 1-4 diols (Jernerén et al., 2010), may explain the observed formation of
475 the *erythro* 7,10-dihydroxyhexadec-8(*E*)-enoic acids (**43**) (Fig. S1).

476 Martinez et al. (2010) previously suggested that fatty acids bind to bacterial 10*S*-DOX
477 via their carboxyl groups at a fixed position relative to the catalytic site. This enzyme, localized
478 in the periplasm (Martinez et al., 2013), should thus be mainly active on FFAs and therefore
479 contribute to the detoxification of these deleterious fatty acids (Monfort et al., 2000; Desbois
480 and Smith, 2010) in the bacterial environment (Martínez et al., 2010). The very high proportions
481 of FFAs (and most notably of palmitoleic acid (**22**)) measured in the SPM samples exhibiting
482 the highest 10*S*-DOX activity certainly supports this hypothesis. Further, the trophic level in
483 April 2018 was characterised by: (i) the dominance of diatoms (notably of *Thalassiosirales*)
484 and (ii) the presence of a very high copepod activity (see Section 4.1).

485 Interestingly, an oxylipin-based chemical defence against copepods was observed
486 previously in the diatom *Thalassiosira rotula* (Pohnert 2000; 2002), being initiated by
487 phospholipases acting immediately after cell damage. This lipase activity leads to the
488 preferential release of free MUFAs and PUFAs, the latter converted further by lipoxygenases
489 to reactive defensive metabolites such as the antiproliferative PolyUnsaturated Aldehydes
490 (PUAs) (Fig. 8), which are well-known to inhibit egg cleavage in copepods (Miralto et
491 al., 1999). In contrast, free MUFAs, which are not affected by lipoxygenases, are released intact
492 outside of wounded diatoms. These compounds (dominated by palmitoleic acid (**22**) in diatoms,
493 Pedersen et al., 1999) exhibit a strong bactericidal action towards marine Gram-negative
494 pathogens (Desbois et al., 2009; Desbois and Smith, 2010). The strong 10*S*-DOX bacterial
495 activity observed in SPM samples in April (Fig. 5) can therefore be attributed to a detoxification
496 strategy allowing bacteria associated to diatoms grazed by copepods to survive the release of

497 bactericidal free palmitoleic acid (**22**) (Fig. 8). 10(*S*)-Hydroperoxyhexadec-8(*E*)-enoic and
498 *threo* 7,10-dihydroxyhexadec-8(*E*)-enoic acids (**30** and **42**) resulting from 10*S*-DOX and diol
499 synthase activities, respectively, may be then transported from the periplasmic space of bacteria
500 to the external medium (Martinez et al., 2013).

501 9- and 10-hydroperoxyacids with an allylic *E* double bond can undergo highly
502 stereoselective allylic rearrangement to 11-*E* and 8-*E* hydroperoxides, respectively (Fig. 7), the
503 extent of which increases with time (Porter et al., 1995). A lower proportion of the 8-*E* isomer
504 observed in the SPM sample collected on 04/30/18 from 25 m depth (10-*E*/8-*E* = 4.5 vs 10-*E*/8-
505 *E* = 1.2 at 5 m) (Fig. 6) thus suggests an involvement of the 10*S*-DOX activity at 25 m and an
506 aging of material collected from a shallower 5 m depth. The highest abundance of the copepod
507 *O. similis* at 25 m observed by Cornwell et al. (2020) likely indicates a strong alteration of
508 diatoms and thus an enhanced production of FFAs, which in turn supports an induction of the
509 bacterial 10*S*-DOX activity at this depth. The ascent of planktonic and bacterial material from
510 25 m to 5 m can be facilitated by the presence of a high proportion of Transparent Exopolymer
511 Particles (TEPs) in the shallower SPM, formed abiotically from dissolved precursors released
512 by phytoplankton and bacteria (Passow, 2000) and composed mainly of surface-active
513 polysaccharides (Mopper et al., 1995). Due to their positive buoyancy, TEPs can provide a
514 means for the upward flux of bacteria and phytoplankton in the marine environment (Azetsu-
515 Scott and Passow, 2004).

516 Allylic rearrangement of hydroperoxides in biological membranes is strongly sensitive to
517 the hydrogen atom donor properties of their surrounding molecules (Porter et al., 1994; 1995).
518 In algal membranes containing a high proportion of PUFAs, which are good hydrogen atom
519 donors, allylic rearrangement should be weak (Fig. 7). In contrast, in bacterial periplasm
520 containing only SFAs and MUFAs (both weak hydrogen atom donors), the rearrangement
521 should be favoured (Fig. 7). The extent of the allylic rearrangement of the different

522 hydroperoxides present in each sample therefore reflects the composition of the organisms
523 (bacteria or phytoplankton) present. The strong allylic rearrangement of 10*S*-
524 hydroperoxyhexadec-8(*E*)-enoic acid (**30**) to 8-hydroperoxyhexadec-9(*E*)-enoic acid (**32**)
525 observed in the SPM sample collected at 5 m on 04/30/18 (Fig. 6A) thus provides further
526 evidence for 10*S*-DOX activity in the bacterial periplasm. Interestingly, in the same samples,
527 the rearrangement of 9-hydroperoxyhexadec-10(*E*)-enoic acid (**31**) (produced abiotically in
528 senescent algae) to the corresponding 11-hydroperoxyhexadec-9(*E*)-enoic acid (**33**) appeared
529 to be only very weak (Fig. 6A).

530

531 **5. Conclusions**

532 Selected lipids (sterols and fatty acids) and their biotic and abiotic oxidation products were
533 quantified in SPM samples collected mainly in 2018 from two depths (5 m and 25 m) at the
534 marine time series station L4 located in the western English Channel. The sterol and fatty acid
535 composition was typical of mixed trophic communities at L4 throughout 2018, with a seasonal
536 evolution from mainly diatoms and copepods in spring to dinoflagellates in late
537 summer/autumn, consistent with recent and long-term taxonomic studies.

538 Abiotic lipid autoxidation and photodegradation were both found to be relatively minor,
539 acting mainly on the most reactive lipids. A slightly greater influence of abiotic degradation,
540 however, was found at 5 m compared to 25 m, likely due to higher irradiance and ascent of
541 older planktonic/bacterial material from deeper to shallower waters.

542 In contrast, significant biotic degradation was evident in samples collected at the end of
543 April. In particular, we observed a strong predominance of certain hydroxyacids linked to
544 specific biotic oxidation process involving bacterial dioxygenase (10*S*-DOX) activity. This
545 contribution from 10*S*-DOX in samples at the end of April was accompanied by a relatively
546 high proportion of FFAs, likely resulting from a chemically-induced defense mechanism by

547 diatoms during times of increased zooplankton (copepod) activity. Since FFAs (dominated by
548 palmitoleic acid in diatoms) exhibit a strong bactericidal action towards marine pathogens such
549 as bacteria, the strong 10S-DOX bacterial activity observed in the April SPM samples points to
550 a detoxification strategy by bacteria against the production of bactericidal free palmitoleic acid
551 (22). We thus propose that this enzyme could be employed by bacteria to detoxify FFAs
552 released by wounded diatoms in the presence of copepods.

553

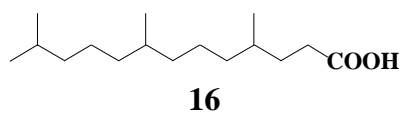
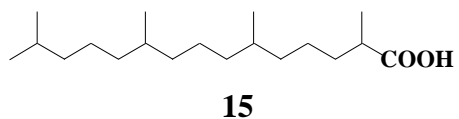
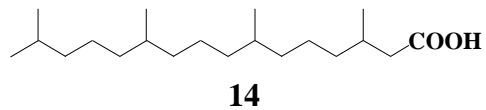
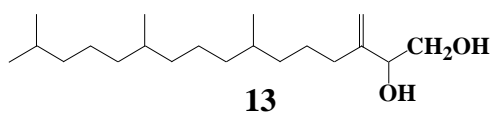
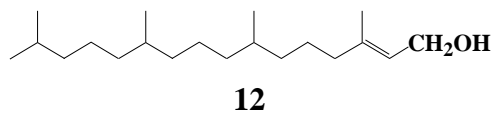
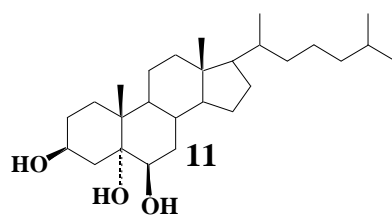
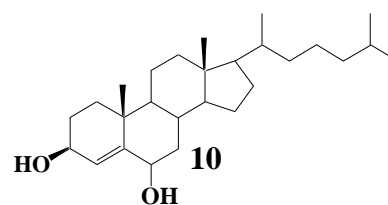
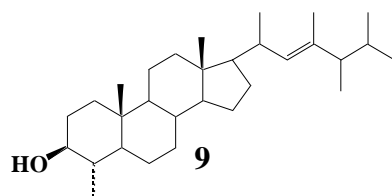
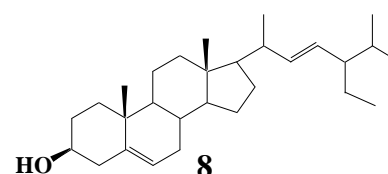
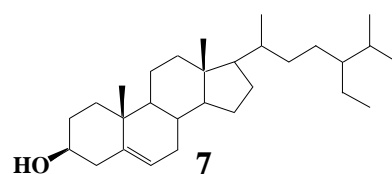
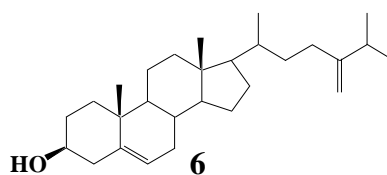
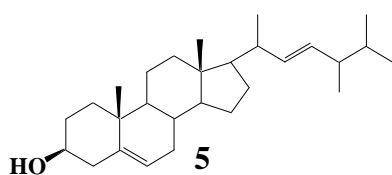
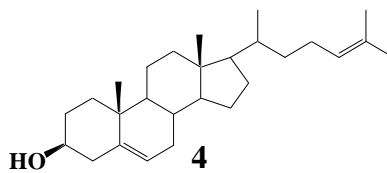
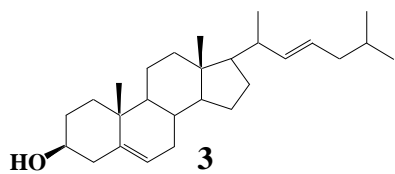
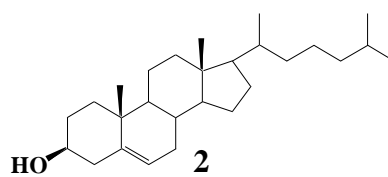
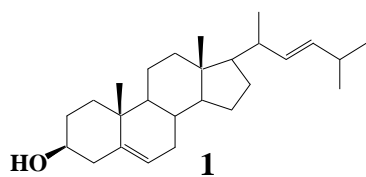
554 **Acknowledgements**

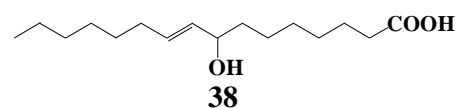
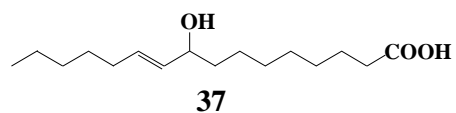
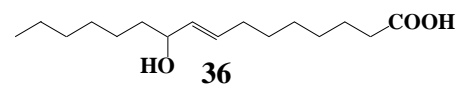
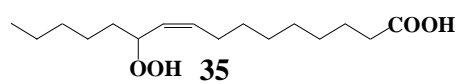
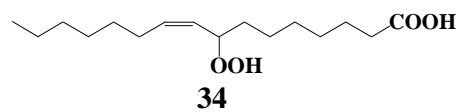
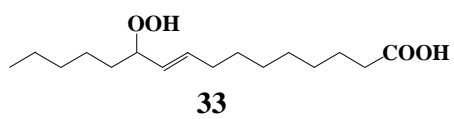
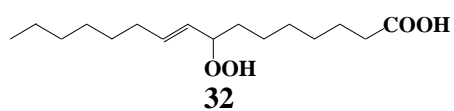
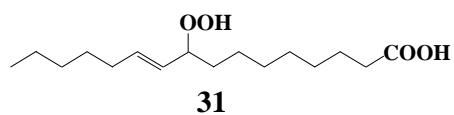
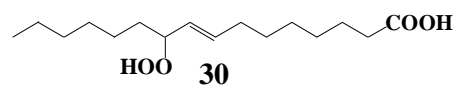
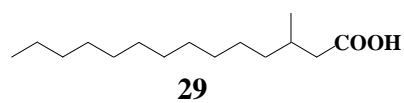
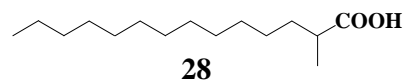
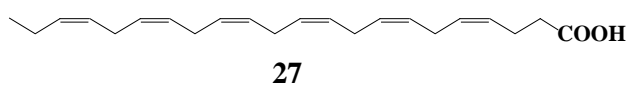
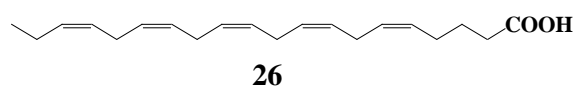
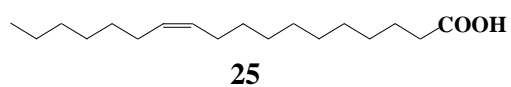
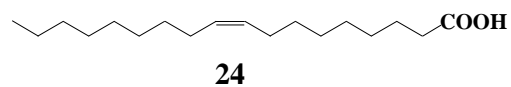
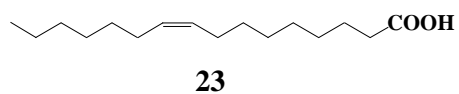
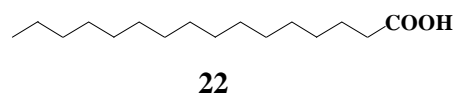
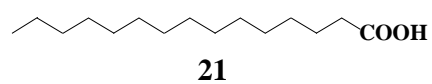
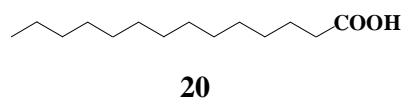
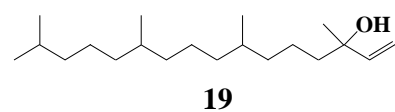
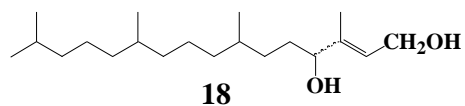
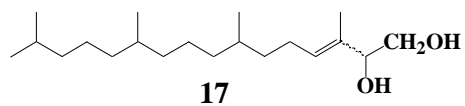
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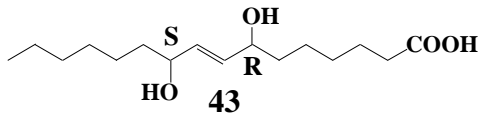
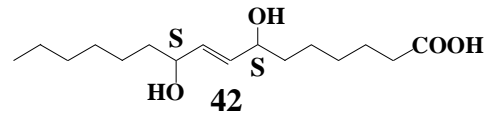
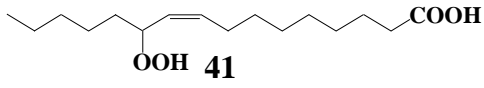
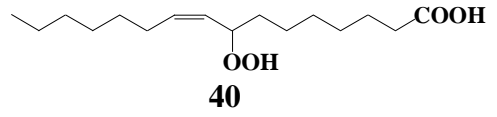
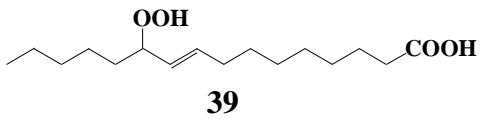
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APPENDIX







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986

987

988 **FIGURE CAPTIONS**

989

990 **Figure 1.** Map of the study area with location of the L4 station investigated.

991

992 **Figure 2.** Time series of sterol concentrations in SPM samples collected at 5 m (A) and 25 m
993 (B) from January to December 2018 at the L4 station.

994

995 **Figure 3.** Time series of acyclic isoprenoid acid concentrations in SPM samples collected at 5
996 m (A) and 25 m (B) from January to December 2018 at the L4 station.

997

998 **Figure 4.** Time series of the proportion of the main classes of fatty acids (SFAs, MUFAs and
999 PUFAs) (A), phytol (**12**) concentration ($\mu\text{g L}^{-1}$) (B) and chlorophyll photooxidation estimate
1000 (%) (C) in SPM samples collected at 5 m from January to December 2018 at the L4 station.

1001

1002 **Figure 5.** Time series of biotic and abiotic degradation percentage of palmitoleic acid (**22**) in
1003 SPM samples collected at 5 m (A) and 25 m (B) from January to December 2018 and at 25 m
1004 from January to December 2019 (C) at the L4 station.

1005

1006 **Figure 6.** Partial ion chromatograms (m/z 199.1518, 213.1675, 329.1968 and 343.2125)
1007 showing the presence of palmitoleic acid (**22**) oxidation products in silylated TLEs in SPM
1008 samples collected at 5 m (A) and 25 m (B) on 04/30/18 at the L4 station.

1009

1010 **Figure 7.** Formation and degradation pathways of 10*S*-hydroperoxyhexadec-8(*E*)-enoic acid
1011 (**30**).

1012

1013 **Figure 8.** Conceptual scheme showing the defense system of diatoms during copepod grazing
1014 and the involvement of FFA detoxification in associated bacteria. (PUA = polyunsaturated
1015 aldehydes, 7,10-DS = 7,10-diol synthase, 10S-DOX = 10S-dioxygenase, 10S-HPHA = 10S-
1016 hydroperoxyhexadecen-8(*E*)-enoic acid, 7,10-DiOHHA = 7,10-dihydroxyhexadecen-8(*E*-
1017 enoic acid).

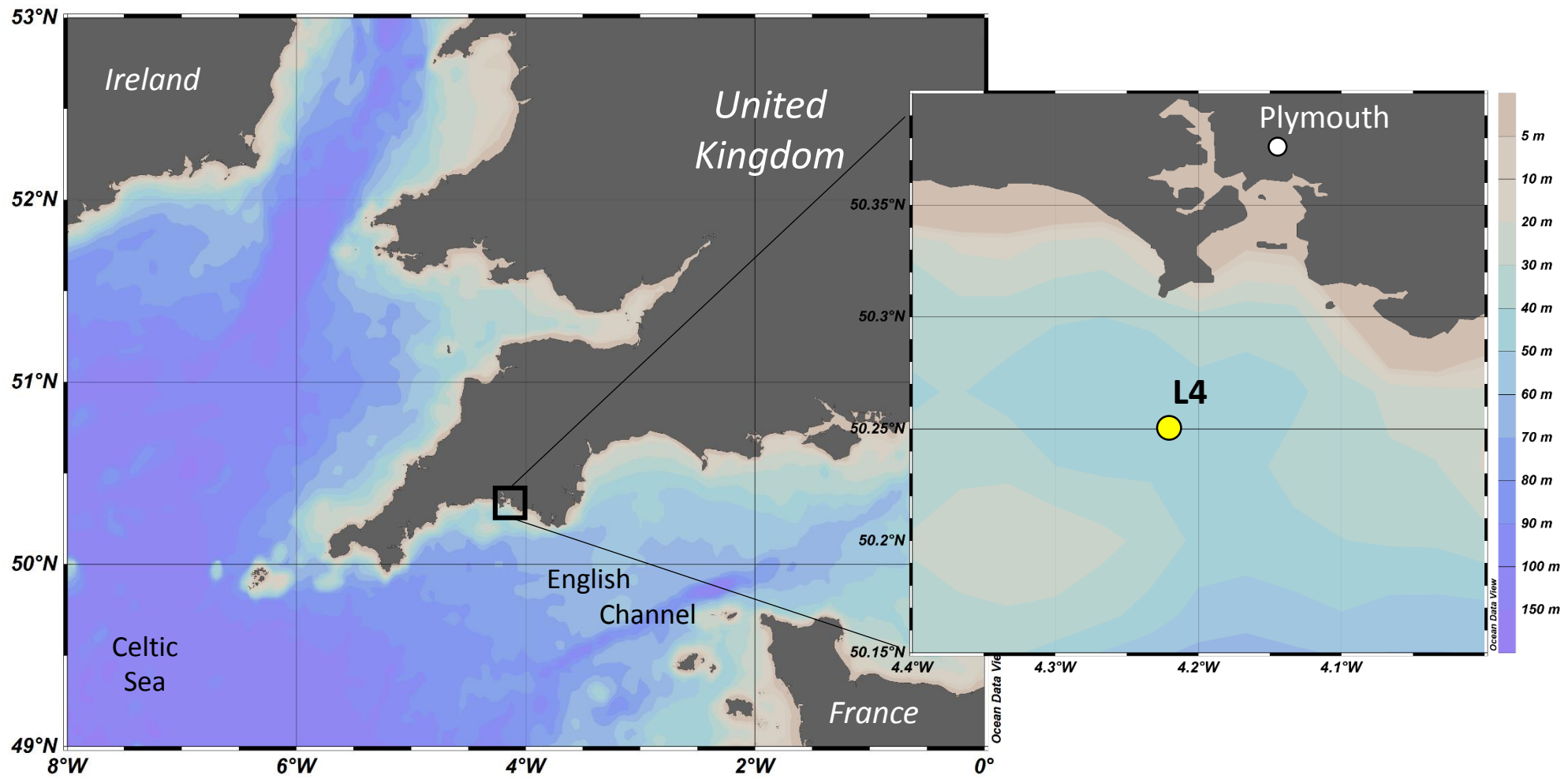
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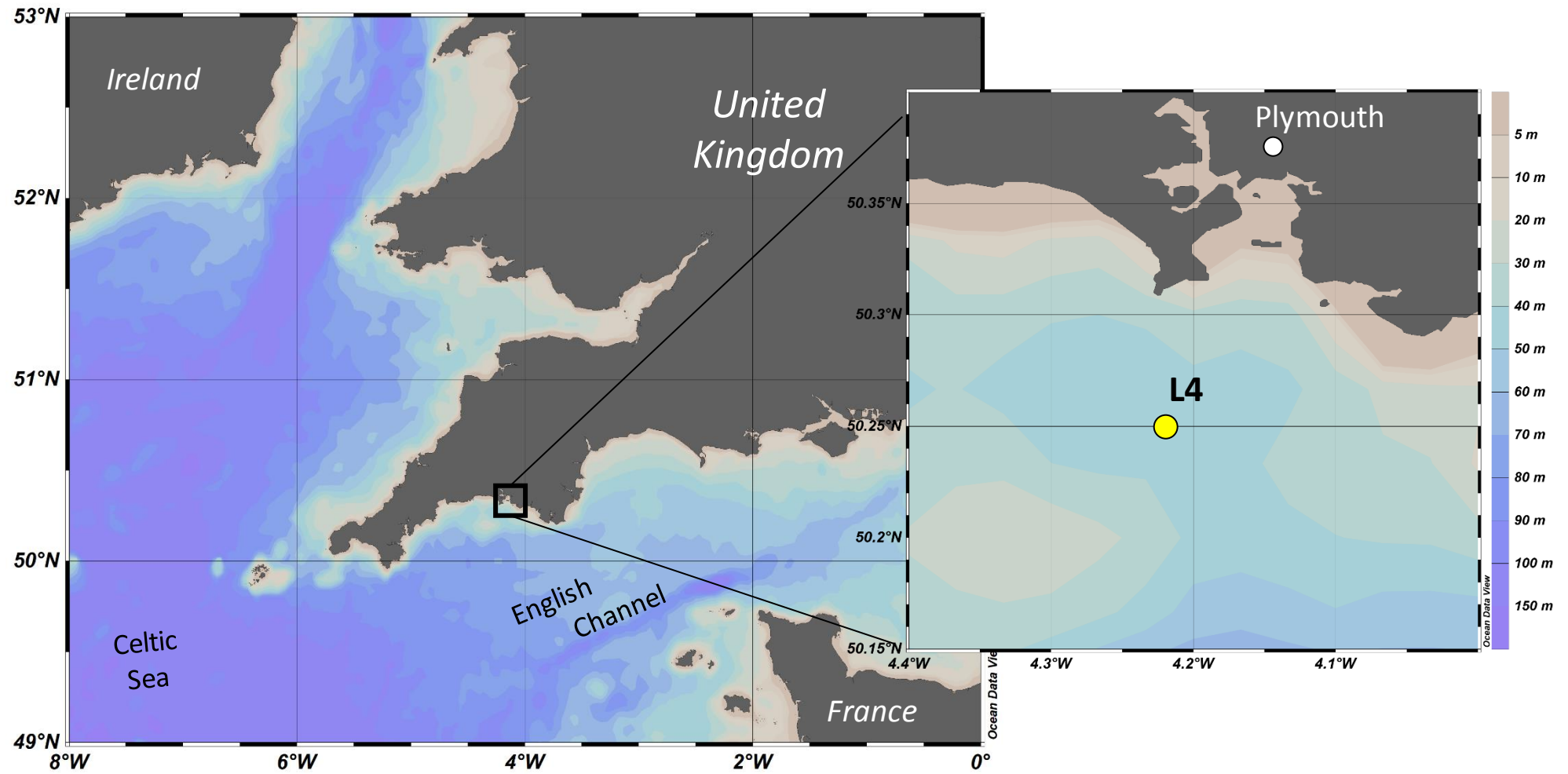
1019 **Supplementary material**

1020

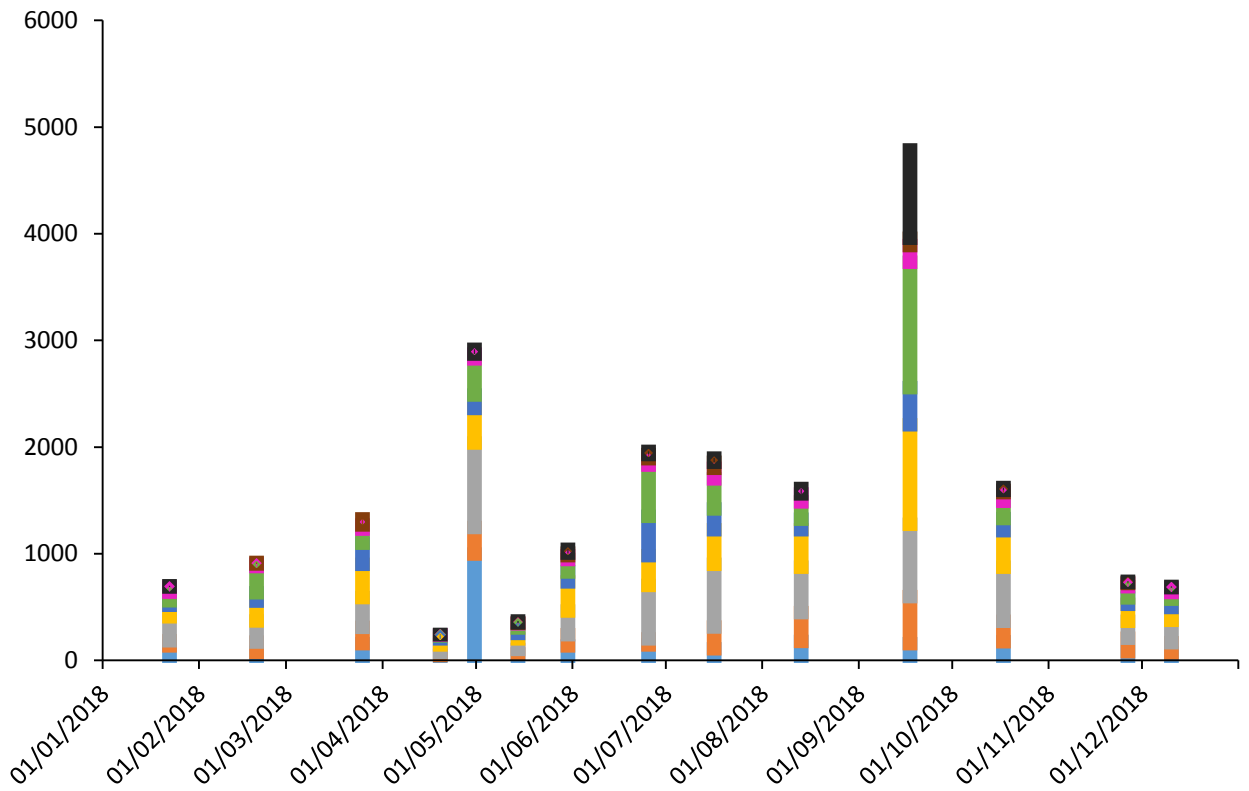
1021 **Figure S1.** Partial ion chromatograms (*m/z* 225.1670, 315.2171, 327.1807 and 417.2808) of
1022 silylated TLE of the SPM sample collected on 04/30/18 at 25 m (A) and standard *threo* 7,10-
1023 dihydroxyhexadec-8(*E*)-enoic acid (**42**) TMS derivative (B).

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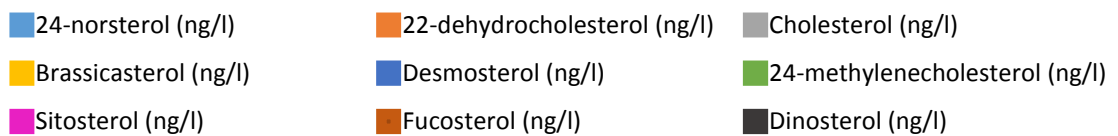
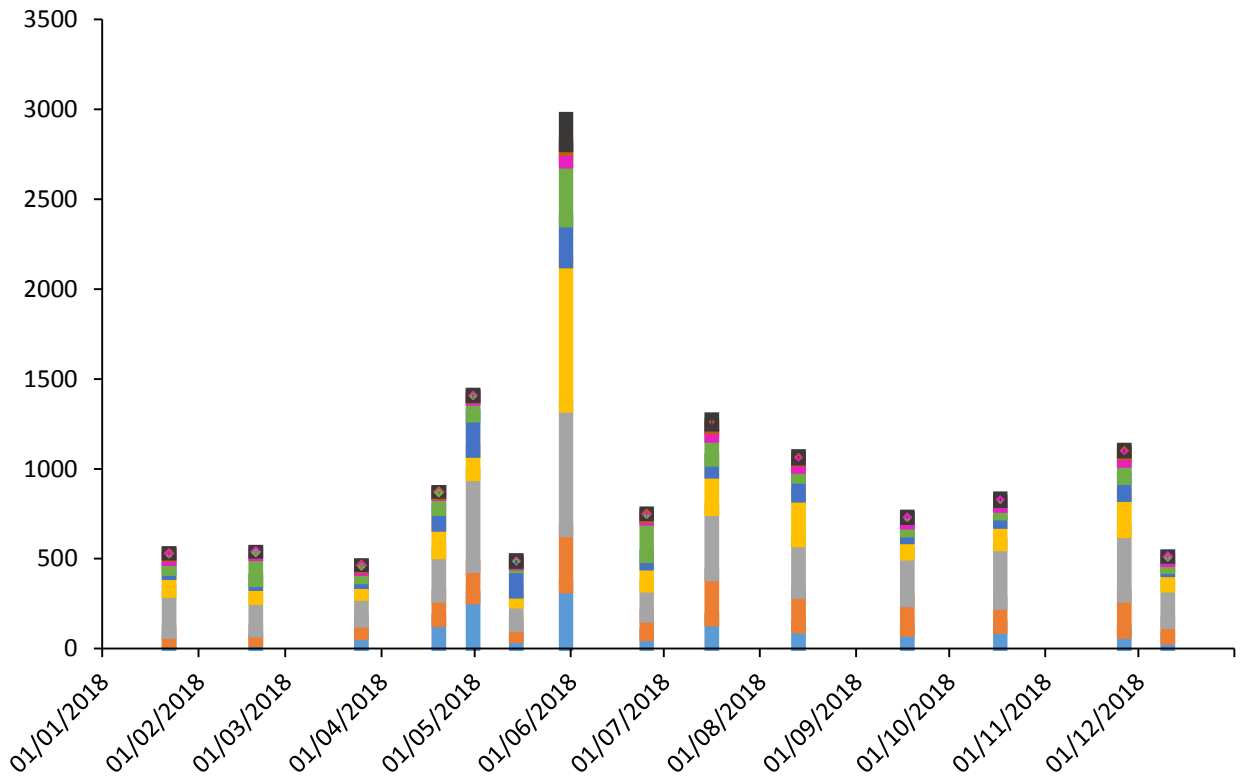




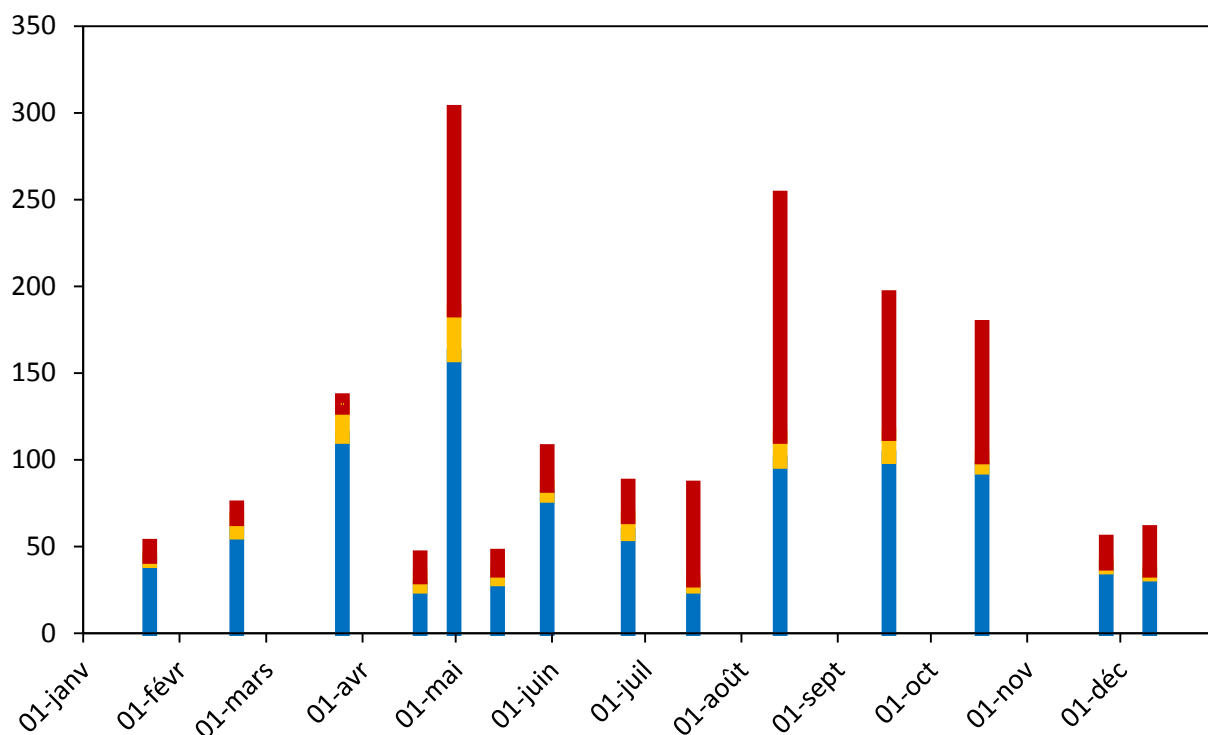
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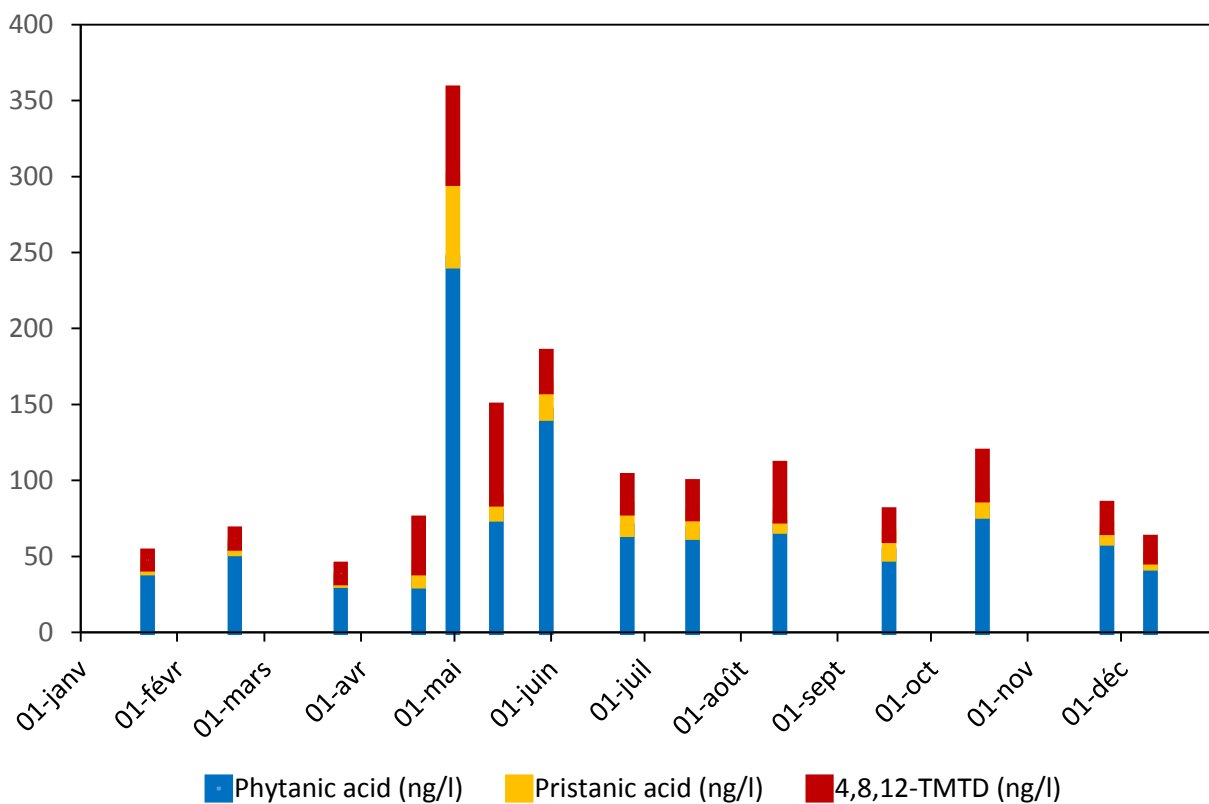
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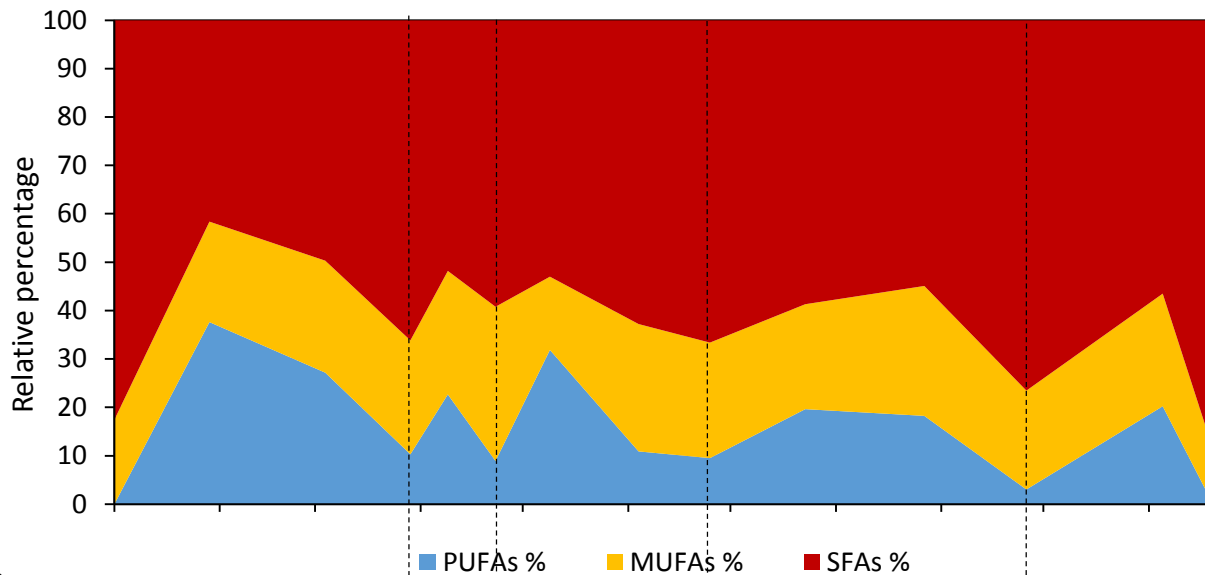
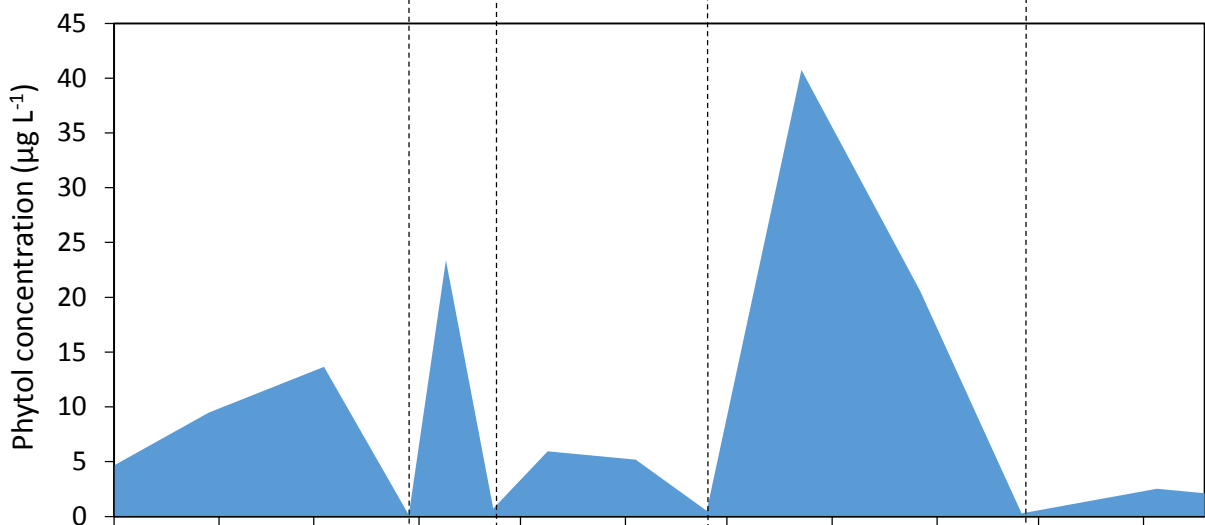
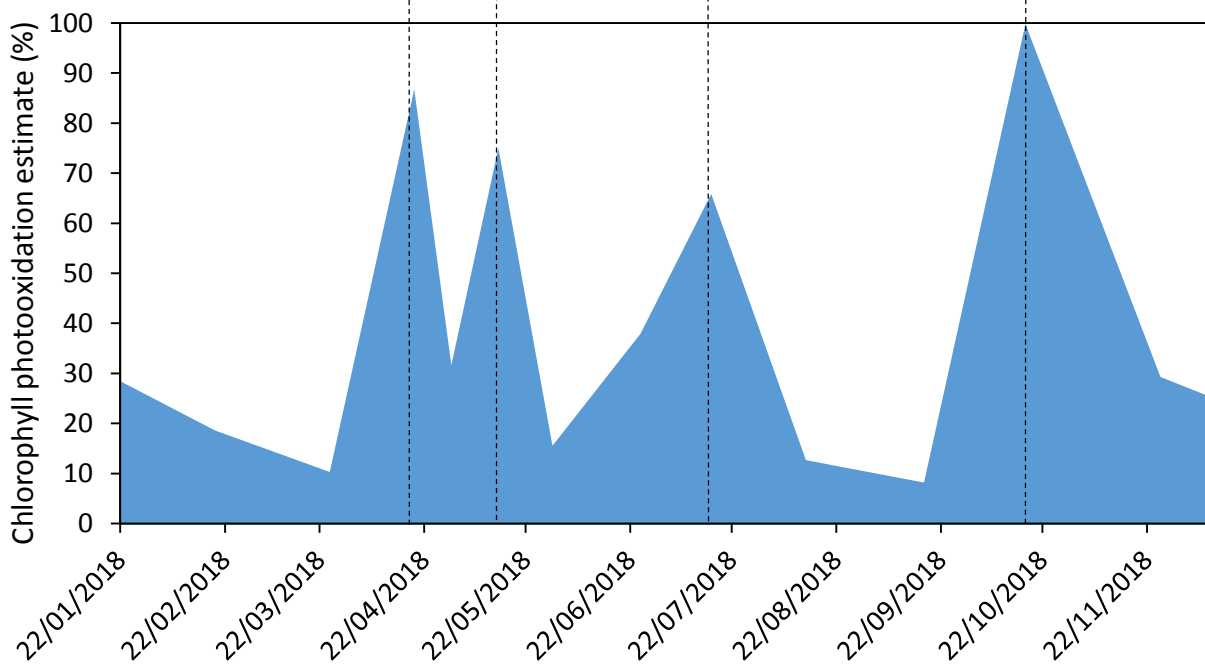


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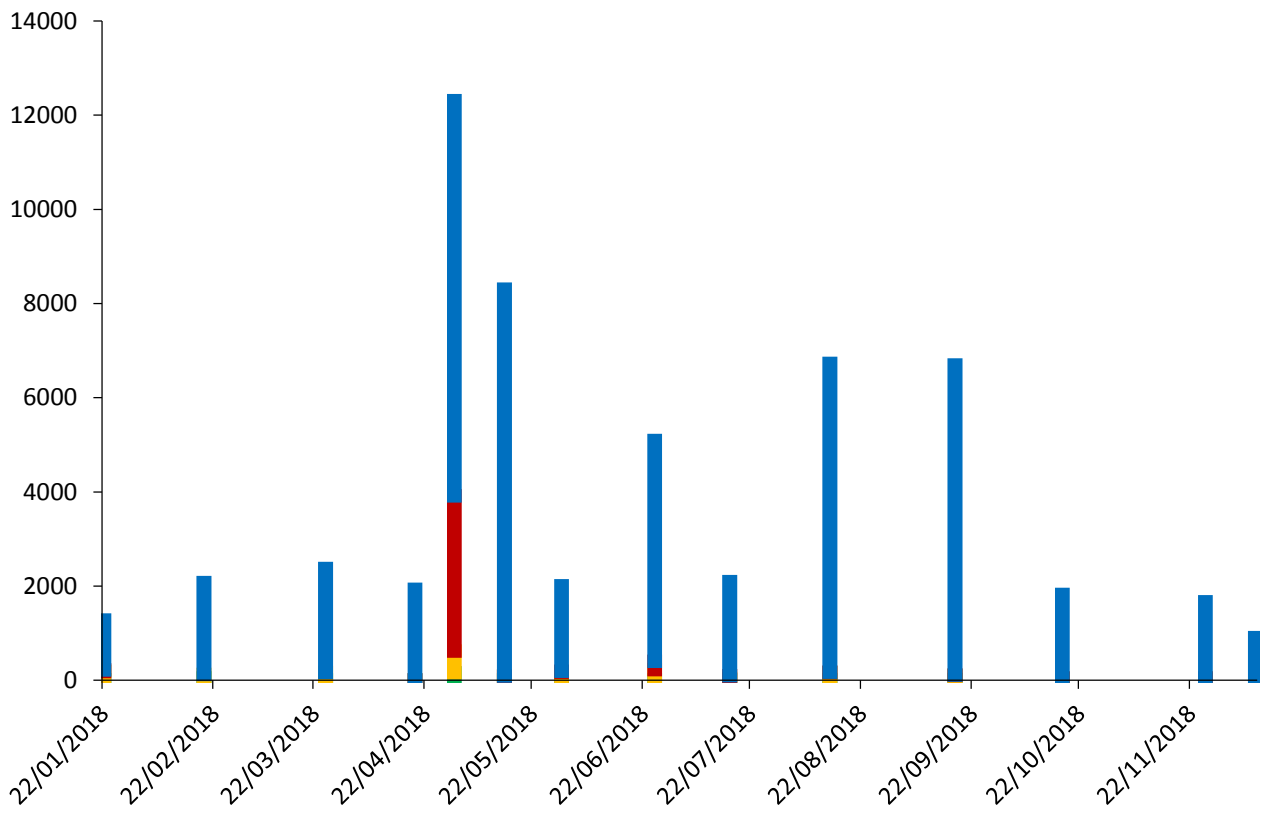


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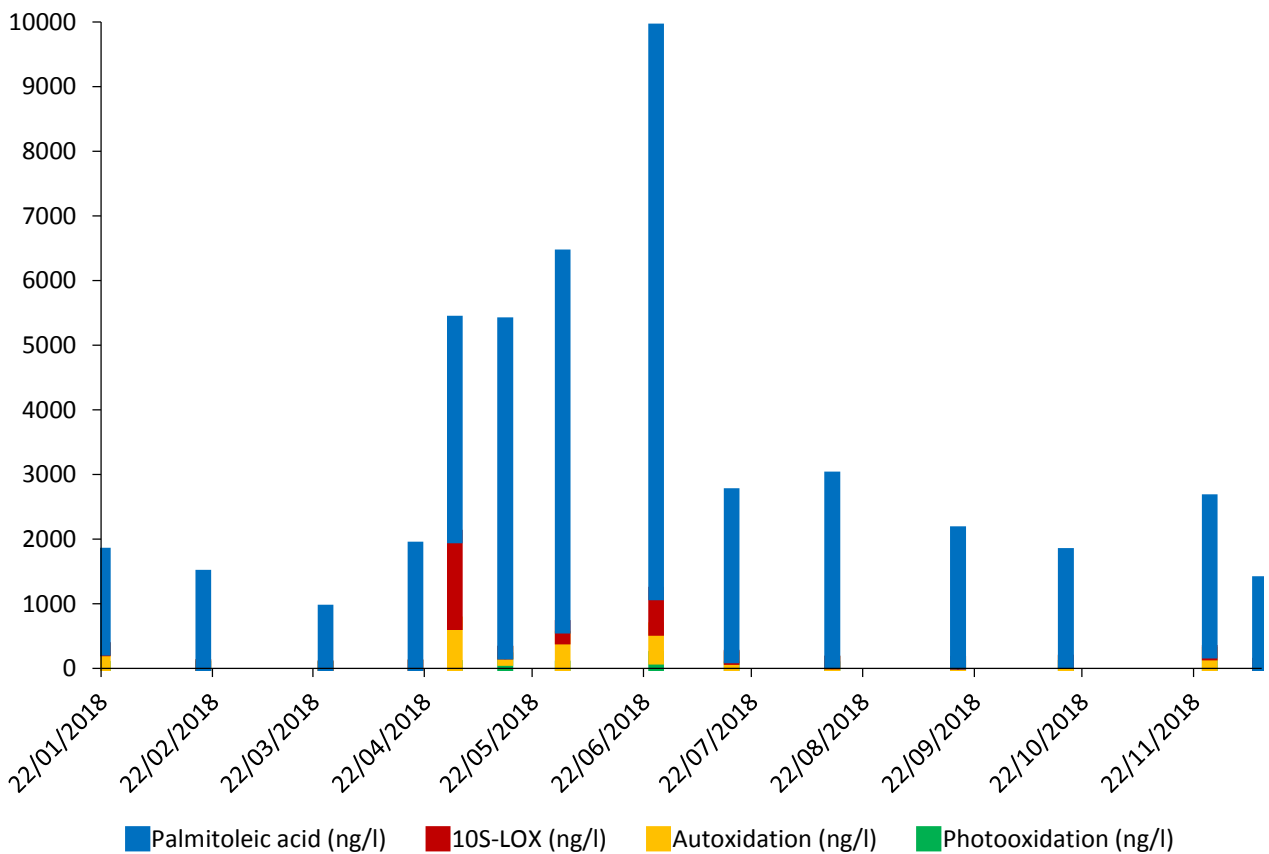


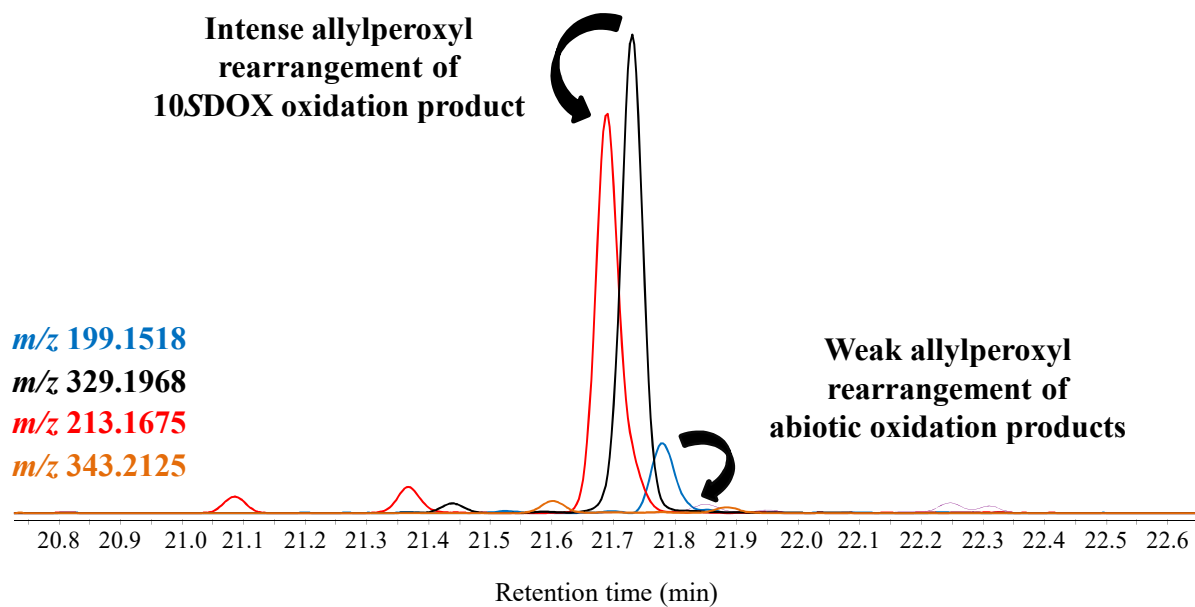
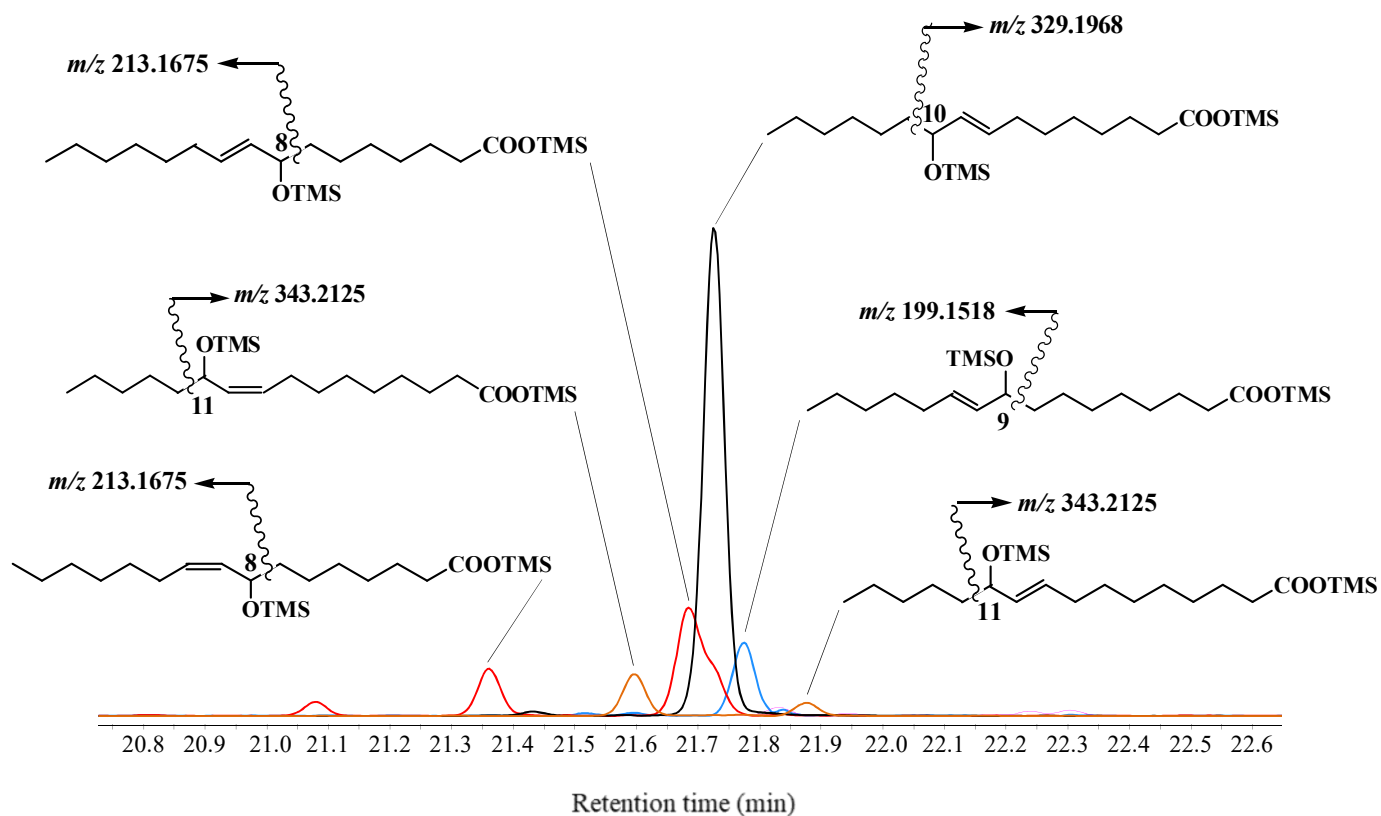
A**B****C**

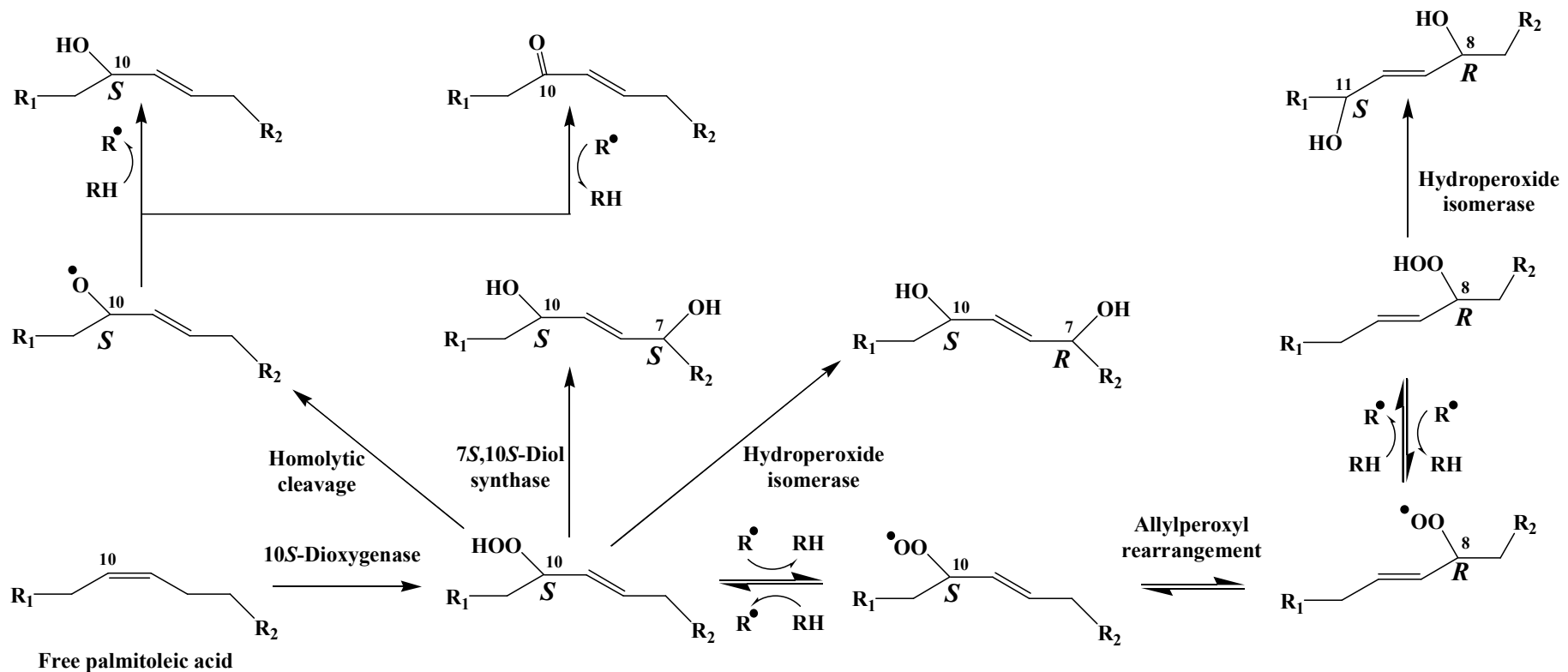
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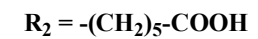
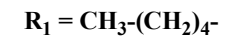
A**B**



**Weak hydrogen donor properties
of MUFA-rich bacterial periplasm**



**Good hydrogen donor properties
of PUFA-rich algal chloroplast**



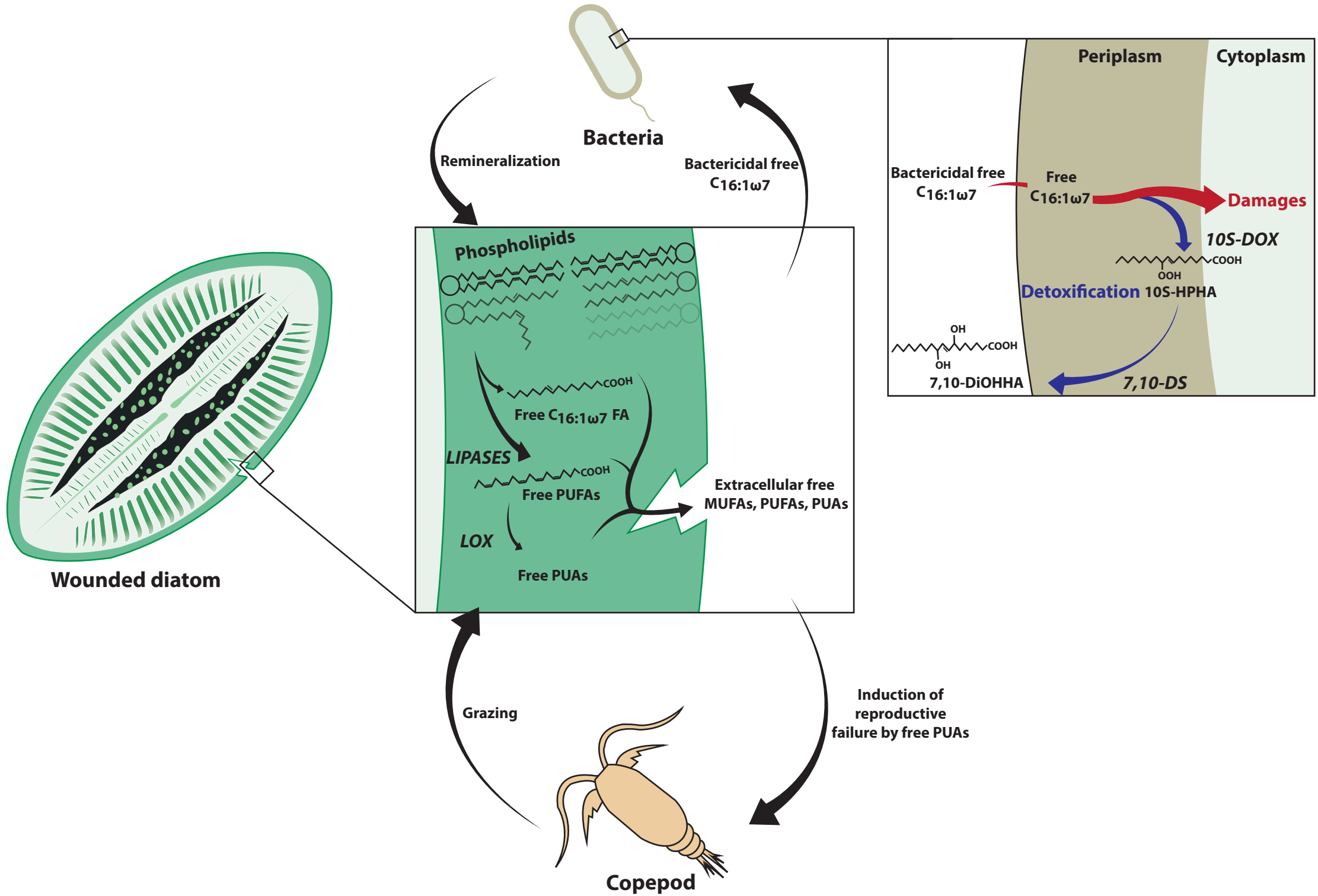


Table 1. Concentrations of sterols and acyclic isoprenoid compounds and chlorophyll photooxidation estimates in spm samples collected at station L4 during the time series 2018 at 5 m.

	01/25	02/18	03/25	04/19	04/30	05/14	05/30	06/25	07/16	08/13	09/17	10/17	11/26	12/10
24-Norcholesta-5,22E-dien-3 β -ol (24-norsterol) ^a	137.1	74.9	156.4	45.8	996.0	62.2	136.9	143.4	109.0	178.6	155.3	174.6	81.5	68.9
Cholesta-5,22E-dien-3 β -ol (22-dehydrocholesterol) ^a	46.9	98.1	152.4	29.4	249.5	40.9	103.7	58.6	203.8	269.1	442.3	192.8	127.8	96.9
Cholest-5-en-3 β -ol (cholesterol) ^a	224.6	196.1	279.4	70.6	791.9	97.9	221.1	500.7	588.9	426.3	679.3	506.5	157.8	211.3
24-Methylcholesta-5,22E-dien-3 β -ol (brassicasterol) ^a	109.2	185.8	312.3	55.9	323.7	51.7	273.6	278.8	323.0	349.3	932.4	340.7	158.1	119.7
Cholest-5,24-dien-3 β -ol (desmosterol) ^a	41.3	77.6	198.7	27.4	128.1	50.8	92.1	368.4	196.2	99.6	348.7	116.0	61.8	79.3
24-Methylcholesta-5,24(28)-dien-3 β -ol (24-methylenecholesterol) ^a	80.2	248.6	132.2	7.9	336.5	38.7	119.0	479.8	281.4	163.5	1173.6	159.9	103.0	60.7
24-Ethylcholest-5-en-3 β -ol (sitosterol) ^a	48.5	23.1	39.6	4.1	47.2	5.6	36.9	60.6	97.8	74.3	156.6	82.7	31.1	45.2
24-Ethylcholesta-5,22E-dien-3 β -ol (fucosterol) ^a	nd ^e	13.8	55.5	nd	nd	5.0	23.2	38.3	57.1	nd	71.0	19.3	8.2	nd
4 α ,23,24-Trimethyl-5 α -cholest-22E-en-3-ol (dinosterol) ^a	10.7	nd	nd	1.2	42.8	17.9	35.0	30.3	38.3	52.0	827.0	29.1	12.1	12.2
Total sterols ^a	698.6	917.9	1326.6	242.2	2215.7	370.7	1041.4	1958.9	1895.6	1612.7	4786.2	1621.6	741.2	693.3
Phytol ^b	4.67	9.47	13.65	0.13	23.37	0.72	5.93	5.17	0.52	40.75	20.57	0.28	2.54	2.13
Phytyldiol ^b	0.11	0.13	0.10	0.02	0.60	0.07	0.07	0.17	0.04	0.37	0.12	0.14	0.06	0.04
Phytanic acid ^a	41.6	58.0	113.1	26.8	160.1	31.1	79.2	57.1	26.8	98.8	101.5	95.3	37.8	33.7
Pristanic acid ^a	2.3	7.7	16.7	5.4	25.9	5.1	5.8	9.8	3.6	14.3	13.1	6.0	2.2	2.3
4,8,12-TMTD acid ^a	5.5	46.2	82.2	11.7	16.1	9.0	10.4	7.5	4.5	19.6	23.8	20.0	6.9	7.1
CPPI ^c	0.018	0.011	0.006	0.115	0.021	0.078	0.009	0.026	0.060	0.007	0.005	0.392	0.019	0.016
Chlorophyll photooxidation estimate (%) ^d	28.5	18.6	10.3	86.7	31.7	75.0	15.5	37.9	65.3	12.7	8.2	99.8	29.3	25.5

^a (ng L⁻¹)

^b (μ g L⁻¹)

^c Chlorophyll Phytyl side-chain Photooxidation Index (molar ratio phytyldiol/phytol).

^d Estimated with the empirical equation: chlorophyll photodegradation % = (1 - [CPPI + 1]^{-18.5}) x 100 (Cuny et al. 2002).

^e Not detected

Table 2. Concentrations of sterols and acyclic isoprenoid compounds and chlorophyll photooxidation estimates in spm samples collected at station L4 during the time series 2018 at 25 m.

	01/25	02/18	03/25	04/19	04/30	05/14	05/30	06/25	07/16	08/13	09/17	10/17	11/26	12/10
24-Norcholesta-5,22 <i>E</i> -dien-3 β -ol (24-norsterol) ^a	38.6	46.2	84.6	88.2	284.1	67.4	344.5	79.2	160.6	120.7	104.1	120.0	90.6	58.4
Cholesta-5,22 <i>E</i> -dien-3 β -ol (22-dehydrocholesterol) ^a	51.9	51.7	69.1	82.0	173.5	62.7	312.2	102.1	251.3	190.5	161.8	132.7	200.8	87.9
Cholest-5-en-3 β -ol (cholesterol) ^a	227.7	182.0	150.0	171.4	511.0	131.0	692.3	168.5	362.4	288.9	259.4	325.4	360.6	203.2
24-Methylcholesta-5,22 <i>E</i> -dien-3 β -ol (brassicasterol) ^a	100.0	78.2	65.8	70.2	130.2	53.5	803.2	121.5	208.7	249.9	91.1	125.0	201.0	84.8
Cholest-5,24-dien-3 β -ol (desmosterol) ^a	23.6	20.8	25.2	184.3	195.6	140.8	227.5	40.9	66.2	106.5	36.8	45.1	94.9	18.3
24-Methylcholesta-5,24(28)-dien-3 β -ol (24-methylenecholesterol) ^a	55.5	145.2	47.4	217.7	95.5	16.6	328.6	207.9	133.3	54.5	45.2	42.6	95.3	38.6
24-Ethylcholest-5-en-3 β -ol (sitosterol) ^a	22.0	14.2	14.6	10.2	11.9	7.8	69.2	15.3	46.4	39.6	24.0	27.1	42.2	19.0
24-Ethylcholesta-5,22 <i>E</i> -dien-3 β -ol (fucosterol) ^a	7.3	nd ^c	5.7	2.4	2.1	1.8	20.1	9.6	16.3	6.4	nd	nd	9.3	nd
4 α ,23,24-Trimethyl-5 α -cholest-22 <i>E</i> -en-3-ol (dinosterol) ^a	5.2	1.4	3.0	1.3	9.5	12.1	150.1	7.6	31.4	16.4	11.8	13.0	12.8	5.3
Total sterols ^a	545.0	539.7	465.4	871.5	1414.9	493.8	2948.8	753.5	1276.7	1072.4	735.9	836.8	1114.7	515.5
Phytol ^b	8.53	8.38	2.83	2.82	12.40	14.20	42.17	26.92	11.97	16.03	6.44	7.21	14.75	6.85
Phytyldiol ^b	0.06	0.12	0.06	0.04	0.16	0.18	0.34	0.48	0.16	0.12	0.08	0.14	0.10	0.10
Phytanic acid ^a	41.9	54.6	33.8	33.4	243.9	77.3	143.6	67.1	65.4	69.4	50.9	79.2	61.6	45.2
Pristanic acid ^a	2.5	3.5	1.5	8.6	54.4	10.1	17.6	14.1	12.2	6.6	12.2	10.8	6.8	4.0
4,8,12-TMTD acid ^a	6.5	7.3	6.9	30.5	55.3	60.1	21.0	19.2	18.9	32.5	14.9	26.6	13.8	10.8
CPPI (%) ^c	0.006	0.012	0.016	0.011	0.011	0.010	0.016	0.014	0.011	0.006	0.010	0.016	0.005	0.012
Chlorophyll photooxidation estimate (%) ^d	10.4	19.6	26.0	17.8	17.8	16.9	11.8	23.3	18.2	10.2	16.7	25.0	9.6	20.0

^a (ng L⁻¹)

^b (μ g L⁻¹)

^c Chlorophyll Phytyl side-chain Photooxidation Index (molar ratio phytyldiol/phytol).

^d Estimated with the empirical equation: chlorophyll photodegradation % = (1 - [CPPI + 1]^{-18.5}) x 100 (Cuny et al. 2002).

^e Not detected

Table 3. Fatty acid concentrations ($\mu\text{g L}^{-1}$) in spm samples collected at station L4 during the time series 2018 at 5 m.

	01/25	02/18	03/25	04/19	04/30	05/14	05/30	06/25	07/16	08/13	09/17	10/17	11/26	12/10
C _{12:0}	0.16	0.08	0.18	0.24	0.31	0.24	0.24	0.55	0.17	0.29	0.43	0.36	0.13	0.11
C _{14:0}	1.38	1.87	2.49	3.54	6.83	6.08	4.09	5.72	2.15	14.71	5.56	2.92	1.65	1.39
BrC _{15:0}	0.20	0.20	0.44	0.63	0.54	0.52	0.71	0.60	0.38	1.32	1.66	0.58	0.21	0.26
C _{15:0}	0.46	0.44	0.81	0.48	1.40	0.75	1.13	1.09	0.54	0.76	0.84	1.20	0.29	0.69
C _{16:4}	nd ^a	0.86	0.53	nd	1.36	nd	2.29	nd	nd	3.77	0.52	nd	0.30	nd
C _{16:1ω7}	1.06	1.95	2.80	2.15	8.39	9.03	1.82	4.69	1.99	6.56	6.58	1.78	1.62	0.90
C _{16:0}	4.80	4.17	6.95	9.27	11.18	15.88	9.33	10.23	6.58	25.69	16.72	9.19	3.35	6.97
C _{18:4}	nd	1.94	3.40	1.53	2.24	1.82	2.24	0.86	0.35	2.14	2.59	0.67	0.84	0.18
C _{18:1ω9}	0.84	1.78	3.04	2.25	2.62	3.70	2.66	3.16	1.14	8.10	3.15	2.13	0.79	0.79
C _{18:1ω7}	0.23	0.45	0.97	1.23	0.73	1.00	0.60	0.82	1.15	2.49	4.07	0.61	0.31	0.34
C _{18:0}	3.10	1.58	2.46	1.69	3.53	2.03	2.22	2.51	2.08	3.63	3.00	2.70	0.99	5.38
C _{20:5}	nd	3.68	1.91	0.94	4.34	2.02	2.34	1.54	0.75	2.20	1.88	nd	0.78	nd
C _{22:6}	nd	1.07	1.44	nd	2.46	nd	3.78	1.20	0.60	7.39	4.37	nd	0.45	nd
Total fatty acids	12.20	20.07	26.81	23.96	45.93	43.07	33.45	32.94	17.87	79.05	51.40	22.12	11.69	17.00
SFAs (%)	82.6	41.6	49.7	66.2	51.8	59.2	53.0	62.8	66.6	58.7	54.9	76.5	56.5	87.0
MUFAs (%)	17.4	20.8	23.1	23.5	25.6	31.9	15.2	26.3	23.9	21.7	26.9	20.4	23.3	11.9
PUFAs (%)	nd	37.6	21.2	10.3	22.8	8.9	31.8	10.9	9.5	19.6	12.2	3.1	20.2	1.1
Diatom fatty acid ratio ^b	0.5	1.1	0.8	0.6	1.5	1.0	0.9	1.0	0.6	1.0	0.8	0.5	1.1	0.3
(MUFAs+PUFAs)/SFAs	0.2	1.4	1.0	0.5	0.9	0.7	0.9	0.6	0.5	0.7	0.8	0.3	0.8	0.2

^a Not detected

^b $(C_{14:0} + C_{16:1\omega7} + \sum C_{16} \text{ PUFAs})/C_{16:0}$

^c $(\sum \text{iso and anteiso } C_{15:0})/C_{15:0}$

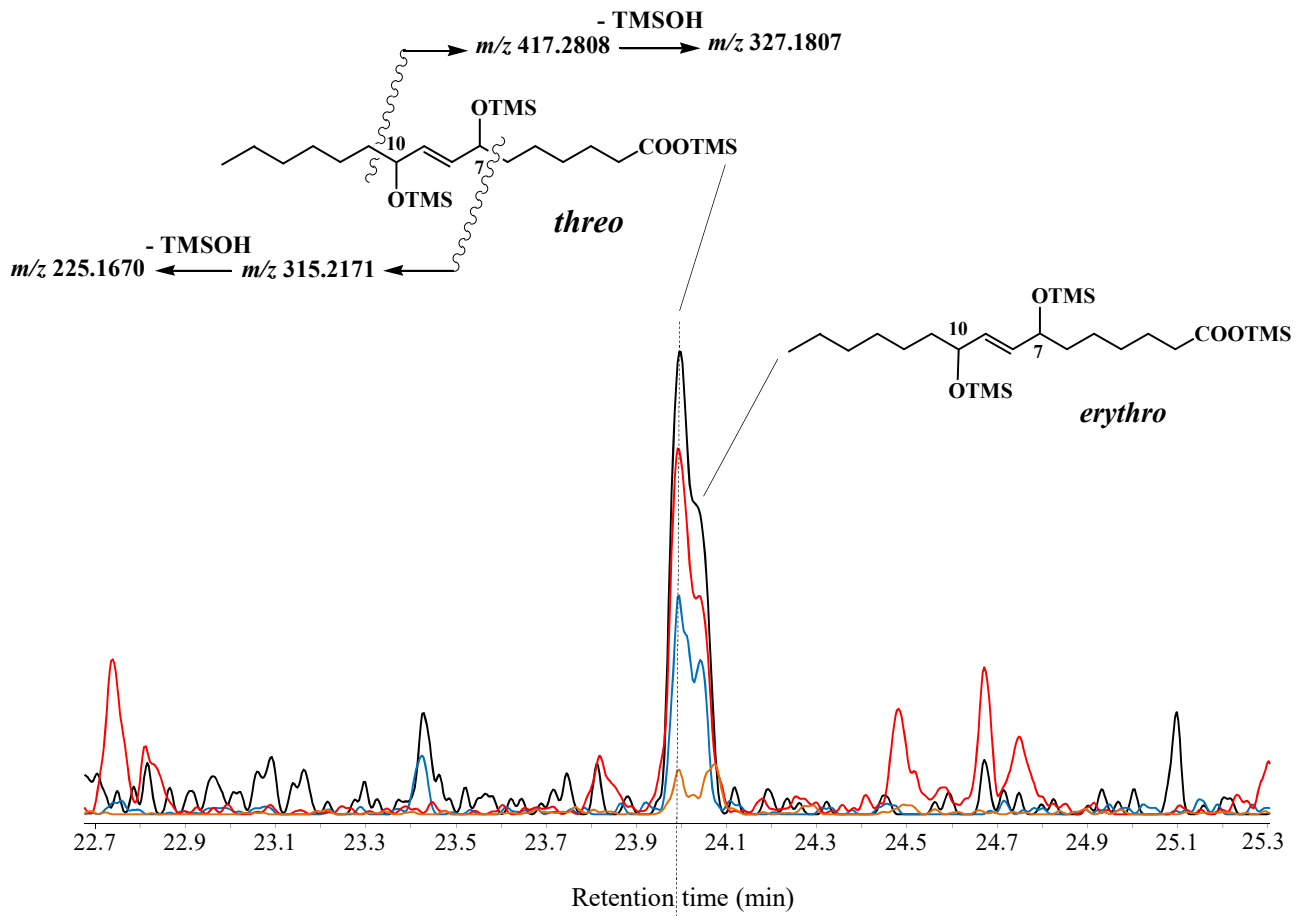
Table 4. Fatty acid concentrations ($\mu\text{g L}^{-1}$) in spm samples collected at station L4 during the time series 2018 at 25 m.

	01/25	02/18	03/25	04/19	04/30	05/14	05/30	06/25	07/16	08/13	09/17	10/17	11/26	12/10
C _{12:0}	0.12	0.01	0.44	0.36	0.07	0.27	0.55	0.74	0.60	0.42	0.36	0.51	0.10	0.29
C _{14:0}	1.52	1.31	1.61	2.42	3.05	4.86	9.81	9.03	2.31	3.66	1.51	2.34	1.98	1.37
BrC _{15:0}	0.25	0.19	0.25	0.04	0.21	0.34	1.29	0.62	0.52	0.70	0.52	0.66	0.27	0.28
C _{15:0}	0.53	0.43	0.57	0.57	0.36	0.65	1.99	0.78	0.67	0.49	0.69	1.18	0.47	0.55
C _{16:4}	nd ^a	0.05	nd	nd	0.55	0.50	0.53	0.71	0.38	1.68	0.41	nd	0.42	0.28
C _{16:1ω7}	1.46	1.38	0.86	2.10	3.31	6.67	5.73	8.71	2.50	2.85	2.00	1.65	2.33	1.26
C _{16:0}	3.30	3.04	5.10	8.18	3.74	10.32	16.26	10.16	4.24	5.07	3.77	6.27	2.91	3.75
C _{18:4}	nd	0.53	0.21	0.75	1.13	1.43	5.19	1.99	0.57	1.45	0.39	0.75	0.97	0.47
C _{18:1ω9}	0.84	0.99	0.49	1.30	1.80	2.23	7.63	3.40	0.82	1.56	1.43	1.53	0.86	0.89
C _{18:1ω7}	0.26	0.27	0.25	0.77	0.39	0.80	1.93	1.11	1.11	1.52	0.74	0.56	0.50	0.35
C _{18:0}	1.46	1.57	2.17	3.22	0.20	1.57	2.74	1.18	1.24	0.81	1.61	1.73	0.63	2.52
C _{20:5}	nd	1.85	0.16	0.50	3.59	2.69	5.96	3.92	1.19	1.88	1.17	0.81	1.07	0.39
C _{22:6}	nd	0.36	nd	nd	2.04	1.21	11.22	2.14	1.26	4.34	1.19	0.92	0.59	0.22
Total fatty acids	9.73	12.00	12.05	20.22	20.46	33.53	71.95	44.69	17.42	27.23	15.81	18.91	13.24	12.69
SFAs (%)	73.7	54.7	83.6	73.2	37.4	53.7	45.4	50.4	55.1	41.0	53.6	67.1	48.0	69.0
MUFAs (%)	26.3	22.0	13.3	20.7	26.9	28.9	21.3	29.6	25.4	21.7	26.4	19.8	27.9	19.7
PUFAs (%)	0	23.3	3.1	6.1	35.7	17.4	33.3	20.0	19.5	37.3	20.0	13.1	24.1	11.3
Diatom fatty acid ratio ^b	0.9	0.9	0.5	0.6	1.9	1.2	1.0	1.8	1.2	1.6	1.0	0.6	1.6	0.8
(MUFAs+PUFAs)/SFAs	0.4	0.8	0.2	0.4	1.7	0.9	1.2	1.0	0.8	1.4	0.9	0.5	1.1	0.5

^a Not detected

^b $(\text{C}_{14:0} + \text{C}_{16:1\omega7} + \sum \text{C}_{16} \text{ PUFAs})/\text{C}_{16:0}$

^c $(\sum \text{iso and anteiso C}_{15:0})/\text{C}_{15:0}$

A**B**