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Biotic and abiotic degradation of suspended particulate lipids along a transect in the Chukchi Sea

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Abstract. Lipids and their degradation products were investigated in samples of suspended particulate matter (SPM) collected in summer 2015 from surface waters of a South-North transect (ca. 65–81°N) of the Chukchi Sea. This material appeared to be composed mainly of diatoms (dominated by Thalassiosirales) and copepod faecal pellet debris. The high solar irradiances measured in the surface waters (up to 500 W m⁻²) favour chlorophyll (sensitizer) photobleaching at the expense of Type II photosensitized oxidation of unsaturated lipid components of phyto- and zooplankton (photodynamic effect). The weak photoreactivity of wax esters of herbivorous zooplankton in these SPM samples contrasts with previous observations of strong photooxidation of these compounds in sinking particles, which suggests that the photodynamic effect should be favoured in large faecal pellets of herbivorous copepods sinking quickly in weakly irradiated zones. Autoxidation (free radical induced oxidation) processes operating in all oxic environments appeared to be particularly efficient in faecal pellets of omnivorous and carnivorous zooplankton and limited in those of herbivorous origin. These differences were attributed to the consumption of algal antioxidants (such as mycosporine-like amino acids and carotenoids) during the diet of omnivorous and carnivorous copepods, favouring the involvement of free radical oxidation processes.

Key words: Chukchi Sea; SPM; Lipids; Biotic and abiotic oxidation.

48 **1. Introduction**

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2
3 49 The Arctic and Antarctic represent the most sensitive regions on Earth in terms of responses to
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5 50 climate change induced by global warming (IPCC, 2013). Sea ice is a particularly characteristic
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8 51 feature of the polar regions and has various roles in controlling local and global climate. During
9
10 52 recent decades, there have been dramatic changes in Arctic sea ice cover and thickness (Comiso
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12
13 53 et al., 2008), and these likely impact the local, regional and global climate through complex
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15 54 coupling mechanisms within the Earth system. Sea ice is also critical for polar ecosystems,
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18 55 providing a host for phototrophic organisms at the base of the food chain, a source of nutrients
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20 56 for other phototrophs, which provide food to primary consumers, and a physical platform for
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22 57 apex marine predators such as polar bears.

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25 58 Sea ice undergoes large seasonal and inter-annual variation. Having reached its maximum
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28 59 extent during late winter, the region of open ocean defined by the retreating ice edge in
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30 60 spring/summer is frequently referred to as the marginal ice zone (MIZ). The MIZ plays host to
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33 61 major spring phytoplankton blooms, stimulated by higher irradiance, elevated nutrient supply
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35 62 and water column stratification. Such spring primary production (PP) in the MIZ drives the
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38 63 Arctic ecosystem and also contributes significantly to the overall carbon cycle by exerting
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40 64 control over atmospheric CO₂ drawdown and subsequent carbon sequestration in marine
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43 65 sediments (Wassman et al., 2008). Increased spatial extent and duration of open waters due to
44
45 66 sea ice loss favors phototrophic activity, and likely explains some of the recent increase in PP
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48 67 in the Arctic (Arrigo et al., 2015).

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50 68 Some of the most dramatic sea ice decline is evident in the MIZ of the Barents Sea, the
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53 69 Chukchi Sea, the Sea of Okhotsk and Baffin Bay (Onarheim et al., 2018), with impacts on both
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55 70 climate and ecology (Serreze et al., 2007; Leu et al., 2011; Post et al., 2013; Renaut et al., 2018).
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58 71 Indeed, the Chukchi Sea is generally considered as one of the most biologically productive
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60 72 regions in the world's oceans (Springer and McRoy, 1993). The hydrography of the Chukchi
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73 Sea is strongly influenced by the advection of water masses from the Bering Sea (Grebmeier et
74 al., 2006), which is particularly strong in summer (Hunt et al., 2013). This inflow of warmer
75 waters has increased in recent times as a response to global warming, with consequences for
76 the spatial coverage of sea ice and timing of retreat (Grebmeier et al., 2006). It is thus very
77 important to study the lower trophic levels in this region, in order to improve our understanding
78 of the effects of sea ice reduction on marine ecosystems (Abe et al., 2020).

79 In the Southern Chukchi Sea, low grazing pressure (resulting from a temporal mismatch
80 between zooplankton and phytoplankton production; Kitamura et al., 2017), fast sinking rates
81 of large diatoms, and shallow bottom depths (Grebmeier et al., 1988, 2006a), result in strong
82 pelagic-benthic coupling leading to increased efficiency of carbon sinking (Bates, 2006; Chen
83 and Borges, 2009). However, these ecosystems are currently undergoing rapid and profound
84 changes due to the effects of climate change, which can modify the ecosystem structure from
85 pelagic-benthic to pelagic-pelagic type structures (Piepenburg, 2005). In the present work, we
86 aimed to monitor phytoplanktonic diversity and degradation state in different suspended
87 particulate matter (SPM) samples collected in summer surface waters across a South-North
88 transect in the Chukchi Sea. For this, we analysed for various lipids and their biotic and abiotic
89 degradation products, owing to their relative stability, specificity, and general suitability as
90 tracers of the origin and fate of organic matter (OM) (Volkman et al., 1998). Moreover, the
91 majority of studies dealing with the degradation of phytoplanktonic OM to date have focused
92 on biotic degradation processes (Afi et al., 1996; Sun et al., 1999; Mäkinen et al., 2017), while
93 the role played by photooxidation and free radical-mediated oxidation (autoxidation) processes
94 in the degradation of lipid components during the senescence of phototrophic organisms has
95 only very recently been investigated (Rontani, 2012; Rontani and Belt, 2020).

96 97 **2. Material and methods**

2.1. Sampling

Seawater sampling was carried out at 14 station over the Chukchi Sea (Table S1) during Korea research ice breaker R/V *Araon* cruise (ARA06B, August 1-22, 2015). A volume of 50-100 L of seawater was directly collected into 50 L carboy bottles from the vessels underway pumped system located at about 5 m below sea level. Filtration on GF/F filters (pre-combusted at 450°C for 6 h before use to avoid contamination) was performed at sea. The samples were frozen on-board (-20°C), freeze dried in the Korean laboratory and then shipped frozen to the UK and French laboratories.

2.2. Lipid extraction

Filters were reduced at room temperature with excess NaBH₄ (70 mg) after adding MeOH (25 mL, 30 min) to reduce labile hydroperoxides (resulting from photo- or autoxidation) to alcohols, which are more amenable to analysis by gas chromatography (GC). A test carried out with methyl oleate confirmed that the conversion of esters to the corresponding *n*-alcohols during the NaBH₄ reduction step of the treatment was negligible (amount of octadec-9-en-1-ol formed < 1% of the initial methyl oleate) and could not interfere with *n*-alkan-1-ol quantification in the different samples. Water (25 mL) and KOH (2.8 g) were then added and the resulting mixture saponified by refluxing (2 h). After cooling, the mixture was acidified (HCl, 2 N) to pH 1 and extracted with dichloromethane (DCM; 3 × 20 mL). The combined DCM extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation at 40°C to give total lipid extracts (TLEs).

2.3. Silylation

122 Dry TLEs and standards were derivatized by dissolving them in 300 μ L pyridine/bis-
123 (trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v/v) and silylated in a heating block
124 (50 $^{\circ}$ C, 1 h). After evaporation to dryness under a stream of N_2 , the derivatized residue was
125 dissolved in ethyl acetate/BSTFA (to avoid desilylation) and analysed by GC-QTOF.

126

127 *2.4. Gas chromatography-EI quadrupole time-of-flight mass spectrometry*

128 Accurate mass measurements were made in full scan mode using an Agilent 7890B/7200
129 GC/QTOF system (Agilent Technologies, Parc Technopolis – ZA Courtaboeuf, Les Ulis,
130 France). A cross-linked 5% phenyl-methylpolysiloxane (Agilent Technologies; HP-5MS Ultra
131 inert, 30 m \times 0.25 mm, 0.25 μ m film thickness) capillary column was used. Analyses were
132 performed with an injector operating in pulsed splitless mode set at 270 $^{\circ}$ C. Oven temperature
133 was ramped from 70 $^{\circ}$ C to 130 $^{\circ}$ C at 20 $^{\circ}$ C min^{-1} and then to 300 $^{\circ}$ C at 5 $^{\circ}$ C min^{-1} . The pressure
134 of the carrier gas (He) was maintained at 0.69×10^5 Pa until the end of the temperature program.
135 Instrument temperatures were 300 $^{\circ}$ C for transfer line and 230 $^{\circ}$ C for the ion source. Nitrogen
136 (1.5 mL min^{-1}) was used as collision gas. Accurate mass spectra were recorded across the range
137 m/z 50–700 at 4 GHz with the collision gas opened. The QTOF-MS instrument provided a
138 typical resolution ranging from 8009 to 12252 from m/z 68.9955 to 501.9706.
139 Perfluorotributylamine (PFTBA) was used for daily MS calibration. Compounds were
140 identified by comparing their TOF mass spectra, accurate masses and retention times with those
141 of standards. Quantification of each compound involved extraction of specific accurate
142 fragment ions, peak integration, and determination of individual response factors using external
143 standards and Mass Hunter software (Agilent Technologies, Parc Technopolis – ZA
144 Courtaboeuf, Les Ulis, France). Saturated (SFAs) and monounsaturated fatty acids (MUFAs)
145 were quantified with structurally similar elaidic and nonadecanoic acid standards, respectively,

146 and the other lipids with an exact standard. The limit of detection (LOD) for each compound
147 was based on a signal-to-noise ratio (S/N) greater than 5. The linear range was determined using
148 values that met the standard analysis criteria of less than 15% deviation across the concentration
149 range. Linear responses (depending on the nature of the silylated analytes) were obtained over
150 2-3 orders of magnitude.

151 The recovery efficiency of polyunsaturated fatty acids (PUFAs) for the sample treatment
152 was checked with a standard of C_{20:5} fatty acid and compared to that obtained for the C_{18:1Δ9}
153 (oleic) acid. Using this approach, we estimate the efficiency of C_{20:5} fatty acid to be ca. 70%
154 compared to that of oleic acid. The sample treatment employed thus induces some losses (likely
155 thermal) of PUFAs.

157 2.5. Chlorophyll-*a* analyses

158 The chlorophyll-*a* (Chl-*a*) concentration was determined onboard using a Trilogy fluorometer
159 (Turner Designs, USA) after 24 h extraction in 90 % acetone at 4°C (Parsons et al., 1984). Chl
160 *a* was measured at 0 and 10 m and we took the mean value to represent the samples collected
161 via the ship's underway system (ca. 5 m).

163 2.6. Standard compounds

164 Phytol, fatty acids, most of the sterols and 2,6,10,14-tetramethylpentadecanoic acid (pristanic
165 acid) were purchased from Sigma-Aldrich (St. Quentin Fallavier, France). 6,10,14-
166 Trimethylpentadecan-2-ol was obtained after oxidation of phytol with KMnO₄ in acetone
167 (Cason and Graham, 1965) and subsequent NaBH₄ reduction of the resulting ketone. The
168 syntheses of 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol), 3,7,11,15-
169 tetramethylhexadec-2(*Z/E*)-en-1,4-diols and 3,7,11,15-tetramethylhexadec-3(*Z/E*)-en-1,2-diols

170 were described previously by Rontani and Aubert (2005). 4,8,12-Trimethyltridecanoic acid
171 (4,8,12-TMTD acid) was synthesized from isophytol (Interchim, Montluçon, France) by a
172 previously described procedure (Rontani et al., 1991). 3,7,11,15-Tetramethylhexadecanoic acid
173 (phytanic acid) was produced in three steps from phytol as described previously (Rontani et al.,
174 2003). 3,7,11,15-Tetramethylhexadecan-1-ol (dihydrophytol) was obtained by hydrogenation
175 of phytol in methanol with Pd-CaCO₃ as a catalyst (Rontani et al., 2003). Type-II
176 photosensitized oxidation of monounsaturated fatty acids and alken-1-ols was carried out in
177 pyridine with hematoporphyrin as sensitizer, while autoxidation was achieved using
178 Fe²⁺/ascorbate (Loidl-Stahlhofen and Spitteller, 1994). Subsequent reduction of the resulting
179 hydroperoxides in methanol with excess NaBH₄ afforded the corresponding hydroxyacids.

181 *2.7. Determination of the double bond position of monounsaturated fatty acids and n-alken-1-* 182 *ols*

183 The double bond positions of monounsaturated fatty acids (MUFAs) were determined via
184 analysis of the TMS derivatives of their oxidation products (allylic hydroxyacids), which are
185 ubiquitous in environmental samples (for a review see Rontani and Belt, 2020). Silylated
186 hydroxyacids affording di-functionalized fragment ions upon electron ionization (EI) (Fig. 2)
187 were selected for this purpose. Monitoring of the accurate mass of these fragment ions (Table
188 S2) allowed an unambiguous assignment of the double bond position of the MUFAs present in
189 the samples investigated (an example is given in Fig. 2). It may be noted that these double bond
190 positions may also be identified (although less clear) by GC-MS using unit masses. However,
191 in the case of *n*-alken-1-ols, the use of accurate masses (Table S3) is needed (Fig. 3). Indeed,
192 unit masses of the fragment ions arising from EI fragmentation of the TMS derivatives of *n*-
193 alken-1-ol oxidation products (diols) interfere with more stable isobaric fragment ions arising

194 from the fragmentation of oxidation products of some MUFAs, which are present in higher
195 proportions than *n*-alken-1-ols in environmental samples.

196 This straightforward method for determining double bond positions only requires adding
197 a simple NaBH₄ reduction step (to reduce unstable hydroperoxyacids to the corresponding
198 hydroxyacids; Marchand and Rontani, 2001) prior to alkaline hydrolysis, which is commonly
199 employed for the treatment of complex lipid extracts (Volkman, 2006).

201 2.8. Chlorophyll photooxidation estimates

202 Type II photosensitized oxidation of the chlorophyll phytyl side-chain leads to the production
203 of 2-hydroperoxy-3-methylidene-7,11,15-trimethylhexadecan-1-ol, which, after NaBH₄
204 reduction, is converted to 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol)
205 (Rontani et al., 1994). This diol constitutes a stable and specific tracer for the photodegradation
206 of the chlorophyll phytyl side-chain (Cuny and Rontani, 1999). The molar ratio
207 phytyldiol:phytol (Chlorophyll Phytyl side-chain Photodegradation Index, CPPI) has been
208 previously proposed to estimate the extent of photodegradation of chlorophylls possessing a
209 phytyl side-chain through use of the empirical equation: chlorophyll photodegradation % = (1
210 - [CPPI + 1]^{-18.5}) × 100 (Cuny et al., 1999)' this equation was employed previously in natural
211 marine samples from various latitudes (For reviews see Rontani and Belt, 2020; Rontani et al.,
212 2021).

214 2.9. Lipid photo- and autoxidation estimates

215 Type-II photosensitized oxidation of Δ⁵-sterols produces mainly unstable Δ⁶-5α-
216 hydroperoxides with smaller amounts of stable and specific Δ⁴-6α/6β-hydroperoxides (Kulig
217 and Smith, 1973). Sterol photooxidation percentage can be estimated on the basis of Δ⁴-

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3 218 3 β ,6 α/β -dihydroxysterols (arising from NaBH₄ reduction of the corresponding
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5 219 hydroperoxides) concentration using the equation: sterol photooxidation % = (Δ^4 -3 β ,6 α/β -
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7 220 dihydroxysterol %) \times (1+0.3)/0.3 (Christodoulou et al., 2009), where the value (0.3)
8
9 221 corresponds to the ratio Δ^4 -6 α/β -hydroperoxides/ Δ^6 -5 α -hydroperoxides found in biological
10 222 membranes (Korytowski et al., 1992). Free radical autoxidation of Δ^5 -stenols yields mainly
11
12 223 unstable and unspecific 7 α -and 7 β -hydroperoxides and, to a lesser extent, specific 5 α/β ,6 α/β -
13
14 224 epoxysterols and their stable hydrolysis products 3 β ,5 α ,6 β -trihydroxysterols (Smith, 1981).
15
16 225 The extent of sterol autoxidation can be estimated after alkaline hydrolysis using the equation:
17
18 226 sterol autoxidation % = (3 β ,5 α ,6 β -trihydroxysterols %) \times 2.4 based on respective formation
19
20 227 rate constants of the different autoxidation products obtained from incubation experiments
21
22 228 (Christodoulou et al., 2010) and calculated previously by Morrissey and Kiely (2006). These
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24 229 equations have been employed previously to obtain reliable estimates of sterol photo- and
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26 230 autoxidation in various marine areas (For reviews see Rontani and Belt, 2020; Rontani et al.,
27
28 231 2021).

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30 232 Photo- and autoxidation of MUFAs and monounsaturated *n*-alken-1-ols yields mixtures
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32 233 of isomeric allylic hydroperoxyacids or hydroperoxyalcohols (Frankel, 1998; Rontani et al.,
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34 234 2012), respectively, which are converted to the corresponding hydroxyacids or diols after
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36 235 NaBH₄-reduction. The relative importance of photo- and autoxidation of these compounds can
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38 236 be readily calculated based on the proportion of *cis* isomers (which are produced specifically
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40 237 by autoxidation; Porter et al., 1995) and the temperature of seawater (Marchand and Rontani,
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42 238 2001).

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45 240 **3. Results**

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242 3.1. Trophic environment across the Chukchi Sea transect

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2 243 The main sterols: 24-norcholesta-5,22*E*-dien-3 β -ol (24-norsterol), 27-nor-24-methylcholesta-
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5 244 5,22-dien-3 β -ol, cholest-5-en-3 β -ol (cholesterol), cholesta-5,22*E*-dien-3 β -ol (22-
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7 245 dehydrocholesterol), cholesta-5,24-dien-3 β -ol (desmosterol), 24-methylcholesta-5,22*E*-dien-
8
9 246 3 β -ol (*epi*-brassicasterol), 24-methylcholesta-5,24(28)-dien-3 β -ol (24-methylenecholesterol),
10
11 247 24-ethylcholest-5-en-3 β -ol (sitosterol) and 24(*E*)-ethylcholesta-5,24(28)-dien-3 β -ol
12
13 248 (fucosterol) were quantified across the transect to estimate the amount and nature of the algal
14
15 249 material present in the SPM samples. The highest values of particulate sterol biomass were
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17 250 observed at stations 03, 02, 01, 09, 13 and 20, with a maximum at Station 03 suggesting the
18
19 251 presence of a bloom event (Table 1, Fig. 4B). In contrast, the other stations, and notably the
20
21 252 under ice station 26, contained relatively low concentrations of such sterols, indicating low
22
23 253 phytoplankton abundances. For the majority of samples, sterol profiles were dominated by 24-
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25 254 norsterol, cholesterol, 22-dehydrocholesterol, *epi*-brassicasterol and 24-methylenecholesterol,
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27 255 the latter being particularly dominant at station 03. The proportion of sitosterol showed a
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29 256 marked increase at stations 21 and 22 (Fig. 4A).
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37 257 Chl-*a*, fatty acid and phytol concentrations (Tables 2 and 3) confirmed the dominance of
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39 258 algal material at stations 03, 02, 01, 09, 13 and 20. The fatty acid profiles showed very low
40
41 259 proportions of PUFAs (mainly C_{16:4}, C_{18:4} and C_{20:5}) along the transect, reaching less than 4%
42
43 260 of total fatty acids at station 03. SFAs were dominated by the classical C_{14:0}, C_{16:0} and C_{18:0}, and
44
45 261 MUFAs by C_{16:1 Δ 9} (palmitoleic acid), C_{18:1 Δ 9} (oleic acid) and C_{18:1 Δ 11} (vaccenic acid) (Table 2).
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49 262 Long-chain saturated and monounsaturated primary alcohols (ranging from C₁₄ to C₂₂)
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51 263 resulting from alkaline hydrolysis of zooplanktonic wax esters (Lee et al., 2006) were also
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53 264 detected, with highest concentrations at station 02 (Table 4). Interestingly, this station also
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55 265 exhibited the highest proportion of C_{20:1} and C_{22:1} *n*-alken-1-ols (Fig. 5A).
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59 266

267 3.2. Biotic and abiotic degradation of phyto- and zooplanktonic lipids

268

269 3.2.1. Chlorophyll

270 Chlorophyll photooxidation estimates ranged from 33% to 96% along the transect (Table
271 3). Several biotic (dihydrophytol, phytanic, pristanic and 4,8,12-TMTD acids) and autoxidative
272 (3,7,11,15-tetramethylhexadec-2(Z/E)-en-1,4-diols, 3,7,11,15-tetramethylhexadec-3(Z/E)-en-
273 1,2-diols, and isophytol) degradation products of the chlorophyll phytyl side-chain could be
274 detected in all samples (Fig. 6A). The phytyl side chain appeared to be strongly degraded at all
275 stations except station 03, this degradation mainly involving autoxidative and biotic processes
276 (Fig. 6B). The percentage of autoxidation products ranged from 4% to 29% of total isoprenoid
277 compounds (Fig. 6B) and from 10% to 190% of the residual phytyl chain. Autoxidation was
278 particularly intense at stations 01, 11, 14, 18, 20, 21 and 26. With the exception of station 03,
279 biotic degradation products of phytol were dominant, ranging from 36% to 78% of total
280 isoprenoid compounds.

281

282 3.2.2. MUFAs, *n*-alken-1-ols and sterols

283 Type II photosensitized oxidation of MUFAs appeared to be very limited except at station 01
284 where 24% of vaccenic acid was photooxidized (Fig. 7C). While palmitoleic acid was very
285 weakly affected by autoxidative processes (Fig. 7A), autoxidation reached 73% and 64% in the
286 case of oleic and vaccenic acids, respectively (Figs. 7B and 7C). Monounsaturated *n*-alken-1-
287 ols arising from the hydrolysis of zooplanktonic wax esters were only weakly oxidized (Fig. 8).
288 Interestingly, in the first part of the transect, photooxidation was more intense in the case of
289 C_{20:1Δ11} and C_{22:1Δ11} *n*-alken-1-ols than for C_{16:1Δ9} and C_{18:1Δ9} (Fig. 8). Due to their relatively low
290 contribution, photo- and autoxidation products of sterols (sum < 10%) were not quantified.

291

292 4. Discussion

293

294 4.1. Trophic environment at the different stations

295 Sterols possess structural characteristics (double bond positions, nuclear methylation and
296 patterns of side-chain alkylation) restricted to a few groups of organisms (for reviews see
297 Volkman, 1986; 2003; Rampen et al., 2010), and are often used to estimate phytoplanktonic
298 diversity (Taipale et al., 2016). The diatom *Thalassiosira* aff. *antarctica* and the dinoflagellate
299 *Gymnodinium simplex* have been proposed as potential sources of 24-norsterol (Rampen et al.,
300 2007), which was found to be present in high proportion (ranging from 15 to 50%) along all the
301 Chukchi Sea transect (Fig. 4A). Sterols that are methylated at the C-4 position including
302 4 α ,23,24-trimethyl-5 α -cholest-22*E*-en-3-ol (dinosterol) are often employed as tracers for the
303 contribution of dinoflagellates in the marine environment (Robinson et al., 1984). The absence
304 (below detection limit) of such sterols at the different stations therefore allowed us to exclude
305 a significant contribution of dinoflagellates across the transect. *T. antarctica*, which is found at
306 high latitudes but not in tropical waters (Hasle and Heimdal, 1968), seems thus to strongly
307 contribute to the phytoplankton community along all the Chukchi Sea transect. This centric
308 diatom also contains a high proportion of 24-methylenecholesterol (Rampen et al., 2007), which
309 is present with 24-norsterol at all stations (proportion ranging from 5 to 23% of total sterols)
310 (Fig. 4A). It seems thus that *T. antarctica* or similar species belonging to the order of
311 Thalassiosirales are one of the main phytoplankton contributors to these SPM samples. This
312 assumption is in good agreement with the dominance of *T. antarctica* and *T. nordenskioeldii*
313 previously observed in surface sediments of the Chukchi Sea (Asthakov et al., 2015). Further,
314 *epi*-brassicasterol, which is also present in significant proportions along all the transect (Fig.
315 4A), suggests the presence of prymnesiophytes and notably of *Phaeocystis pouchetii*, whose
316 sterol content comprises almost entirely this sterol (Nichols et al., 1991), and is widely

1 distributed in the Arctic (Riisgaard et al., 2015). The increasing proportions of sitosterol
2 observed between stations 11 and 22 could potentially be attributed to the presence of increasing
3 proportions of the diatoms *Asterionella glacialis*, *Haslea ostrearia* or *Amphiprora hyalina*
4 (Volkman, 2003). Finally, the relatively high proportions of cholesterol present in most of the
5 samples (Fig. 4A) suggest the occurrence of zooplanktonic material. Indeed, it is well-known
6 that herbivorous and omnivorous crustaceans convert dietary phytosterols to cholesterol
7 (Grieneisen, 1994; Behmer and Nes, 2003).

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324 The presence of a high proportion of zooplanktonic material in the different samples is
325 supported further by the detection of *n*-alkan-1-ols (Table 4) arising from alkaline hydrolysis
326 of wax esters, which are generally the main storage lipids of marine zooplankton in high-
327 latitude species (Lee et al., 2006). The most common *n*-alkan-1-ols of the wax esters of
328 herbivorous copepods that undergo diapause (common in the Arctic) are C_{20:1Δ11} and C_{22:1Δ11},
329 while omnivorous or carnivorous zooplankton generally show a predominance of C_{14:0} and C_{16:0}
330 *n*-alkan-1-ols (Lee and Nevenzel, 1979; Albers et al., 1996). The proportion of herbivorous and
331 omnivorous/carnivorous zooplankton was thus estimated on the basis of *n*-alkan-1-ol
332 composition. The results obtained (Fig. 5B) show highest herbivorous zooplanktonic
333 contribution at station 02 (where *Calanus glacialis* and *Eucalanus bungii* appeared to be
334 dominant, Kim et al., 2020), which exhibits the highest concentration of *n*-alkan-1-ols (Table
335 4, Fig. 5A). Further, the very low amounts of the C_{20:5} acid, a well-known component of
336 numerous zooplankton species (Cass et al., 2014), suggests the presence of fecal pellets, where
337 PUFAs are generally only present in low proportions (Harvey et al., 1987; Prahl et al., 1985)
338 compared to zooplanktonic organisms. Fecal pellets generally settle out of the water column
339 relatively quickly. Although coprophagy is usually the more important source of fecal pellet
340 degradation (Iversen and Poulsen, 2007), they also experience fragmentation (coprorhexy)

1 341 leading to the formation of small slowly sinking particles (Smetacek, 1980), which could have
2 342 been collected during the sampling.
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4 343 The presence of PUFAs in only trace amounts is very surprising; indeed, these
5 344 compounds are generally major components of high-altitude phytoplankton blooms (Parrish et
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7 345 al. 2005; Leu et al. 2006; Marmillot et al. 2020). We suggest that the relatively low proportions
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9 346 of PUFAs observed may be attributed to: (i) a highly detritic state of all the SPM samples
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11 347 investigated, (ii) a degradation of the more labile components of these samples (including
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13 348 PUFAs) between sampling and analysis (ca. 5 years) despite storage at -20 °C, or (iii) thermal
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15 349 losses during the treatment (see section 2.4). Although PUFAs appeared to be strongly
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17 350 degraded, the detection of residual amounts of the unusual fatty acids C_{16:4} (synthesized by
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19 351 diatoms; Volkman, 2006) and C_{18:4}, a well-known acid component of copepod wax esters
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21 352 (Kattner, 1989; Graeve and Kattner, 1992), is in good agreement with the trophic environment
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23 353 described above. The C_{18:4} fatty acid is also present in high proportion in *Phaeocystis* spp.
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25 354 (Sargent et al., 1985), but in this case it is accompanied by C_{18:5} and C_{22:6} fatty acids, which are
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27 355 absent in the SPM samples. The main source of the C_{18:4} fatty acid in our SPM samples seems
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29 356 thus to be copepod wax esters.
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41 358 *4.2. Biotic and abiotic degradation of phyto- and zooplanktonic lipids*

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45 360 *4.2.1. Chlorophyll*

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48 361 It was demonstrated recently that high solar irradiances favour photobleaching of chlorophyll
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50 362 (sensitizer) at the expense of Type-II (i.e. involving singlet oxygen) photosensitized oxidation
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52 363 of lipids (the photodynamic effect) (Amiriaux et al., 2016; Rontani et al., 2021). Since the SPM
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54 364 samples investigated in the present work were collected near to the surface (5 m), thereby
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56 365 receiving highest solar irradiance (up to 500 W m⁻², Dr. Ha, unpublished results), the elevated
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366 CPPI-based chlorophyll photodegradation estimates are not surprising (Table 3). Further, we
367 note that even at station 03, 45% of chlorophyll was photooxidized, suggesting the diatoms
368 were in a poor physiological state, despite an apparent bloom event.

369 Isoprenoid compounds resulting from the degradation of the chlorophyll phytyl side-
370 chain were not only useful for quantifying chlorophyll photodegradation (see section 2.7), but
371 also for identifying the importance of autoxidative and biotic alteration of primary production.
372 Autoxidation of the phytyl chain affords mainly isophytol (Rontani and Galeron, 2016),
373 3,7,11,15-tetramethylhexadec-2(Z/E)-en-1,4-diols and 3,7,11,15-tetramethylhexadec-3(Z/E)-
374 en-1,2-diols (Rontani and Aubert, 2005) (Fig. 9), which are specific tracers of these degradative
375 processes. The detection of significant proportions of these compounds in some SPM samples
376 (Fig. 6) thus demonstrates the important role played by autoxidation in the degradation of
377 primary producers.

378 Pelagic crustaceans assimilate the chlorophyll phytyl chain when feeding herbivorously
379 (Prahl et al., 1984; Harvey et al., 1987). During this metabolism, phytol is successively
380 hydrogenated to dihydrophytol, oxidized to phytanic acid, and then cleaved to pristanic and
381 4,8,12-TMTD acids by way of classical α - and β -oxidation sequences (Fig. 9) (for a review see
382 Rontani and Volkman, 2003). Such isoprenoid compounds have been detected previously in
383 different *Calanus* species (Avigan and Blumer, 1968; Prahl et al., 1984). As such, while phytol
384 logically dominates isoprenoid compounds at station 03 due to a declining bloom event mainly
385 composed of weakly altered diatoms, the other stations exhibit a strong dominance of phytanic
386 and pristanic acids (Fig. 6B), which confirms a strong contribution of zooplanktonic material.

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388 4.2.2. Unsaturated fatty acids

389 Photodegradation rates of unsaturated fatty acids increases, logically, with their degree of
390 unsaturation (Frankel, 1998), such that PUFAs are very reactive towards Type-II

391 photosensitized oxidation processes (Frankel, 1998; Rontani et al., 1998). Unfortunately, the
392 resulting oxidation products cannot be used as quantitative tracers of Type-II photooxidation
393 processes in the environment due to the instability of the primary oxidation products formed
394 (Rontani and Belt, 2020). However, it was demonstrated previously that PUFAs are
395 photodegraded approximately 5 times faster than MUFAs in dead cells of diatoms (Rontani et
396 al., 2011). Based on the very weak photooxidation percentage of MUFAs in our SPM samples
397 (Fig. 7; mean value $1.9 \pm 4.2\%$), the contribution of Type-II photosensitized oxidation processes
398 to the degradation of PUFAs thus appeared to be very weak ($\sim 10\%$). This very weak
399 photooxidative alteration of PUFAs and MUFAs results likely from the limitation of the
400 photodynamic effect under high solar irradiances (Amiriaux et al., 2016; Rontani et al., 2021).

401 Whereas autoxidation of palmitoleic acid was limited to 25% in SPM samples (Fig. 7A),
402 it reached 73% in the case of oleic acid (Fig. 7B). These differences of reactivity may be
403 attributed to the origins of these MUFAs. Indeed, although palmitoleic and oleic acids are not
404 unambiguous biomarkers of phytoplankton and zooplankton inputs (Wakeham and Canuel,
405 1988), they are often used to obtain relative indication of the predominance of algal vs.
406 zooplanktonic sources (Tolosa et al., 2004). Palmitoleic acid, which is a major fatty acid of
407 diatoms (Volkman et al., 1989; Dunstan et al., 1993), is also present in several bacteria (e.g., de
408 Carvalho and Caramujo, 2014), and may be found in high proportion in storage lipids of
409 zooplankton feeding on diatoms (Lee et al., 2006). In contrast, omnivorous and carnivorous
410 zooplankton species are characterized by wax esters with high amounts of oleic acid (Lee et al.,
411 2006). However, we note that *Phaeocystis* spp. may also contain elevated levels of oleic acid
412 (Dalsgaard et al., 2003). On the basis of high proportions of phytanic and pristanic acids
413 observed in all SPM samples (Fig. 5), we consider that the major source of oleic acid to be
414 omnivorous zooplankton (more precisely euphausiids or *Metridia pacifica* detected in the
415 samples analysed, Kim et al., 2020) rather than prymnesiophytes. Autoxidation seems thus to

416 be stronger in faecal pellets of omnivorous and carnivorous zooplankton than in diatoms or
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2 417 herbivorous zooplankton feeding on diatoms. Further, we note that the highest autoxidation
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4 418 percentages of oleic acid were observed at stations 01, 11, 14, 18, 20, 21 and 26, which also
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7 419 exhibit the highest autoxidation of the chlorophyll phytyl side-chain (Fig. 6B).

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10 420 Based on: (i) pseudo-first order autoxidative degradation rates of palmitoleic and C_{20:5}
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12 421 acids previously measured during incubation of dead diatom cells (1.5×10^{-3} and $2.7 \times 10^{-2} \text{ h}^{-1}$,
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14 422 respectively; Rontani et al., 2014), and (ii) the mean autoxidation percentage ($14.4 \pm 7.7\%$)
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16 423 of palmitoleic acid observed in the different SPM samples (Fig. 6A), an important contribution
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18 424 of autoxidation to the disappearance of PUFAs in these samples may be expected. However, it
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20 425 is well known that PUFAs are also significantly reduced relative to total fatty acids during
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22 426 passage through the gut of copepods (Harvey et al., 1987; Prahl et al., 2009). Consequently,
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24 427 due to the important contribution of zooplanktonic faecal pellets to the SPM samples analysed,
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26 428 an important degradation of PUFAs during copepod grazing is very likely. Note that a
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28 429 significant degradation during the storage and the treatment cannot be totally excluded.

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34 430 Surprisingly, vaccenic acid, well-known to be specific to bacteria (Lambert and Moss,
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36 431 1983; Sicre et al., 1988), also appeared to be strongly autoxidized (Fig. 7C). Autoxidation states
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38 432 of vaccenic and oleic acids are not significantly different (Kruskal-Wallis, $n=26$ $p = 0.817 >$
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40 433 0.05), while the autoxidation state of vaccenic acid is significantly different to that of
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42 434 palmitoleic acid (Kruskal-Wallis, $n=26$ $p = 0.00025 < 0.05$). Autoxidation of vaccenic acid
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44 435 seems thus to mainly intervene in omnivorous or carnivorous zooplanktonic faecal pellets,
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46 436 rather than in heterotrophic bacteria associated to diatom phytodetritus or present in faecal
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48 437 pellets of herbivorous zooplankton feeding on diatoms. Interestingly, the lipid composition of
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50 438 bacterivorous ciliates resembles that of their prey (Harvey et al., 1987; Boëchat and Adrian,
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52 439 2005). Recently, the presence of high proportions of *trans* MUFAs in SPM samples collected
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54 440 under sea ice in Baffin Bay was attributed to the ingestion of bacteria stressed by salinity in
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441 internal brines of sea ice by sympagic ciliates, and the direct incorporation of these highly
442 isomerized dietary fatty acids (Burot et al., 2021). A trophic link between copepods and ciliates
443 has been well established (Pierce and Turner 1992), and some authors have shown that lipids
444 of bacterial origin can be transferred up the food web without modification to copepods that
445 consume bacterivorous ciliates (Ederington et al., 1995). The presence of both vaccenic and
446 oleic acids in copepod wax esters, as in the case of some euphausiids (Lee et al., 2006), could
447 thus explain their similar autoxidative reactivity (Figs. 7B and 7C).

448 449 *4.2.3. Monounsaturated n-alkan-1-ols*

450 Although Type II photosensitized oxidation of monounsaturated *n*-alkan-1-ols was also
451 relatively weak (Fig. 8), likely due to the strong chlorophyll photobleaching, it is interesting to
452 note that C_{20:1Δ11} and C_{22:1Δ11} *n*-alkan-1-ols (specific to herbivorous copepod wax esters; Lee et
453 al., 2006) were more photooxidized in the first five stations (01, 02, 03, 09, and 11) than the
454 non-specific C_{16:1Δ9} and C_{18:1Δ9} *n*-alken-1-ols (Kruskal-Wallis, n=20 p = 0.00516 < 0.05).
455 Previously, a strong photooxidation of C_{20:1Δ11} and C_{22:1Δ11} *n*-alken-1-ols was observed in
456 sinking particles collected in summer at 100 m in the Beaufort Sea (Rontani et al., 2012), and
457 attributed to a very high efficiency of Type-II photosensitized oxidation processes in faecal
458 pellets of herbivorous copepods. A very efficient transfer of singlet oxygen from more or less
459 digested diatoms to the wax esters present in the lipid droplets trapped in faecal pellets (Najdek
460 et al., 1994) was also proposed. The strongest photooxidation observed in the Beaufort Sea
461 likely results from a fast transfer of faecal pellets to deep waters where the intensity of solar
462 irradiance should be sufficiently weak to favour the photodynamic effect at the expense of
463 chlorophyll photobleaching. The weak and selective photooxidation of C_{20:1Δ11} and C_{22:1Δ11} *n*-
464 alken-1-ols observed during the present study confirms: (i) the involvement of this process in
465 faecal pellets of herbivorous copepods, and (ii) the key role played by solar irradiance and

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2 467 sinking rates in the efficiency of the photodynamic processes. Due to the intensity of solar
3 irradiance during summers, only the chlorophyll of senescent diatom cells and the debris of
4 herbivorous zooplankton faecal pellets (which are suspended in surface waters of the Chukchi
5 468 Sea), is thus strongly affected by photooxidation processes.
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9 470 Monounsaturated *n*-alkan-1-ols also appeared to be weakly affected by autoxidative
10 processes in our Chukchi Sea samples (Fig. 8). Since autoxidation of monounsaturated long-
11 chain MUFAs and *n*-alkan-1-ols involves attack of the allylic positions of their isolated double
12 471 bonds (Frankel, 1998), their degradation rates should be very similar and only weakly impacted
13 by esterification. The differences in reactivity observed between these alcohols and oleic and
14 472 vaccenic acids (Figs. 7B and 7C) are thus very surprising. Autoxidation of wax esters of
15 omnivorous or carnivorous copepods containing high amounts of oleic acid and of the
16 473 unreactive C_{14:0} and C_{16:0} alcohols (Albers et al., 1996) seems thus to be strongly favoured (Fig.
17 474 7B), while wax esters of herbivorous copepods dominated by C_{20:1Δ11} and C_{22:1Δ11} *n*-alken-1-ols
18 and C_{14:0}, C_{16:0}, C_{20:1} and C_{22:1} fatty acids (Lee et al., 2006) are only weakly affected (Fig. 8). It
19 475 was previously observed that herbivorous amphipods are somewhat resistant to oxidative stress
20 due to the presence of high concentrations of antioxidants (i.e. mycosporine-like amino acids
21 476 and carotenoids) ingested from their algal diet (Abele and Puntarulo, 2004; Obermüller et al.,
22 2005; Obermüller, 2006), while carnivorous species are very sensitive to this stress due to their
23 477 lower accumulation of algal antioxidants via the food chain (Obermüller et al., 2005). The
24 478 differences in autoxidative reactivity observed in the present work between oleic acid (main
25 acid counterpart of omnivorous or carnivorous copepod wax esters; Albers et al., 1996) and
26 479 C_{20:1Δ11} and C_{22:1Δ11} *n*-alken-1-ols (main alcohol counterparts of herbivorous copepod wax
27 480 esters; Lee et al., 2006) thus complement these previous findings.
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56 489 It is generally considered that sinking of zooplanktonic faecal pellets to the seafloor is
57 strongly limited by coprophagy (Paffenhöfer and Knowles, 1979) and bacterial decomposition
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2 491 (Smetacek, 1985). In the case of faecal pellets of carnivorous or omnivorous zooplankton,
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5 492 autoxidation processes seem thus to also contribute to their degradation.
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7 494 **4. Conclusions**

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9 495 Analysis of the lipid content of SPM samples collected in surface waters of the Chukchi Sea
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12 496 enabled us to confirm: (i) their detritic character, (ii) the dominance of diatoms
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14 497 (Thalassiosirales) among primary producers, and (iii) the presence of high proportions of
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16 498 zooplanktonic (copepods) faecal pellet debris during the summer period. Type II
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19 499 photosensitized oxidation of phyto- and zooplanktonic lipids (photodynamic effect) appeared
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22 500 to be relatively limited, likely due to the enhancement of photobleaching of chlorophyll
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24 501 (sensitizer) by the high solar irradiance observed near to the surface. The weak photooxidation
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27 502 of zooplanktonic wax esters observed in these SPM samples contrasts with the strong
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29 503 photooxidative alteration of these compounds previously observed in sinking particles collected
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31 504 from the Beaufort Sea in summer (Rontani et al., 2012). The photodynamic effect seems thus
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34 505 to be favoured in large faecal pellets of herbivorous copepods sinking quickly in weakly
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36 506 irradiated zones. In contrast, autoxidative processes, which can operate in all oxic aquatic
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39 507 environments (Schaich, 2005) and potentially affect all unsaturated lipids (Rontani, 2012;
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41 508 Rontani and Belt, 2020), acted more intensively in faecal pellets of omnivorous or carnivorous
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44 509 copepods than in those of herbivorous counterparts. Such differences of reactivity were
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46 510 attributed to the consumption of algal antioxidants during the diet of omnivorous or carnivorous
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49 511 copepods, which should favour the establishment of free radical oxidation processes.
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10 520 **References**

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FIGURE CAPTIONS

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5 801 **Figure 1.** Map of the study area with location of the stations investigated in Chukchi Sea. The

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7 802 line corresponds to the limit of ice at the time of sampling.

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12 804 **Figure 2.** GC-QTOF determination of the double bond position of MUFAs with the TMS

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14 805 derivatives of their oxidation products in the SPM sample collected at station 02.

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60 821 **Figure 3.** GC-QTOF determination of the double bond position of monounsaturated *n*-alkan-
61 1-ols with the TMS derivatives of their oxidation products in the SPM sample collected at
62 station 02.

63 811 **Figure 4.** Relative proportions (A) and concentrations (ng L^{-1}) (B) of sterols in SPM samples
64 collected at the different stations investigated.

65 814 **Figure 5.** Concentrations ($\mu\text{g L}^{-1}$) of *n*-alkan-1-ols (A) and proportions of herbivorous and
66 omnivorous or carnivorous zooplankton (B) in SPM samples collected at the different stations
67 investigated.

68 818 **Figure 6.** Concentrations (ng L^{-1}) of chlorophyll phytyl side-chain and its main degradation
69 products (A) and estimates of the proportion of its biotic, autoxidative and photooxidative
70 degradation (B) in SPM samples collected at the different stations investigated.

71 822 **Figure 7.** Relative percentage of intact, autoxidized and photooxidized palmitoleic (A), oleic
72 (B) and vaccenic (C) acids in SPM samples collected at the different stations investigated.

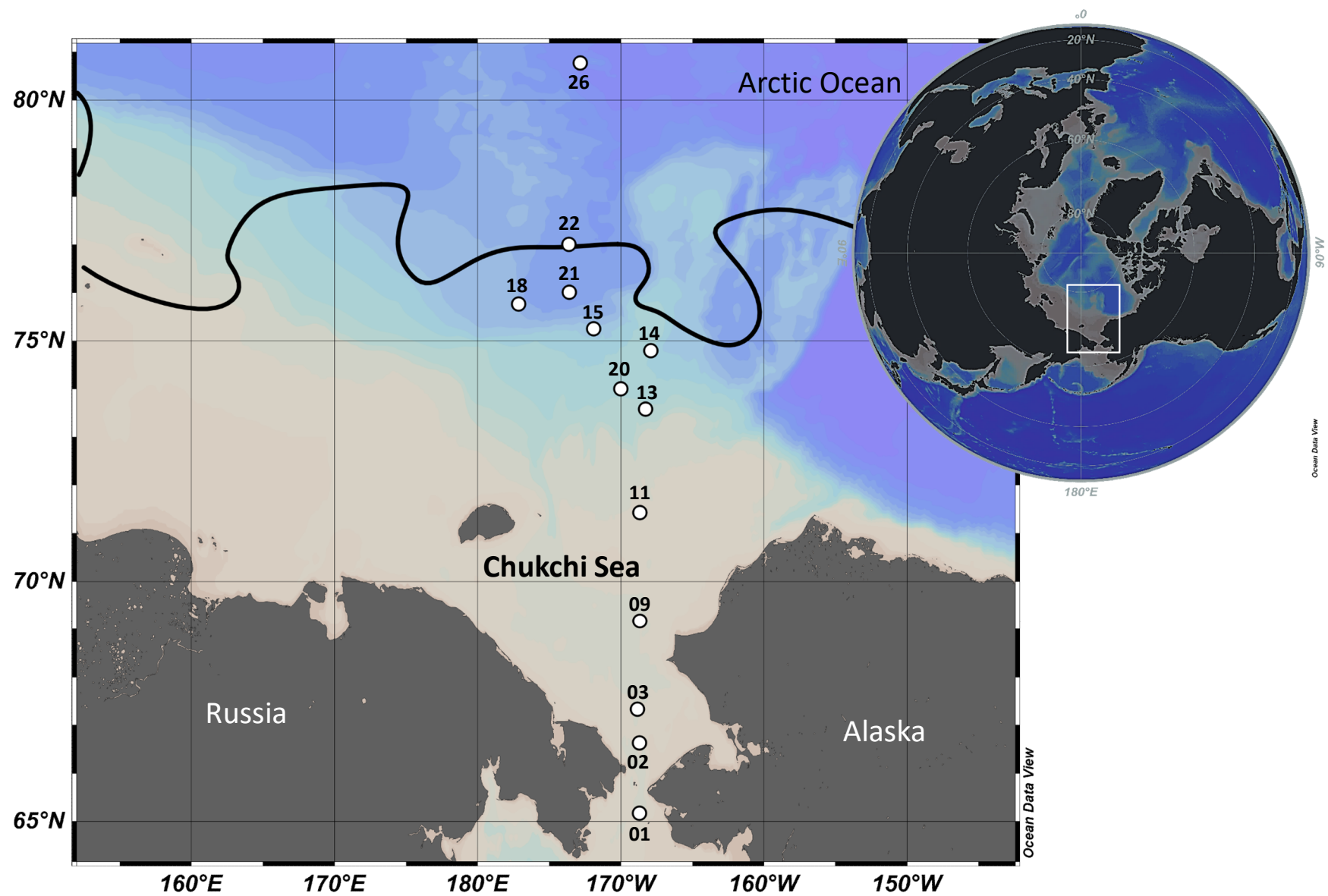
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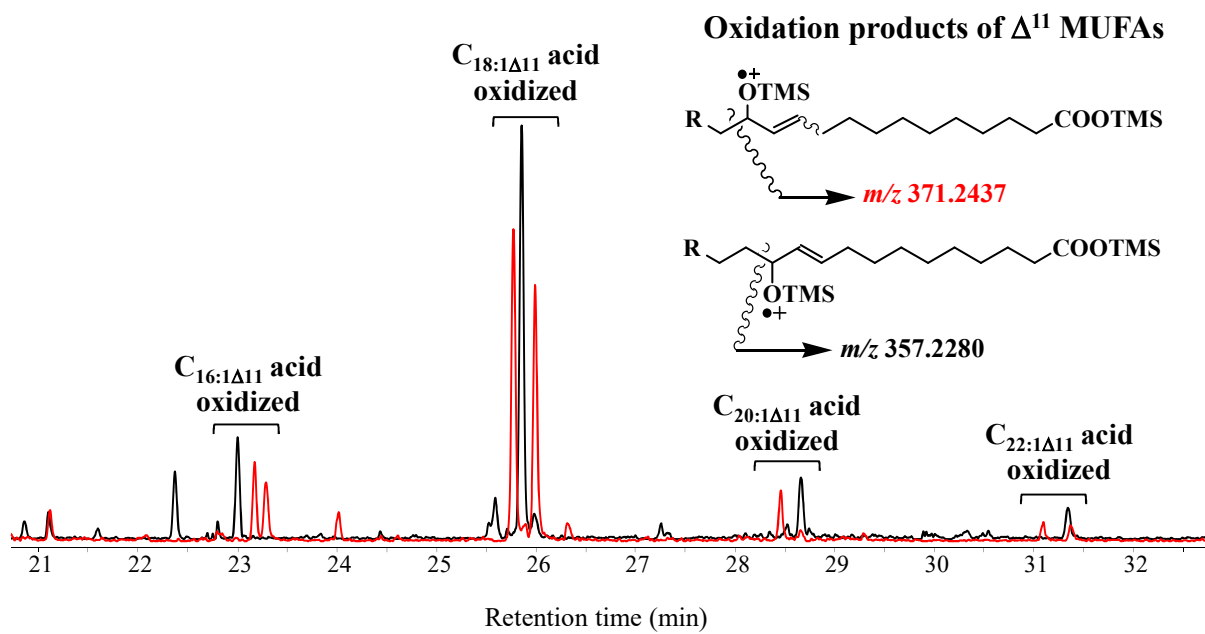
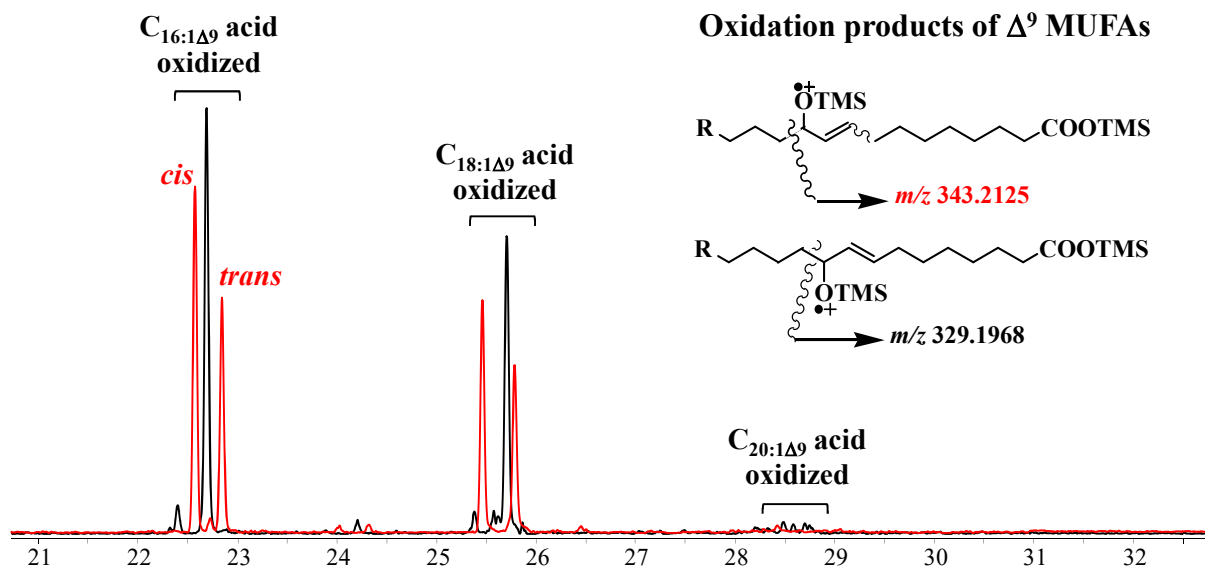
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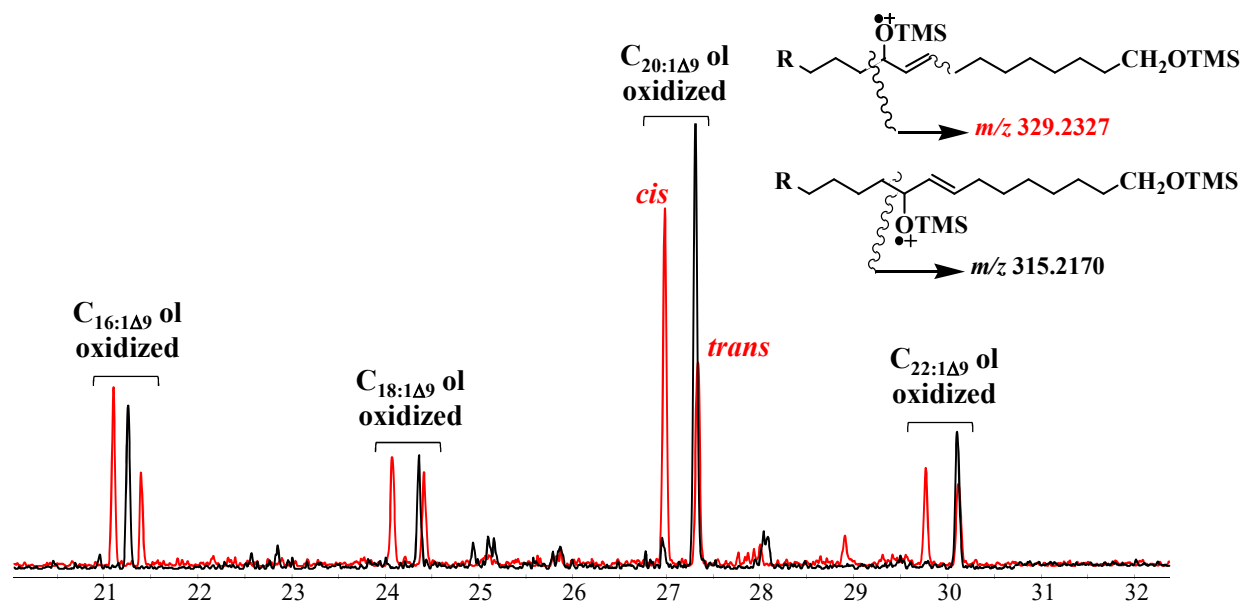
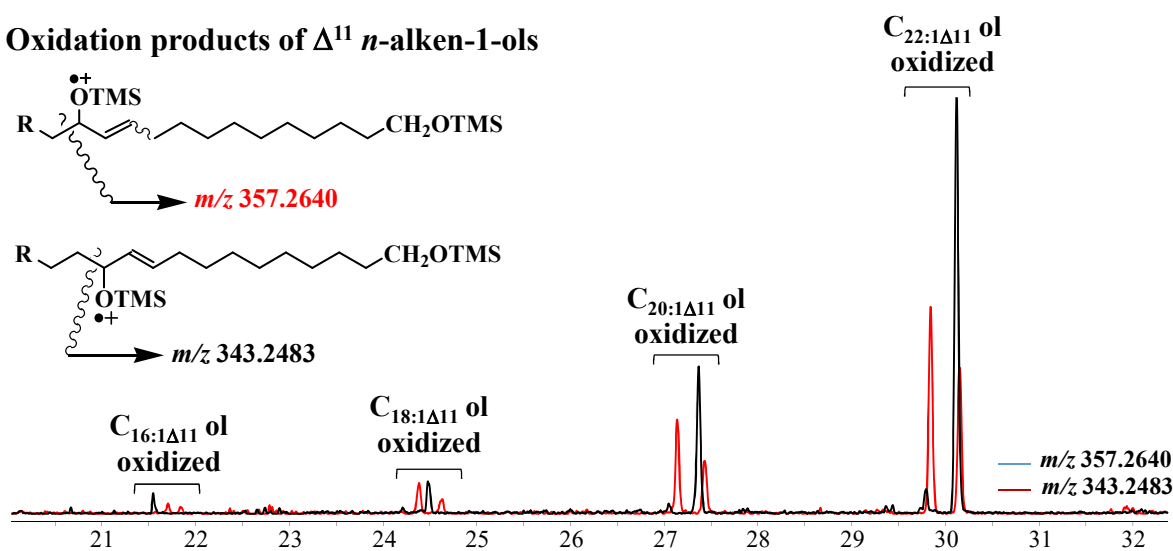
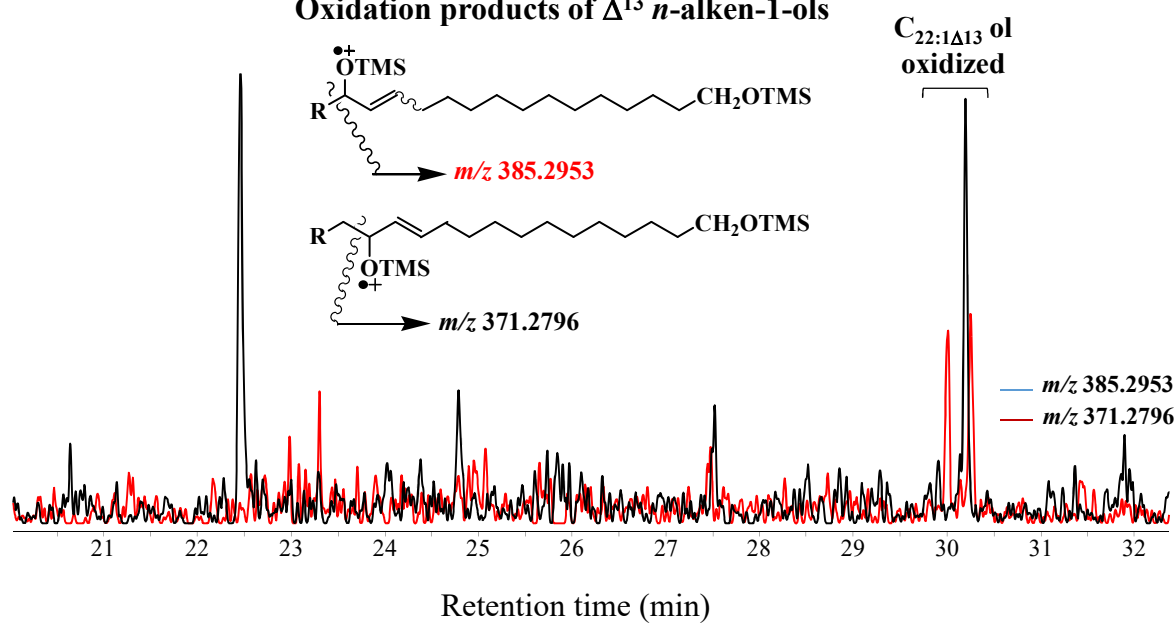
825 **Figure 8.** Relative percentage of intact, autoxidized and photooxidized C_{16:1Δ9}, C_{18:1Δ9}, C_{20:1Δ11}
826 and C_{22:1Δ11} *n*-alkan-1-ols in SPM samples collected at the different stations investigated.

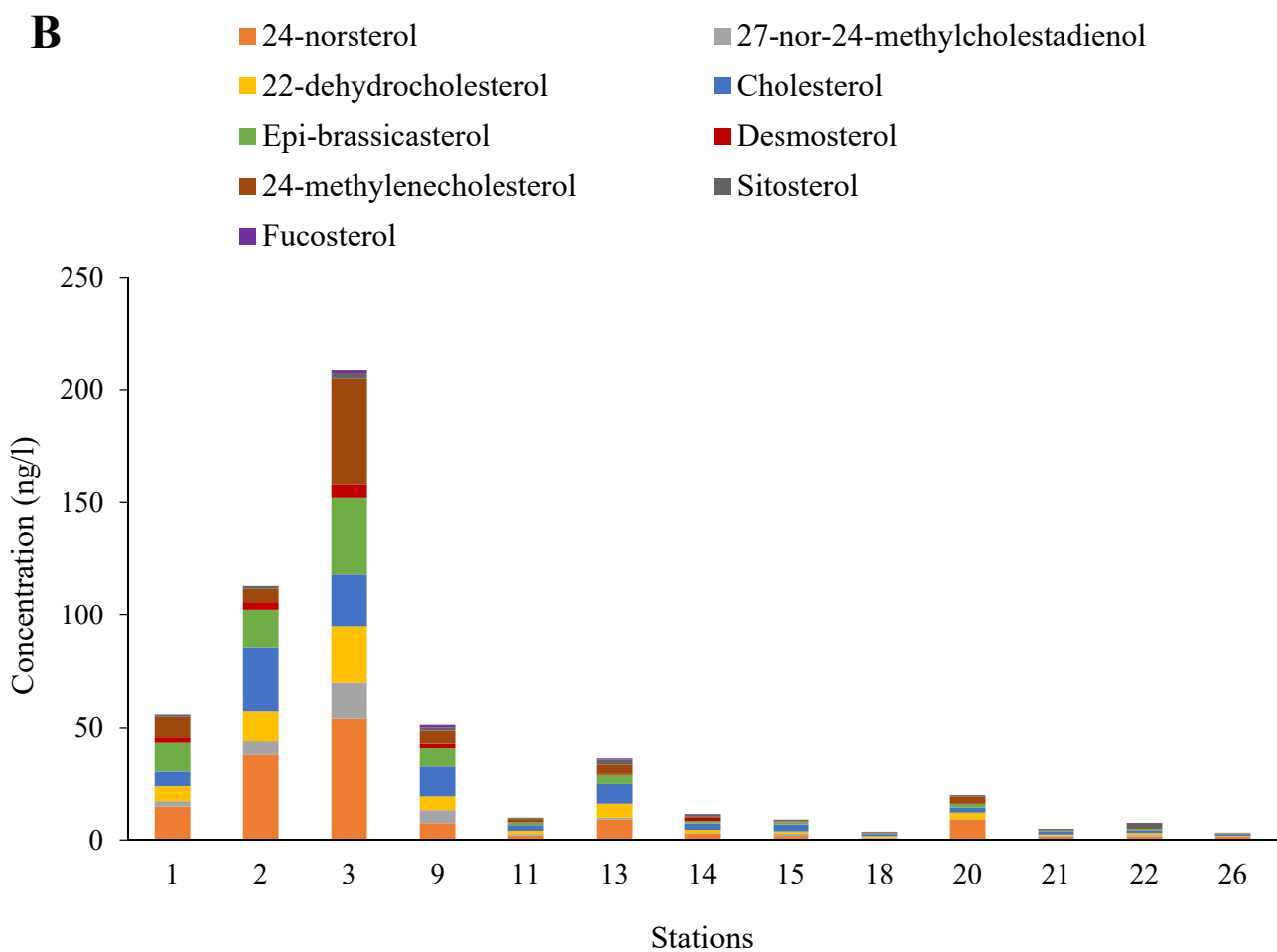
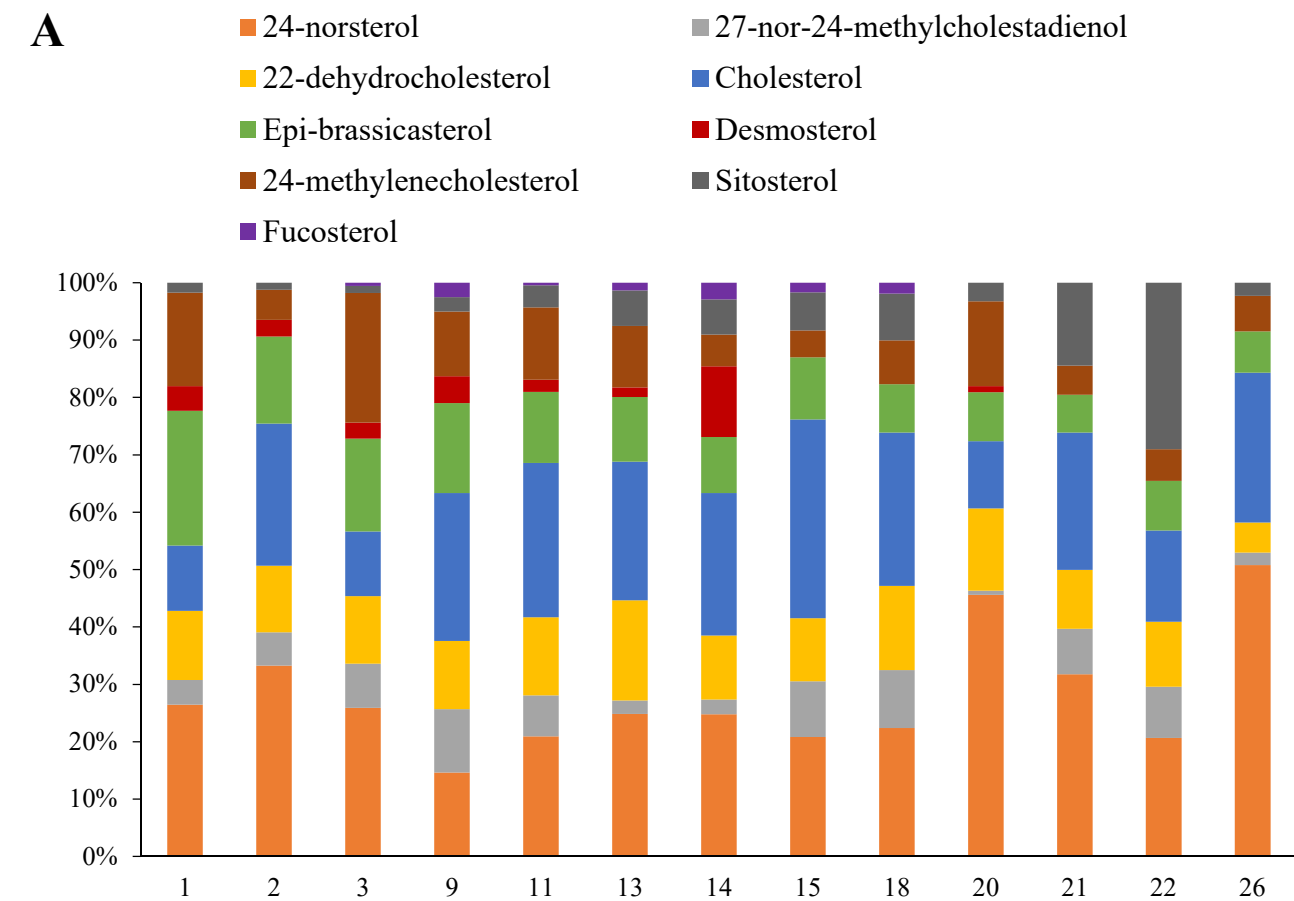
827
828 **Figure 9.** Biotic and abiotic degradation of the chlorophyll phytyl side-chain (compounds in
829 blue were quantified during the present work).

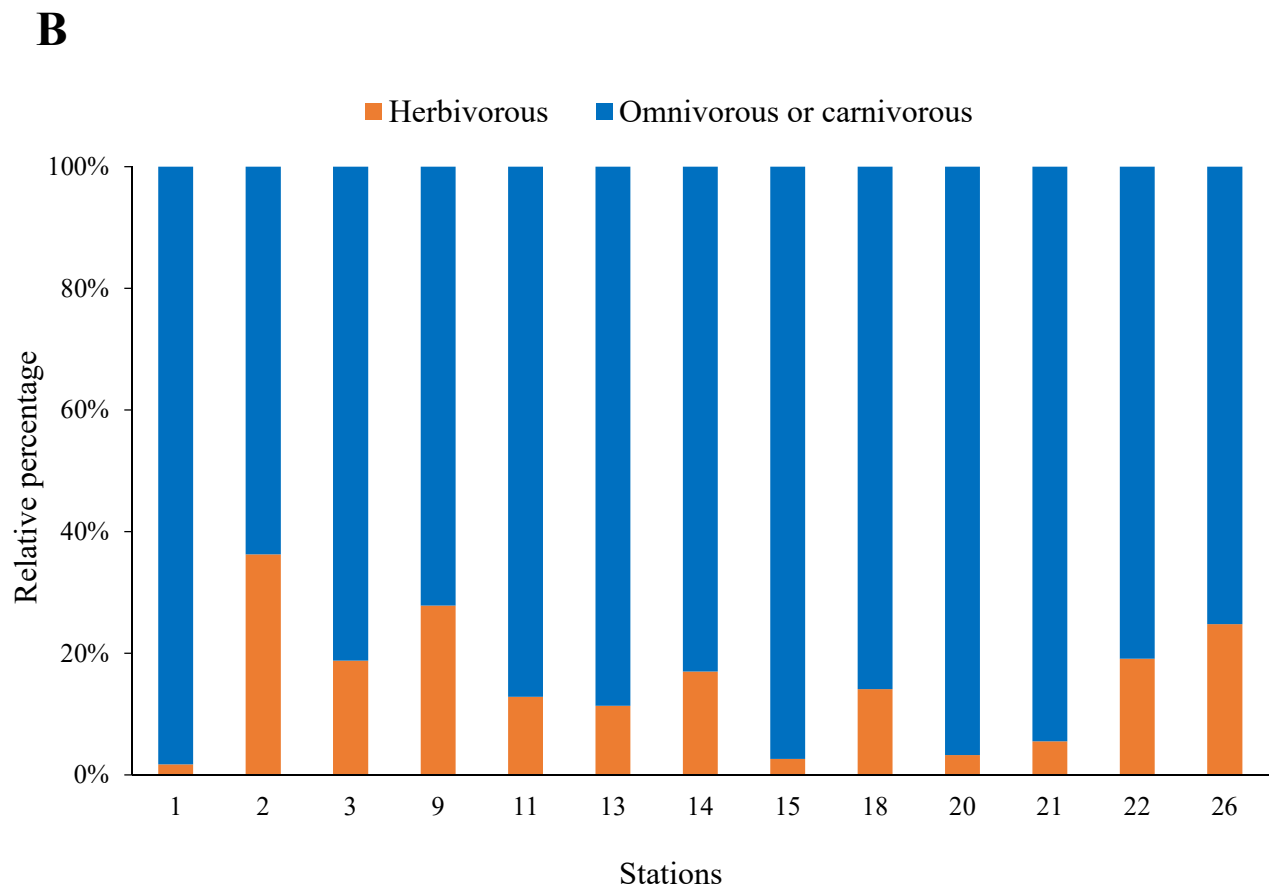
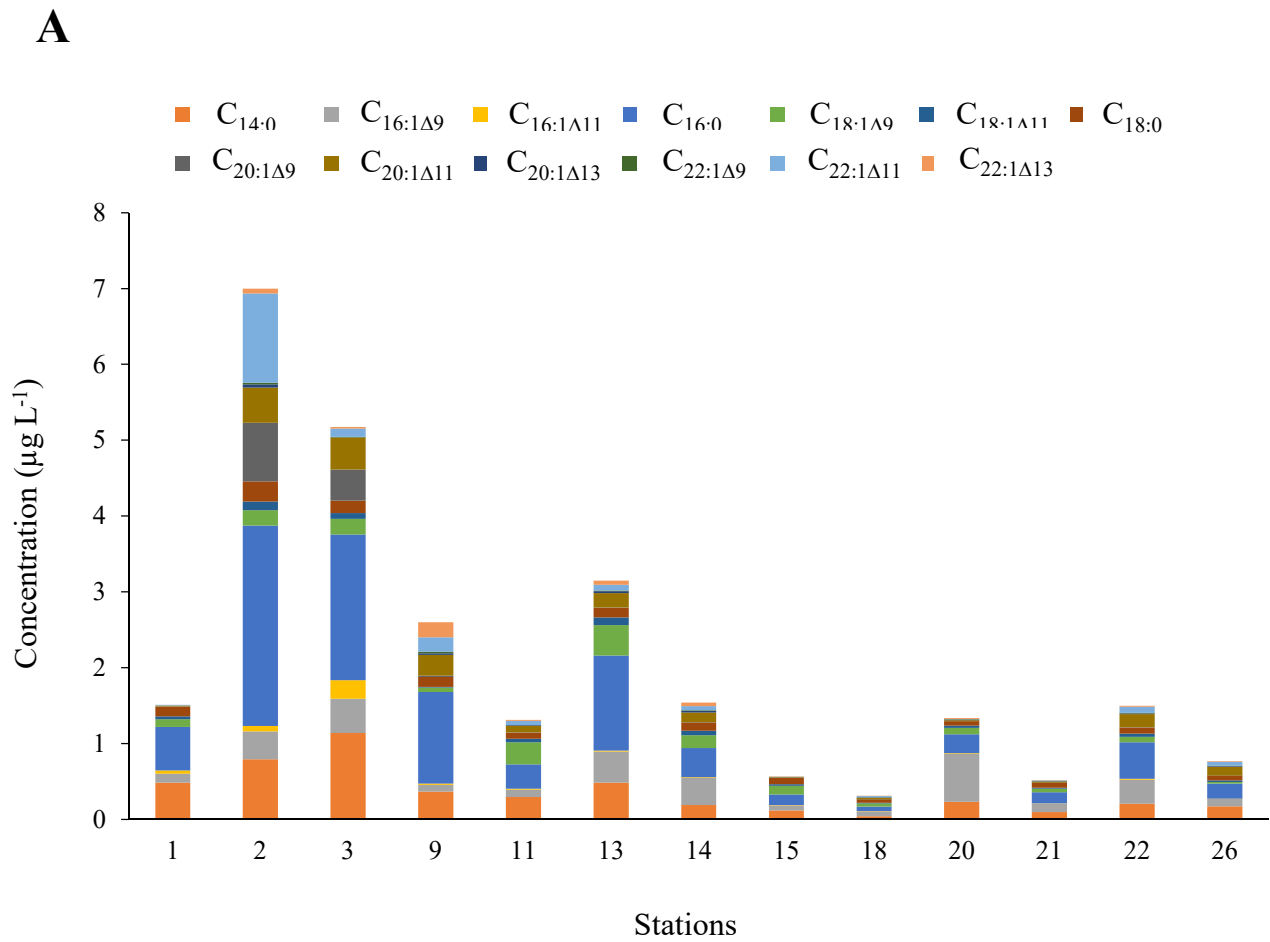
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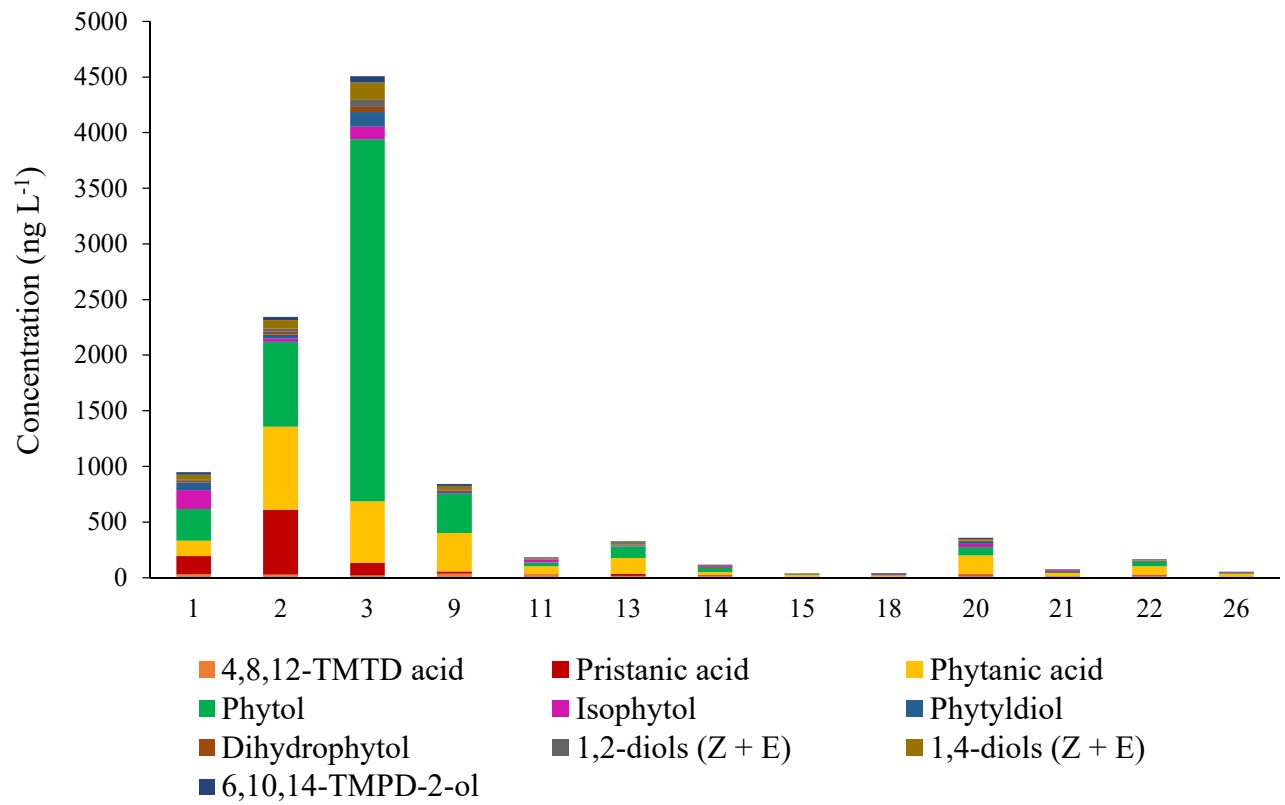
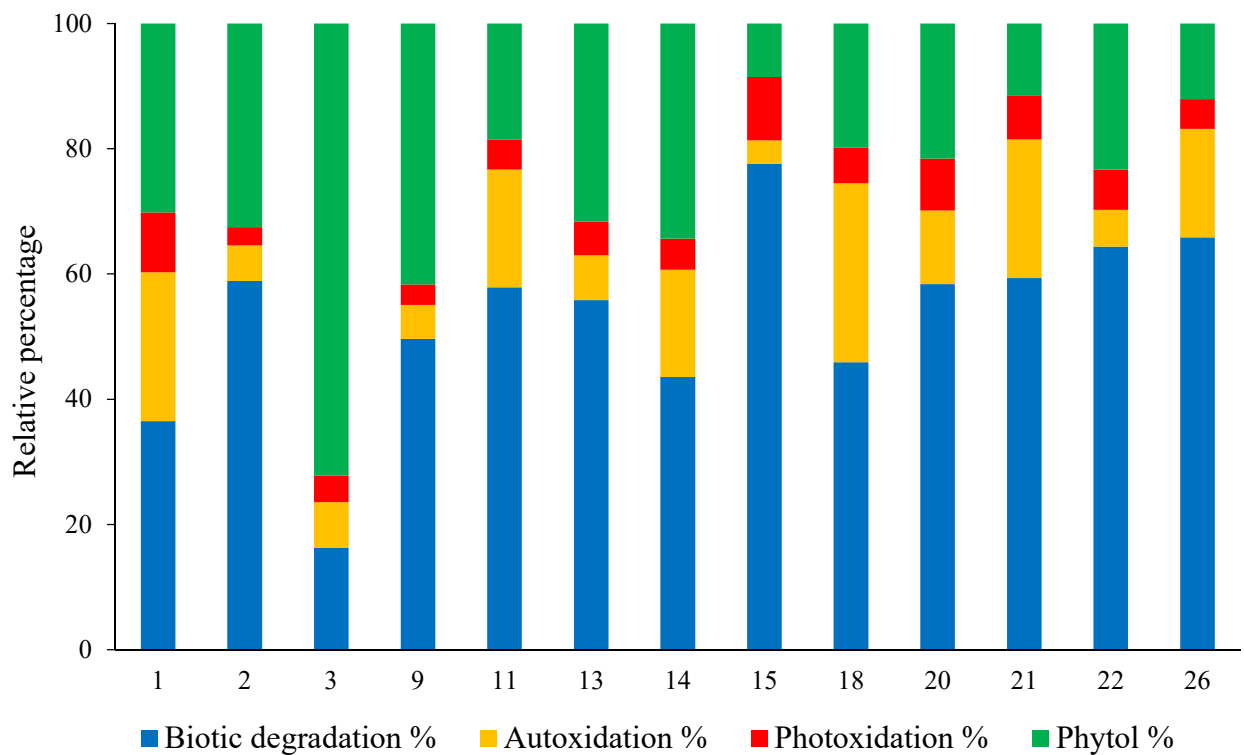


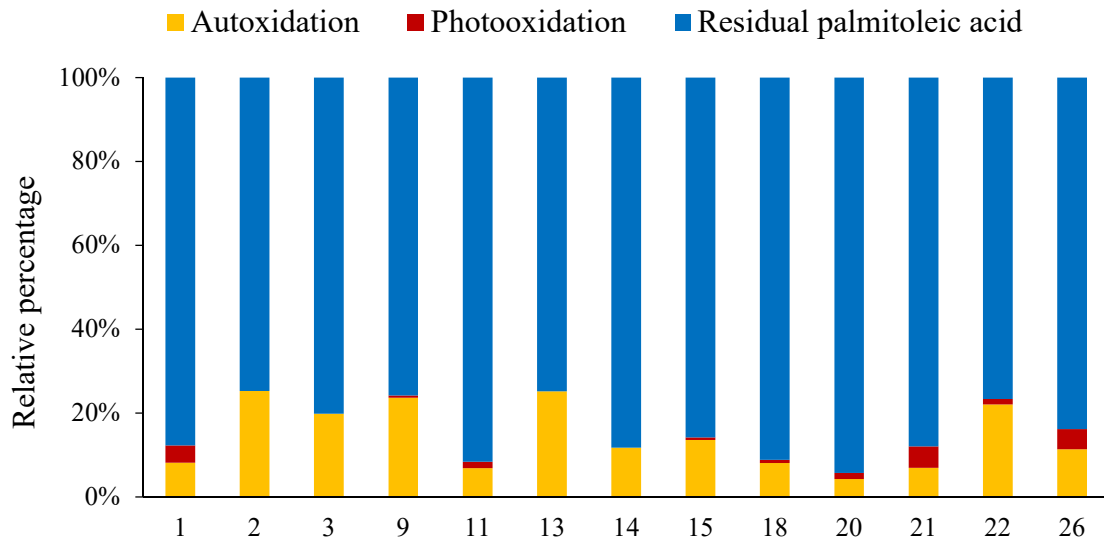
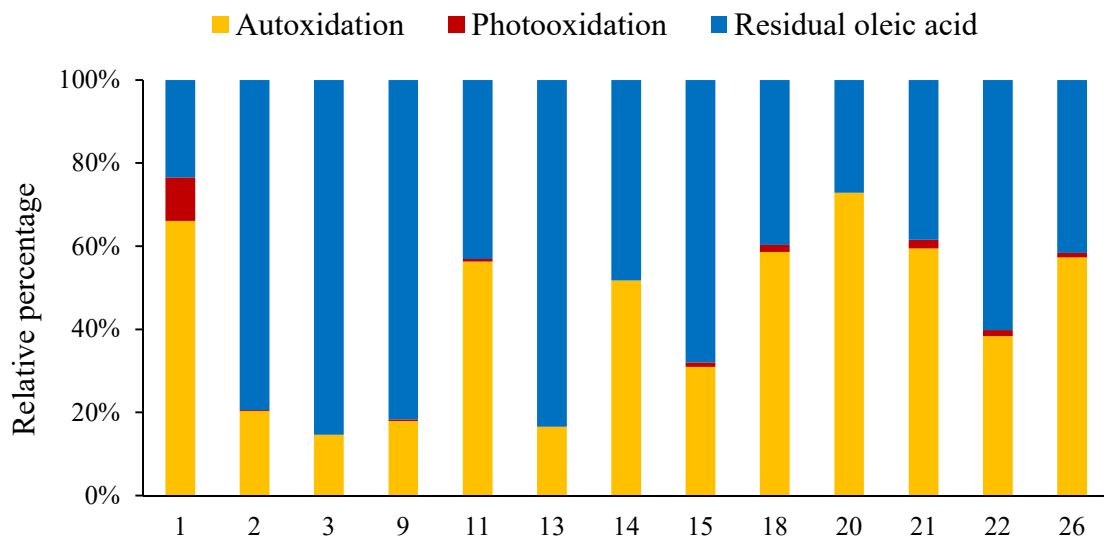
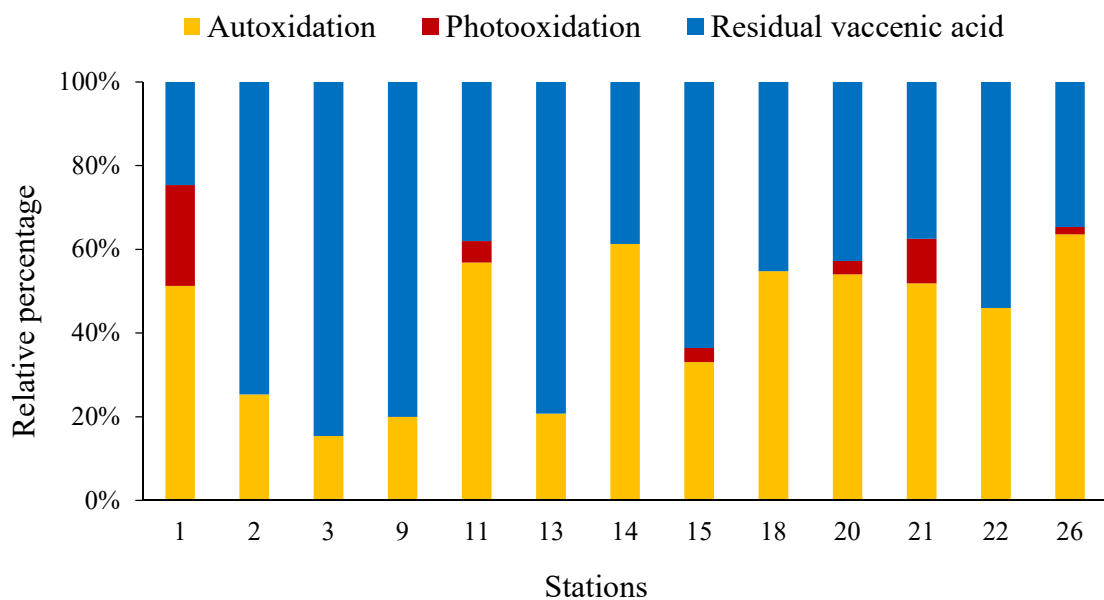


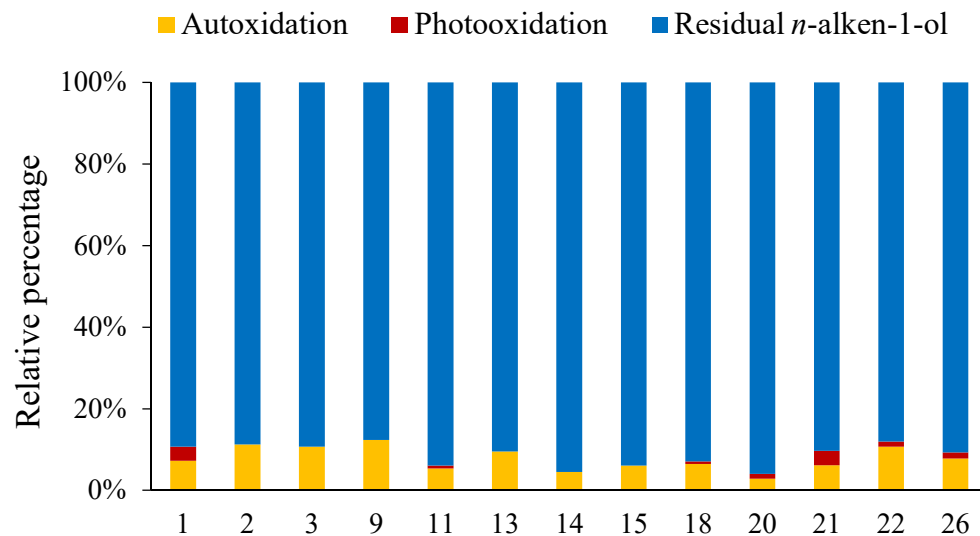
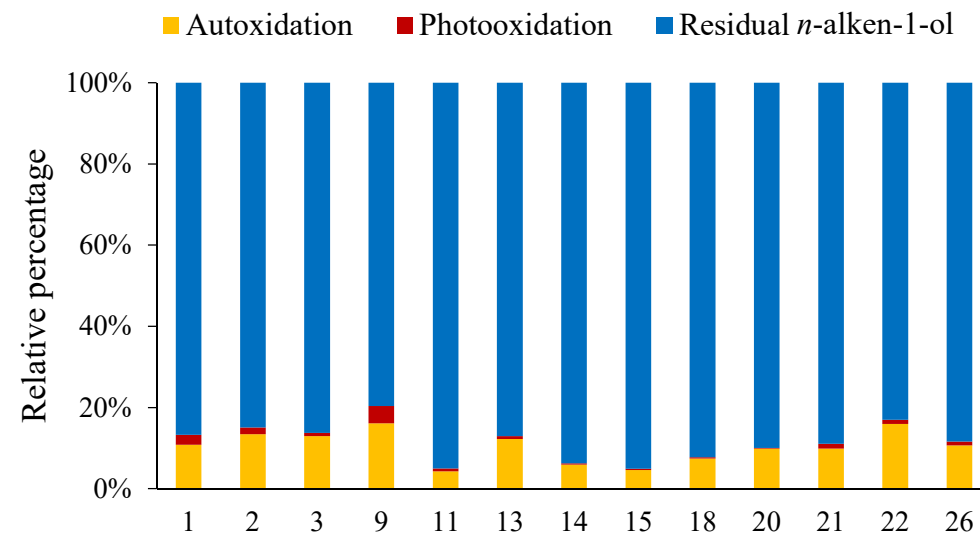
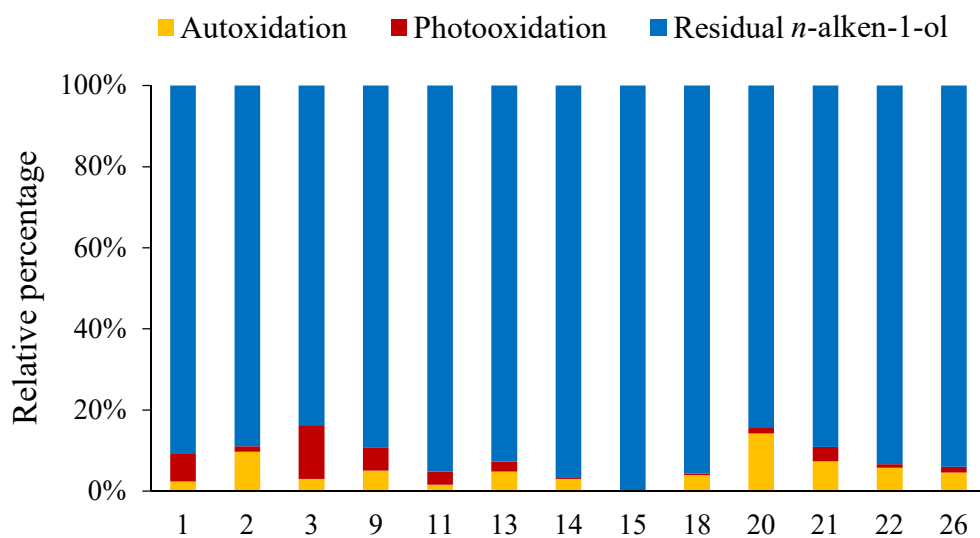
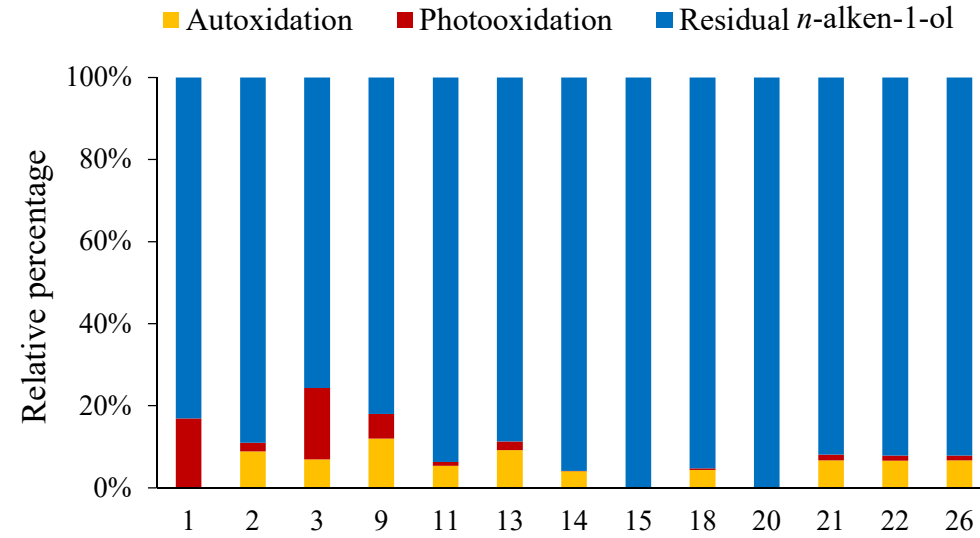
Oxidation products of Δ^9 *n*-alken-1-olsOxidation products of Δ^{11} *n*-alken-1-olsOxidation products of Δ^{13} *n*-alken-1-ols





A**B**

A**C_{16:1Δ9} fatty acid****B****C_{18:1Δ9} fatty acid****C****C_{18:1Δ11} fatty acid**

C_{16:1Δ9} *n*-alken-1-ol**C_{18:1Δ9} *n*-alken-1-ol****C_{20:1Δ11} *n*-alken-1-ol****C_{22:1Δ11} *n*-alken-1-ol**

Stations

Stations

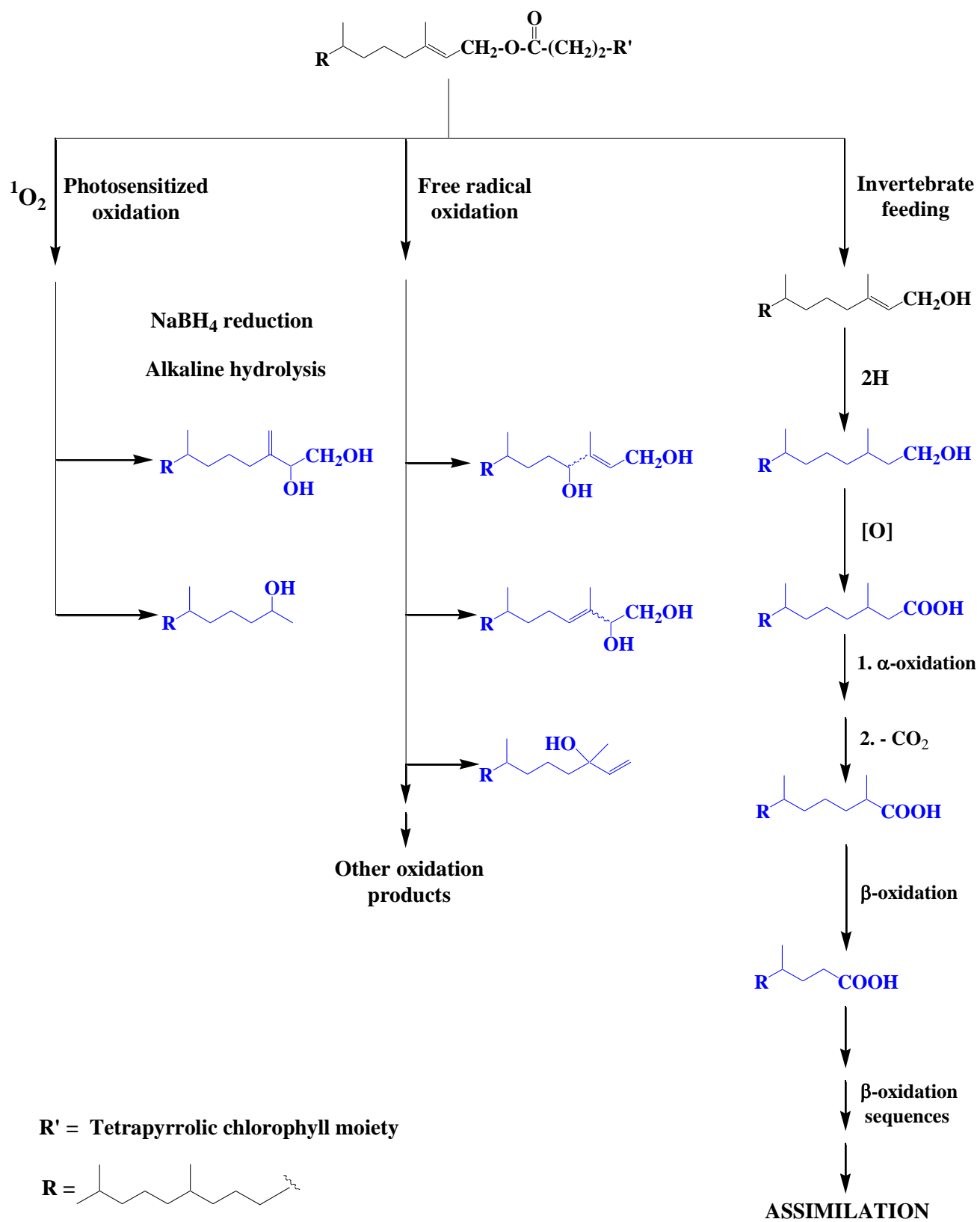


Table 1

Concentrations (ng L⁻¹) of the main sterols in the samples investigated.

Sterol	St 01	St 02	St 03	St 09	St 11	St 13	St 14	St 15	St 18	St 20	St 21	St 22	St 26
24-norcholesta-5,22 <i>E</i> -dien-3β-ol	14.8	37.7	54.1	7.5	2.0	9.0	2.9	1.9	0.8	9.1	1.6	1.6	1.6
27-nor-24-methylcholesta-5,22-dien-3β-ol	2.4	6.5	16.0	5.7	0.7	0.9	0.3	0.9	0.4	0.1	0.4	0.7	0.1
Cholesta-5,22 <i>E</i> -dien-3β-ol	6.7	13.1	24.6	6.1	1.3	6.3	1.3	1.0	0.5	2.9	0.5	0.9	0.2
Cholest-5-en-3β-ol	6.4	28.1	23.5	13.2	2.6	8.7	2.9	3.1	1.0	2.3	1.2	1.2	0.8
24-methylcholesta-5,22 <i>E</i> -dien-3β-ol	13.1	17.1	33.8	8.1	1.2	4.1	1.1	1.0	0.3	1.7	0.3	0.7	0.2
Cholesta-5,24-dien-3β-ol	2.4	3.3	5.9	2.4	0.2	0.6	1.4	nd ^a	nd	0.2	nd	nd	nd
24-methylcholesta-5,24(28)-dien-3β-ol	9.1	6.0	47.1	5.8	1.2	3.9	0.6	0.4	0.3	3.0	0.2	0.4	0.2
24-ethylcholest-5-en-3β-ol	1.0	1.4	2.5	1.3	0.4	2.2	0.7	0.6	0.3	0.6	0.7	2.2	0.1
24(<i>E</i>)-ethylcholesta-5,24(28)-dien-3β-ol	nd	nd	1.2	1.3	0.1	0.5	0.3	0.2	0.1	nd	nd	nd	nd
Total	55.9	113.2	208.8	51.4	9.8	36.1	11.6	9.0	3.6	20.0	4.9	7.6	2.2

^a nd = not detected (< 0.1 ng L⁻¹)

Table 2

Concentrations ($\mu\text{g L}^{-1}$) of saturated and monounsaturated fatty acids in the samples investigated. PUFAs present in very weak proportion (reaching less than 4% at station 03) were not included in this table.

Station	C _{14:0}	C _{16:1Δ9}	C _{16:1Δ11}	C _{16:0}	C _{18:1Δ9}	C _{18:1Δ11}	C _{18:0}	C _{20:1Δ9}	C _{20:1Δ11}	C _{20:1Δ13}	C _{22:1Δ9}	C _{22:1Δ11}	C _{22:1Δ13}	Total
01	2.67	1.09	0.08	8.58	0.33	0.15	0.30	0.02	0.06	0.04	0.01	0.13	0.01	13.5
02	6.36	9.20	0.86	14.41	3.75	1.81	1.88	0.26	0.35	0.07	0.23	0.24	0.06	39.5
03	12.61	17.95	2.93	18.52	3.78	2.19	1.21	0.05	0.12	0.03	0.03	0.23	0.06	59.7
09	2.90	3.28	0.55	8.18	1.63	0.95	1.33	0.02	0.23	0.05	0.08	0.57	0.03	19.8
11	0.55	0.58	0.03	2.47	0.32	0.10	0.21	0.01	0.11	0.03	0.03	0.29	0.02	4.7
13	2.51	6.53	0.18	6.31	3.43	0.71	0.62	0.02	0.14	0.06	0.03	0.25	0.03	20.8
14	0.46	1.60	0.02	3.08	0.80	0.11	0.42	0.01	0.08	0.02	0.01	0.17	0.01	6.8
15	0.75	0.88	0.03	3.35	1.12	0.19	1.79	nd	0.02	0.01	nd	0.12	0.02	8.3
18	0.17	0.57	nd ^a	1.56	0.17	0.04	0.30	nd	0.03	0.01	0.01	0.30	0.01	3.3
20	1.47	8.97	nd	7.08	0.53	0.25	0.38	0.02	0.06	0.04	nd	0.12	0.02	18.9
21	0.52	1.10	0.02	2.58	0.25	0.05	0.27	nd	0.03	0.01	nd	0.18	0.01	5.0
22	1.57	5.64	0.10	4.69	2.14	0.27	0.89	nd	0.08	0.02	0.02	0.03	0.01	15.5
26	0.27	0.52	0.02	2.06	0.17	0.04	0.33	nd	0.05	0.01	0.02	0.04	0.01	3.5

^a nd = not detected ($< 0.01 \mu\text{g L}^{-1}$)

Table 4

Concentrations ($\mu\text{g L}^{-1}$) of *n*-alkan-1-ols in the samples investigated.

Compounds	St 01	St 02	St 03	St 09	St 11	St 13	St 14	St 15	St 18	St 20	St 21	St 22	St 26
C _{14:0}	0.24	0.40	0.57	0.18	0.15	0.24	0.10	0.06	0.02	0.12	0.05	0.10	0.09
C _{16:1Δ9}	0.12	0.36	0.45	0.09	0.10	0.41	0.36	0.07	0.07	0.63	0.11	0.32	0.10
C _{16:1Δ11}	0.04	0.07	0.24	0.02	0.01	0.01	0.01	0.01	nd ^a	0.01	0.01	0.01	nd
C _{16:0}	0.26	1.20	0.87	0.55	0.15	0.57	0.18	0.06	0.03	0.11	0.07	0.22	0.09
C _{18:1Δ9}	0.10	0.20	0.21	0.06	0.29	0.40	0.17	0.11	0.04	0.08	0.05	0.07	0.02
C _{18:1Δ11}	0.04	0.11	0.07	0.01	0.05	0.10	0.06	0.02	0.01	0.03	0.01	0.04	0.02
C _{18:0}	0.13	0.27	0.16	0.13	0.08	0.13	0.11	0.09	0.05	0.06	0.07	0.08	0.06
C _{20:1Δ9}	0.01	0.77	0.41	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd
C _{20:1Δ11}	0.02	0.46	0.42	0.28	0.09	0.19	0.13	0.01	0.02	0.01	0.01	0.17	0.11
C _{20:1Δ13}	nd	0.04	nd	0.02	0.01	0.02	0.02	nd	nd	nd	nd	0.01	0.01
C _{22:1Δ9}	nd	0.02	0.01	0.02	nd	0.01	0.01	nd	nd	0.01	nd	0.01	0.01
C _{22:1Δ11}	0.01	1.18	0.11	0.19	0.05	0.07	0.06	nd	0.02	nd	0.01	0.08	0.05
C _{22:1Δ13}	nd	0.06	0.02	0.20	0.01	0.05	0.05	nd	nd	0.01	nd	0.01	0.01
Total	0.96	5.16	3.56	1.76	0.99	2.22	1.24	0.43	0.26	1.09	0.38	1.13	0.58

^a nd = not detected ($< 0.01 \mu\text{g L}^{-1}$)

Table S1

Coordinates and sampling dates of the different stations sampled.

Station	Sampling date	Latitude (°N)	Longitude (°W)
01	02/08/2015	65.173	168.690
02	02/08/2015	66.630	168.688
03	02/08/2015	67.333	168.834
09	03/08/2015	69.167	168.668
11	04/08/2015	71.430	168.670
13	04/08/2015	73.581	168.283
14	05/08/2015	74.798	167.899
15	05/08/2015	75.250	171.901
18	07/08/2015	75.761	177.152
20	08/08/2015	76.007	173.608
21	08/08/2015	73.999	169.997
22	09/08/2015	77.006	173.617
26	13/08/2015	80.774	172.849

Table 3

Concentrations of isoprenoid compounds, chlorophyll and chlorophyll photooxidation estimates in the samples investigated.

	St 01	St 02	St 03	St 09	St 11	St 13	St 14	St 15	St 18	St 20	St 21	St 22	St 26
3,7,11,15-tetramethylhexadec-2-en-1-ol (Phytol) ^a	286	762	3253	351	34	104	40	3	8	77	9	39	6
4,8,12-trimethyltridecanoic acid (4,8,12-TMTD acid) ^a	29	28	20	35	33	17	19	4	6	18	10	20	8
2,6,10,14-tetramethylpentadecanoic acid (Pristanic acid) ^a	167	585	113	20	4	17	4	3	1	11	3	7	2
2,6,10,14-tetramethylhexadecanoic acid (Phytanic acid) ^a	139	745	553	346	64	143	26	20	10	169	30	77	23
3,7,11,15-tetramethylhexadec-1-en-3-ol (Isophytol) ^a	169	27	113	7	28	3	12	nd ^e	9	27	15	1	7
3-methylidene-7,11,15-trimethylhexadecan-1, 2-diol ^a	68	39	134	10	3	5	1	1	1	18	2	5	1
3,7,11,15-tetramethylhexadecan-1-ol (Dihydrophytol) ^a	14	24	46	17	4	7	1	2	1	10	2	4	1
3,7,11,15-tetramethylhexadec-3-en-1,2-diols (<i>Z</i> and <i>E</i>) ^a	10	29	61	10	2	5	2	1	1	5	1	2	1
3,7,11,15-tetramethylhexadec-2-en-1,4-diols (<i>Z</i> and <i>E</i>) ^a	46	77	156	28	5	15	5	1	2	10	1	6	1
6,10,14-trimethylpentadecan-2-ol ^a	23	30	59	18	6	12	4	3	2	12	3	6	2
Total	951	2346	4508	842	183	328	114	38	41	357	76	167	52
CPPI ^b	0.191	0.041	0.033	0.022	0.072	0.041	0.028	0.173	0.071	0.187	0.180	0.096	0.104
Chlorophyll ^c	2.50	2.01	7.17	0.68	0.27	0.29	0.16	0.04	0.06	1.01	0.09	0.13	0.11
Chlorophyll photooxidation estimate (%) ^d	96.1	52.7	45.3	33.0	72.2	52.8	40.5	94.8	71.8	95.8	95.4	81.5	84.0

^a (ng L⁻¹)^b Chlorophyll Phytol side-chain Photooxidation Index (molar ratio 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol /phytol)^c (µg L⁻¹)^d Estimated with the empirical equation: chlorophyll photodegradation % = (1 - [CPPI + 1]^{-18.5}) x 100 (Cuny et al. 2002).^e nd = not detected (< 1 ng L⁻¹)

Table S2

Accurate masses of the main fragment ions produced during EI fragmentation of silylated monounsaturated fatty acid autoxidation products.

Parent fatty acid	<i>m/z</i>	<i>m/z</i>	<i>m/z</i>	<i>m/z</i>
C _{16:1} Δ ₉	199.1518 ^a	213.1675 ^a	329.1968 ^b	343.2125 ^b
C _{16:1} Δ ₁₁	171.1206	185.1363	357.2280	371.2437
C _{16:1} Δ ₁₃	143.0748	157.1051	385.2592	399.2749
C _{18:1} Δ ₉	227.1830	241.1987	329.1968	343.2125
C _{18:1} Δ ₁₁	199.1518	213.1675	357.2280	371.2437
C _{18:1} Δ ₁₃	171.1206	185.1363	385.2592	399.2749
C _{20:1} Δ ₉	255.2139	269.2295	329.1968	343.2125
C _{20:1} Δ ₁₁	227.1830	241.1987	357.2280	371.2437
C _{20:1} Δ ₁₃	199.1518	213.1675	385.2592	399.2749
C _{22:1} Δ ₉	283.2451	297.2607	329.1968	343.2125
C _{22:1} Δ ₁₁	255.2139	269.2295	357.2280	371.2437
C _{22:1} Δ ₁₃	227.1830	241.1987	385.2592	399.2749

^a Fragments containing the terminal methyl group.

^b Fragments containing the trimethylsilyl ester group.

Table S3

Accurate masses of the main fragment ions produced during EI fragmentation of silylated monounsaturated *n*-alken-1-ol autoxidation products.

Parent <i>n</i> -alkenol	<i>m/z</i>	<i>m/z</i>	<i>m/z</i>	<i>m/z</i>
C _{16:1Δ9}	199.1518 ^a	213.1675 ^a	315.2170 ^b	329.2327 ^b
C _{16:1Δ11}	171.1206	185.1363	343.2483	357.2640
C _{16:1Δ13}	143.0748	157.1051	371.2796	385.2953
C _{18:1Δ9}	227.1830	241.1987	315.2170	329.2327
C _{18:1Δ11}	199.1518	213.1675	343.2483	357.2640
C _{18:1Δ13}	171.1206	185.1363	371.2796	385.2953
C _{20:1Δ9}	255.2139	269.2295	315.2170	329.2327
C _{20:1Δ11}	227.1830	241.1987	343.2483	357.2640
C _{20:1Δ13}	199.1518	213.1675	371.2796	385.2953
C _{22:1Δ9}	283.2451	297.2607	315.2170	329.2327
C _{22:1Δ11}	255.2139	269.2295	343.2483	357.2640
C _{22:1Δ13}	227.1830	241.1987	371.2796	385.2953

^a Fragments containing the terminal methyl group.

^b Fragments containing the terminal trimethylsilyl ether group.