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Control of the preservation of sympagic algal material in surficial sediments of central and eastern Baffin Bay by bactericidal hydroperoxides and free fatty acids

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Control of the preservation of sympagic algal material in surficial sediments of central and eastern Baffin Bay by bactericidal hydroperoxides and free fatty acids --Manuscript Draft--

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Abstract:	<p>Monounsaturated fatty acids and their oxidation products were quantified in surficial sediments (0–1 cm) dominated by sympagic (ice-associated) material released at the end of the ice melt collected in summer in central and eastern Baffin Bay during the 2016 GreenEdge campaign. Sympagic algae preservation towards bacterial mineralization was monitored based on intact and oxidized C16:1ω7 (palmitoleic) acid, and oxidation products of C18:1ω7 (vaccenic) and C16:1ω5 acids provided insights on the photooxidative and autoxidative alterations of bacteria present in these sediment samples. Preservation of sympagic algal material appeared to be highest at the stations that were relatively unaffected by copepod grazing and that contained strongly autoxidized (and thus inactive) bacteria. Analysis of sinking particles collected with a drifting trap showed an intense flux of highly photooxidized ice algae in early July that was dominated by <i>Navicula</i> spp. and associated with bacteria that had also been strongly altered by photooxidative processes. It is proposed that subsequent homolytic decomposition of the hydroperoxides resulting from this intense photooxidation may have driven the strong autoxidation of sympagic algae and bacteria observed in the sediments. The lack of colonization of sympagic material by active benthic bacteria observed at some of the stations investigated was attributed to its high content in deleterious autoxidative hydroperoxides and free fatty acids (reaching for example 107% and 22% of residual palmitoleic acid, respectively, at station 605).</p>
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RONTANI Jean-François
DR2 (CNRS)

Marseille, the 22 July 2022

To the attention of: Prof T. BIANCHI

Editor in Chief of Marine Chemistry

Dear Dr. Bianchi,

You will find herewith a paper entitled “*Control of the preservation of sympagic algal material in surficial sediments of central and eastern Baffin Bay by bactericidal hydroperoxides and free fatty acids*” submitted for publication in the journal Marine Chemistry. In this paper, we analyzed sediment and sinking particles collected in 2016 in the Baffin Bay (GreenEdge Campaign) and used oxidation products of monounsaturated acids to demonstrate the role played by oxidative stress of bacteria on the preservation of the sympagic algal material.

Sincerely yours

RONTANI Jean-François

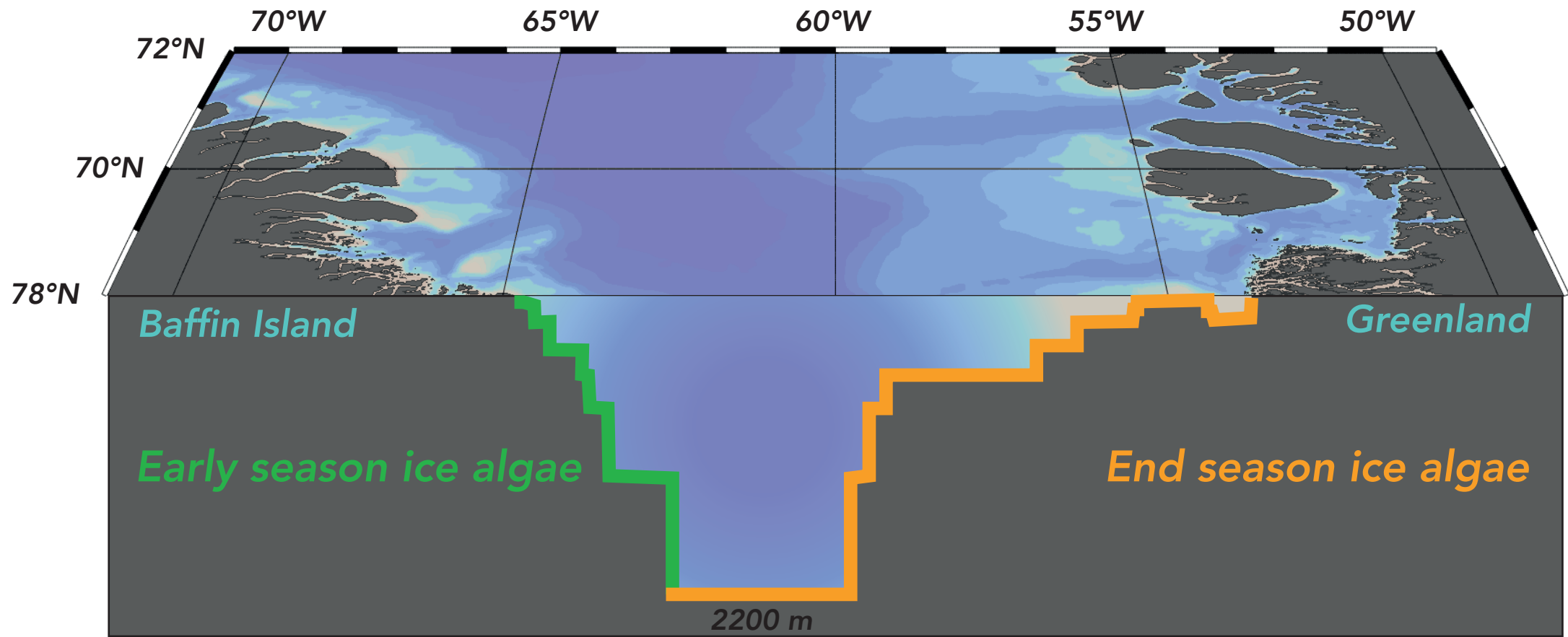
Sediments and sinking particles from central and eastern Baffin Bay were analyzed

Ice algae released at the end of the ice melt strongly dominate these sediments

Highly photooxidized ice algae and bacteria sink in the water column in early July

Preservation of ice algal material is well correlated with bacteria oxidation state

Hydroperoxides and FFAs prevent ice algae colonization by benthic bacteria



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23 8 Rontani Jean-François^{a*}, Lalande Catherine^b, Laure Vilgrain^{c,d}, Vaultier
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Abstract. Monounsaturated fatty acids and their oxidation products were quantified in surficial sediments (0–1 cm) dominated by sympagic (ice-associated) material released at the end of the ice melt collected in summer in central and eastern Baffin Bay during the 2016 GreenEdge campaign. Sympagic algae preservation towards bacterial mineralization was monitored based on intact and oxidized C_{16:1ω7} (palmitoleic) acid, and oxidation products of C_{18:1ω7} (vaccenic) and C_{16:1ω5} acids provided insights on the photooxidative and autoxidative alterations of bacteria present in these sediment samples. Preservation of sympagic algal material appeared to be highest at the stations that were relatively unaffected by copepod grazing and that contained strongly autoxidized (and thus inactive) bacteria. Analysis of sinking particles collected with a drifting trap showed an intense flux of highly photooxidized ice algae in early July that was dominated by *Navicula* spp. and associated with bacteria that had also been strongly altered by photooxidative processes. It is proposed that subsequent homolytic decomposition of the hydroperoxides resulting from this intense photooxidation may have driven the strong autoxidation of sympagic algae and bacteria observed in the sediments. The lack of colonization of sympagic material by active benthic bacteria observed at some of the stations investigated was attributed to its high content in deleterious autoxidative hydroperoxides and free fatty acids (reaching for example 107% and 22% of residual palmitoleic acid, respectively, at station 605).

Key words: Central and Eastern Baffin Bay; Surficial sediments; Sinking particles; MUFA oxidation products; Sympagic algae preservation; Bacteria oxidation.

48 1. Introduction

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3 49 In the Arctic Ocean, primary production is mainly supported by pelagic phytoplankton,
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5 50 sympagic algae generally dominated by pennate diatoms growing in the bottommost
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7 51 centimetres of the sea ice (Poulin et al., 2011; Hop et al., 2020) and epiphytic centric diatoms
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9 52 (mainly *Melosira arctica*) anchored to ice floes (Gosselin et al., 1997; Boetius et al., 2013).
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12 53 Global warming is expected to have dramatic consequences in terms of timing, magnitude, and
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14 54 spatial distribution of both ice-associated and pelagic primary production (Kohlbach et al.,
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16 55 2016). Sympagic and epiphytic ice algae are released into the under-ice environment during the
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18 56 spring ice melt, prior to the pelagic phytoplankton bloom (Fortier et al., 2002; Gradinger, 2009;
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20 57 Leu et al., 2015). Ice-algal production tends to be of lower magnitude than pelagic production
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22 58 (Leu et al., 2011), but ice algae are nevertheless generally assumed to be a major source of
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24 59 organic matter reaching the seafloor (Boetius et al., 2013; Amiraux et al., 2017; Lalande et al.,
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26 60 2019; Yunda-Guarin et al., 2020). This large contribution to the carbon sink results from: (i)
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28 61 strong aggregation of these organisms due to their production of high concentrations of
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30 62 extracellular polymeric substances (EPSs) that shield the biogenic silica of diatom frustules
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32 63 against dissolution (Moriceau et al., 2007) and induce rapid settling in the water column
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34 64 (Riebesell et al., 1991), (ii) a mismatch between zooplanktonic grazing and sympagic algal
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36 65 fluxes (Nadaï et al., 2021), and (iii) the poor physiological state of their associated bacterial
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38 66 communities (Amiraux et al., 2017; Amiraux et al., 2020).
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47 67 Sympagic bacteria are strongly damaged by osmotic stress in hypersaline brine channels
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49 68 during the early stages of ice melt (Amiraux et al., 2017) and by bactericidal free fatty acids
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51 69 (FFAs; mainly palmitoleic acid) released by sympagic algae in response to light stress later in
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53 70 the season (Amiraux et al., 2020). Recently, it was observed that this light stress also favours
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55 71 the transfer of singlet oxygen ($^1\text{O}_2$) from senescent sympagic algae to their attached bacteria,
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57 72 inducing oxidative alterations in these organisms (Burot, 2022). This combination of stresses
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73 means that a significant fraction of the bacteria associated to the sympagic algae released in the
74 water column during ice melt is either dead or non-growing (inactive) (Amiriaux et al., 2020;
75 Burot et al., 2021).

76 Recently, the detection of high proportions of *trans* vaccenic acid produced by bacterial
77 *cis-trans* isomerase (CTI) under hypersaline conditions (Guckert et al., 1986; Heipieper et al.,
78 2003) in surface sediments of the Beaufort Sea and northern and western Baffin Bay confirmed
79 that ice algal material released during the early stages of ice melt is a major contributor to these
80 sediments (Amiriaux et al., 2021). The surprising lack of colonization of this material by
81 healthy-state pelagic or benthic bacteria was attributed to its high content of bactericidal-free
82 palmitoleic acid attested by the presence of 10*S*-hydroxyhexadec-8(*trans*)-enoic acid resulting
83 from 10*S*-DOX bacterial detoxification (Martínez et al., 2010; Rontani and Belt, 2020). The
84 fact that sediments of central and eastern Baffin Bay lack CTI activity (Amiriaux et al., 2021)
85 despite being mainly composed of sympagic material (Yunda-Guarin et al., 2020) suggests a
86 strong contribution of ice algae released at the end of ice melt to these sediments, and thus a
87 different timing of sedimentation than in the Beaufort Sea and northern and western Baffin Bay.

88 Here we analyzed surface sediments (0–1 cm) collected at nine stations in central and
89 eastern Baffin Bay during the 2016 GreenEdge campaign (Fig. 1) in order to determine which
90 factors—mismatch between zooplanktonic grazing and ice algae flux, presence of bactericidal
91 free fatty acids, or bacterial oxidative stress—are responsible for the preservation of the
92 sympagic material in this region. The algae and lipid contents of sinking particles collected with
93 a drifting sediment trap anchored to an ice floe during the same campaign were also analyzed
94 to support the findings.

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96 2. Experimental

97 2.1. Sampling

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3 98 Sediment samples were collected using an USNEL box corer (50×50×40 cm) on board
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5 99 the CCGS Amundsen from June to July 2016 as part of the GreenEdge campaign (Fig. 1). From
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7
8 100 each box core, 3–5 g of intact sediment (0–1 cm) was collected and immediately frozen at -80
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10 101 °C for later analysis.

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13 102 A time-series sediment trap (Technicap PPS4, France; 12 sampling cups) anchored to an
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16 103 ice floe at 25 m under the ice collected sinking particles from 15 June to 9 July 2016. The
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18 104 sediment trap named ‘Crosby’ was deployed at 68.597°N, 59.936°W on June 14 and recovered
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21 105 at 67.769°N, 59.134°W on July 11, 2016 (Fig. 1). Drift was tracked using two ARGOS beacons
22
23 106 attached to a mast connected to the line holding the sediment trap. The irregular signal
24
25 107 emissions of the ARGOS beacons prevented continuous monitoring of sediment trap position.
26
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28 108 Prior to deployment, the sediment trap collection cups were filled with filtered seawater
29
30 109 adjusted to a salinity of 38 with NaCl and 4% formalin to preserve samples during deployment
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33 110 and after recovery. The carousel holding the sampling cups was programmed to rotate every
34
35 111 two days.

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38 112 The sediment trap sample cups were gently shaken before taking subsamples with a
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41 113 modified micropipette to collect large particles for measurements of chlorophyll *a* (Chl *a*) and
42
43 114 algal cells. Subsamples for Chl *a* measurements were filtered onto 0.7-µm pore-size GF/F
44
45 115 filters, extracted in acetone for 24 h at -20 °C, and measured on a Turner Design fluorometer
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48 116 (Welschmeyer, 1994). For the enumeration of algal cells, subsample volumes were adjusted to
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50
51 117 3 mL with filtered seawater before being placed in an Utermöhl chamber. A minimum of 300
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53 118 algal cells were counted and identified by inverted microscopy at 100×, 200× or 400× depending
54
55 119 on cell size according to the Utermöhl method (Utermöhl, 1931). Subsamples for lipid analysis
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58 120 were filtered through pre-weighed Whatman GF/F filters (0.7-µm pore-size, 25 or 47-mm
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60 121 diameter, pre-combusted for 4 h at 450 °C) and kept frozen (< -20 °C) prior to analysis.

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3 123 *2.2. Lipid analysis*

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9 125 *2.2.1. Lipid extraction*

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12 126 Samples aliquoted samples of sediments and GF/F filters carrying sinking particles were

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14 127 reduced with excess NaBH₄ after addition of MeOH (25 mL; 30 min) to reduce labile

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16 128 hydroperoxides to alcohols, making them more amenable to gas chromatography-mass

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18 129 spectrometry (GC-MS) analysis. Water (25 mL) and KOH (2.8 g) were then added and the

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20 130 resulting mixture was saponified by refluxing (2 h). After cooling, the mixture was acidified

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22 131 (HCl, 2 N) to pH 1 and extracted with dichloromethane (DCM, 3 × 20 mL). The DCM extracts

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24 132 were combined and concentrated by rotary evaporation at 40 °C to give total lipid extracts

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26 133 (TLEs). Highly-branched isoprenoids (HBI) quantification in ‘Crosby’-trap sinking particulate

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28 134 samples required further separation of the TLEs, which were therefore fractionated using

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30 135 column chromatography (silica; Kieselgel 60, 8 × 0.5 cm). HBI alkenes were obtained by

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32 136 elution with hexane (10 mL).

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35 137 The relative proportions of hydroperoxides and their ketonic and alcoholic degradation

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37 138 products in sediments collected at stations 403 and 605 were estimated via a different process

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39 139 (Rontani et al., 2018) based on ultrasonic extraction of lipids with chloroform-MeOH-water

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41 140 (1:2:0.8, v/v/v), separation of the supernatant by centrifugation at 3500 g, evaporation to

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43 141 dryness, and division of the residue into two equal parts. The first sub-sample was acetylated

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45 142 in acetic anhydride-pyridine (1:2, v/v) overnight to convert hydroperoxides to the

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47 143 corresponding ketones (Mihara and Tateba, 1986), then evaporated to dryness and saponified.

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49 144 The second sub-sample was evaporated to dryness, reduced with NaBD₄, and saponified.

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145 Quantification of FFAs was carried out on lipid fractions resulting from ultrasonic
146 extraction (as described above) of the sediment samples.

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148 2.2.2. *Derivatization*

149 TLEs were silylated by dissolving them in 300 μ L of a mixture of pyridine and BSTFA
150 (Supelco; 2:1, v/v) and heating to 50 $^{\circ}$ C for 1 h. After evaporation to dryness under a stream of
151 N_2 , the derivatized residue was dissolved in a mixture of hexane and BSTFA (to avoid
152 desilylation) and analyzed by gas chromatography–tandem mass spectrometry (GC-MS/MS)
153 and gas chromatography–EI quadrupole time-of-flight mass spectrometry (GC-QTOF).

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155 2.2.3. *Gas chromatography–tandem mass spectrometry*

156 GC-MS/MS analyses were performed using an Agilent 7890A/7000A tandem quadrupole
157 gas chromatograph system (Agilent Technologies, Courtaboeuf, Les Ulis, France) with a cross-
158 linked 5% phenyl-methylpolysiloxane capillary column (Agilent; HP-5MS, 30 m \times 0.25 mm,
159 film thickness 0.25 μ m). Analyses were performed with an injector operating in pulsed splitless
160 mode set at 270 $^{\circ}$ C, and oven temperature was ramped from 70 $^{\circ}$ C to 130 $^{\circ}$ C at 20 $^{\circ}$ C min^{-1} ,
161 then to 250 $^{\circ}$ C at 5 $^{\circ}$ C min^{-1} and finally to 300 $^{\circ}$ C at 3 $^{\circ}$ C min^{-1} . Pressure of the carrier gas (He)
162 was held at 0.69×10^5 Pa until the end of the temperature program and then ramped from 0.69
163 $\times 10^5$ Pa to 1.49×10^5 Pa at 0.04×10^5 Pa min^{-1} . The mass spectrometry conditions were:
164 electron energy, 70 eV; source temperature, 230 $^{\circ}$ C; quadrupole 1 temperature, 150 $^{\circ}$ C;
165 quadrupole 2 temperature, 150 $^{\circ}$ C; collision gas (N_2) flow, 1.5 mL min^{-1} ; quench gas (He) flow,
166 2.25 mL min^{-1} ; mass range, 50–700 Daltons; cycle time, 313 ms. Oxidation products of
167 monounsaturated fatty acids (MUFAs) were assigned by comparing retention times and mass
168 spectra against standards (see section 2.2.5). Quantification was carried out with external

169 standards in multiple reaction monitoring (MRM) mode. Precursor ions were selected from the
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2 170 more intense ions (and specific fragmentations) observed in electron ionization (EI) mass
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5 171 spectra.

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11 173 *2.2.4. Gas chromatography–EI quadrupole time-of-flight mass spectrometry*

14 174 Accurate mass measurements were made in full scan mode using an Agilent 7890B/7200
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17 175 GC/QTOF system (Agilent Technologies, Courtaboeuf, Les Ulis, France) with a cross-linked
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19 176 5% phenyl-methylpolysiloxane (Agilent Technologies; HP-5MS Ultra inert, 30 m × 0.25 mm,
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22 177 0.25 µm film thickness) capillary column. Analyses were performed with an injector operating
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25 178 in pulsed splitless mode set at 270 °C. Oven temperature was ramped from 70 °C to 130 °C at
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27 179 20 °C min⁻¹ and then to 300 °C at 5 °C min⁻¹. Pressure of the carrier gas (He) was maintained
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30 180 at 0.69 × 10⁵ Pa until the end of the temperature program. Instrument temperatures were 300
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32 181 °C for the transfer line and 230 °C for the ion source. Nitrogen (1.5 mL min⁻¹) was used as
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34 182 collision gas. Accurate mass spectra were recorded across the range *m/z* 50–700 at 4 GHz with
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37 183 the collision gas opened. The QTOF-MS instrument provided a typical resolution ranging from
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39 184 8009 to 12252 from *m/z* 68.9955 to 501.9706. Perfluorotributylamine (PFTBA) was used for
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42 185 daily MS calibration. Compounds were identified by comparing their TOF mass spectra,
43
44 186 accurate masses and retention times against standards (see section 2.2.5).

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50 188 *2.2.5. Standard compounds*

53 189 Hexadec-9(*cis*)-enoic (palmitoleic) and octadec-11(*cis*)-enoic (vaccenic) acids were
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56 190 purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Hexadec-11(*cis*)-enoic acid
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59 191 was purchased from Alpha chemistry (New York, USA). Autoxidation products of these

192 MUFAs were produced by Fe²⁺/ascorbate-induced oxidation (Loidl-Stahlhofen et al., 1994).
193 Subsequent reduction of the resulting isomeric hydroperoxyacids in methanol with excess
194 NaBH₄ afforded the corresponding hydroxyacids.

196 2.2.6. Estimation of autoxidative, photooxidative and 10S-DOX degradation of MUFAs

197 Photo- and autoxidation of MUFAs yields mixtures of isomeric allylic hydroperoxyacids
198 (Frankel, 1998), which are converted to the corresponding hydroxyacids after NaBH₄ reduction.
199 The relative importance of photooxidation and autoxidation of these compounds can be readily
200 calculated based on proportion of *cis* isomers (which are produced specifically by autoxidation;
201 Porter et al., 1995) and temperature of the seawater (Frankel, 1998; Marchand and Rontani,
202 2001). The role played by 10S-DOX activity in the degradation of palmitoleic acid was
203 estimated based on the difference between (10-*trans* + 8-*trans*) and (9-*trans* + 11-*trans*)
204 hydroxyacids as previously described (Galeron et al., 2018; Rontani et al., 2018).

206 2.3. Copepod concentration and activity measurement

207 During short and intense pulse of algal production in Arctic spring blooms, copepods,
208 especially *Calanus* spp. herbivores, feed on sympagic and pelagic algae in order to fuel eggs
209 production and build lipid stocks to survive the next winter in diapause (Daase et al., 2021). To
210 have a proxy of the potential grazing pressure on sympagic material, we calculated the
211 concentration of copepods (especially *Calanus* spp.) and their feeding activities. To have more
212 robust interpretations, we both used data from *in situ* quantitative imaging of zooplankton and
213 microscope counts after zooplankton net sampling.

214 During the GreenEdge cruise, the 5HD Underwater Vision Profiler (UVP5, a quantitative
215 imaging system for plankton and particles, Picheral et al. 2010) was deployed at more than 150

216 stations across the ice edge (Fig. 2A, grey points). UVP5 data are useful to obtain *in situ*
217 copepod concentrations and look at individual morphologies on the images (see detailed
218 methodology in Vilgrain et al. 2021). Vertical tows with a 200- μm mesh were performed at 20
219 of these stations to sample and count zooplankton under the microscope (Fig. 2A, small black
220 dots).

221 To make the two types of data comparable and focus on *Calanus* species, we calculated
222 copepod concentrations from nets integrated by square meter over the whole water column, but
223 only for *Calanus* species that are presumably found within a surface layer during the spring
224 bloom. The UVP data does not have the image resolution power needed to select a given
225 species, but we integrated copepod concentrations by cubic metre only from a surface layer
226 (80 m). As we know that the device images only capture large copepods ($>700 \mu\text{m}$), it will be
227 mostly *Calanus* species that get counted within this depth range.

228 Copepod concentrations computed from the UVP may be underestimated because the
229 device only sees large individuals ($> 700 \mu\text{m}$) in small volumes (1 L every 5 cm on average).
230 However, as recently demonstrated, concentrations calculated from UVP data are reliable if
231 integrated over a large part of the water column (Barth & Stone, 2022). Indeed, relative
232 comparison between copepod concentrations from nets and UVP are consistent in our dataset
233 (see Fig. 2B and 2D). Net data are scarce, especially for stations with OWD close to 0, which
234 makes it useful and instructive to compare stations using the numerous UVP casts. Note that it
235 was not possible to calculate copepod concentrations at station 600 with the UVP5 due to a
236 technical issue, and that no net sampling was performed at station 713. Furthermore, several
237 (up to three) CTD-UVP casts were done per station at different hours of the day.

238 Finally, we used a feeding activity indicator for the surface copepod community,
239 computed from individual position on images in Vilgrain et al. (2021). This indicator is
240 calculated by the fourth axis of a PCA in which copepods are positioned according to

241 morphological characteristics. PC4 values represent the complexity of the perimeter of an
242 object and thus the visibility of copepod appendages, supposed to be more important if they are
243 actively feeding. Over hundreds of images by casts, the average PC4 value for a subpart of the
244 community will be high if many of individuals have their appendages spread out, indicating the
245 activity of this community (see Vilgrain et al. 2021 for the detailed methodology).

247 *2.4 Statistical analysis*

248 As the variables investigated are non-parametric, Spearman correlations were performed
249 to determine the correlation between concentration of palmitoleic acid and its oxidation
250 products and (i) percent autoxidation of vaccenic acid, (ii) percent autoxidation of C_{16:1 ω 5} acid,
251 and (iii) primary production (Chl *a*) in the euphotic layer from Lafond et al. (2019).

253 **3. Results and discussion**

255 *3.1. Surface sediment samples*

256 Yunda-Guarin et al. (2020) previously used the sympagic carbon (%), an HBI-based
257 index (Brown et al., 2014, 2018; Brown and Belt, 2017) to estimate the relative contribution of
258 both sympagic and pelagic carbon in sediments collected during the 2016 GreenEdge campaign,
259 and found that the contribution of sympagic carbon was >89% at all the stations investigated
260 here, except for station 418 where its contribution was only 60%. We can thus consider that
261 most of the organic carbon present in the sediments analyzed arises from sea ice algae.

262 The main MUFAs present in the different sediment samples analyzed were C_{16:1 ω 7}
263 (palmitoleic), C_{16:1 ω 5}, C_{18:1 ω 9} (oleic) and C_{18:1 ω 7} (vaccenic) acids. Palmitoleic acid is found in

264 several bacteria (De Carvalho and Caramujo, 2014), but it is also the major fatty acid found in
1
2 265 diatoms (Volkman et al., 1989; Fahl and Kattner, 1993; Leu et al., 2010). Because of the
3
4 266 dominance of diatom biomass (compared to bacteria) in the Arctic, this MUFA is generally
5
6
7 267 considered as a robust marker of primary producers in this region (Marmillot et al., 2020).
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9
10 268 Vaccenic and C_{16:1 ω 5} acids are well-known bacterial fatty acids (Lambert and Moss, 1983;
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12 269 Guezennec and Fiala-Medioni, 1996; Blumenberg et al., 2005). If C_{16:1 ω 5} acid is also present in
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14 270 some fungi (Ngosong et al., 2012), the lack of ergosterol (a well-known fungal sterol, Newell
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16
17 271 et al., 1988) observed in all the sediment samples analyzed here, allowed to exclude these
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20 272 organisms as potential sources of this MUFA. In contrast, oleic acid is the most widely-
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22 273 distributed fatty acid in nature and is present in numerous marine organisms, including
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24 274 omnivorous and carnivorous zooplankton species, bacteria, phytoplankton and cyanobacteria
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27 275 (Harwood and Russel, 1984; Lee et al., 2006; Leyton et al., 2011). Oleic acid was therefore
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29 276 ruled out in this study due to its lack of specificity. Although MUFAs are less reactive to
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32 277 photooxidation and autoxidation processes than their polyunsaturated counterparts (Frankel,
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34 278 1998), their oxidation products are sufficiently stable and specific to be used as tracers of these
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37 279 processes in the marine environment (Rontani, 2021). In order to monitor the preservation and
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39 280 oxidative alteration of sympagic material and its attached bacteria, we quantified palmitoleic,
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42 281 vaccenic and C_{16:1 ω 5} acids and their oxidation products in the different sediment samples.

44 282 Concentrations of residual palmitoleic acid and its oxidation products were highly
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46 283 variable (sum ranging from 1.5 $\mu\text{g g}^{-1}$ at station 403 to 86.5 $\mu\text{g g}^{-1}$ at station 707), and sympagic
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49 284 material was clearly present in highest amounts at the stations 409, 605 and 707 (Table 1, Fig.
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51 285 3A). This variability could be attributed to differences in primary production at these different
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54 286 stations. However, the correlation between concentrations of palmitoleic acid and its oxidation
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56 287 products in sediments and primary production (Chl *a*) measured during the GreenEdge
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59 288 campaign in the corresponding euphotic layers (Lafond et al., 2019) was not significant

289 (Spearman's $p > 0.05$). The observed differences in preservation are thus probably the result of
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2 290 copepod grazing and bacterial mineralization efficiency.
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5 291 Oxidative degradation of sympagic algae was also highly variable (ranging from 3.8% at
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7 292 station 713 to 92.5% at station 409) (Fig. 3B), and involved both abiotic (photooxidation,
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9 autoxidation) and biotic (10S-DOX oxidation) processes. Interestingly, the less mineralized
10 293 sympagic material samples were also the most oxidized samples (Fig. 3). 10S-DOX
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12 294 (dioxygenase) activity was previously attributed to a detoxification strategy allowing bacteria
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14 295 associated to sympagic diatoms to survive the production of bactericidal FFAs by these algae
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16 296 during the later stages of ice melt (Amiriaux et al., 2020). The proportions of free palmitoleic
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18 297 acid measured at stations 403 and 605 (6.4% and 22.0% of total acid, respectively; Table 2) that
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20 298 presented contrasting 10S-DOX activities (Table 1) confirmed this assumption. Bactericidal
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22 299 FFAs (mainly palmitoleic acid) are released by sympagic algae during the later stages of ice
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24 300 melt under the effect of light stress (Amiriaux et al., 2020). The high proportions of these
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26 301 compounds observed here suggest a significant contribution of sympagic algae released at the
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28 302 end of ice melt to the sediments investigated. This assumption is well supported by the lack of
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30 303 bacterial CTI activity (resulting from osmotic stress in hypersaline brines during the early stages
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32 304 of ice melt; Amiriaux et al., 2017) in these sediments (Amiriaux et al., 2021).
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41 306 The bacterial vaccenic and C_{16:1 ω 5} acids appeared to be only weakly affected by
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43 307 photooxidation processes (Table 1, Fig. 4), with percent photooxidation values ranging from
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45 308 0.0 to 4.2% and 0.0 to 11.1%, respectively. In contrast, their autoxidation percentages were
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47 309 highly variable (Table 1, Fig. 4), ranging from 0.0 to 75.9% for vaccenic acid and from 0.0 to
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49 310 67.8% for C_{16:1 ω 5} acid. Note that the percentages of bacterial fatty acid autoxidation were
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51 311 highest at stations 409, 605 and 707 (Fig. 4) where the preservation of sympagic algal organic
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53 312 carbon was also highest (Fig. 3A). The good correlation between concentration of palmitoleic
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55 313 acid and its oxidation products and percent autoxidation of vaccenic and C_{16:1 ω 5} acids
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2 314 (Spearman's rho of 0.96 and 0.80, respectively; $p < 0.05$) confirmed that the preservation of
3 315 sympagic algal material increases exponentially with autoxidation state of the attached bacteria.

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5 316 Interestingly, at stations presenting the highest contents of ice algal material, the profiles
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7 317 of allylic hydroxyacids resulting from the oxidation of algal and bacterial MUFAs and
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9 318 subsequent NaBH₄ reduction of the corresponding hydroperoxyacids showed a dominance of
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11 319 *cis* isomers (Fig. 5A). Autoxidation of MUFAs starts by the abstraction of an allylic hydrogen
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13 320 atom. In the case of palmitoleic or vaccenic acid, this attack affords radicals at positions 10 and
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15 321 13, which then react with molecular oxygen to produce the corresponding *cis* hydroperoxyl
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17 322 radicals (Fig. 6). These radicals can then either abstract a hydrogen atom from another molecule
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19 323 to produce *cis* allylic hydroperoxides or undergo allylic rearrangements affording *trans* isomers
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21 324 (Porter et al., 1995) (Fig. 6). The presence of good hydrogen atom donors thus favours the
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23 325 formation of *cis* isomers instead of *trans* ones. The strong dominance of *cis* isomers observed
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25 326 at stations 409, 605 and 707 (Fig. 5A) was thus attributed to the presence of high amounts of
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27 327 hydroperoxides, which are excellent hydrogen atom donors (Porter et al., 1995). NaBH₄
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29 328 reduction (carried out in order to avoid thermal breakdown of hydroperoxides during the
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31 329 treatment) reduces hydroperoxy and keto groups to the corresponding hydroxyl groups. The
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33 330 sum of hydroperoxyacids, ketoacids and hydroxyacids is thus quantified in the form of
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35 331 hydroxyacids. In order to confirm the presence of hydroperoxyacids in these samples, we
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37 332 applied a different treatment (see section 2.2) to sediments from two stations contrastingly
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39 333 affected by autoxidation processes, i.e. station 403 (weakly affected) and station 605 (strongly
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41 334 affected). Comparison of the amounts of hydroxyacids present after acetylation and NaBD₄
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43 335 reduction then made it possible to estimate the amount of hydroperoxyacids and hydroxyacids
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45 336 present in the samples, and deuterium labelling (via NaBD₄ reduction) enabled us to estimate
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47 337 the proportion of ketoacids (Rontani et al., 2012). The results obtained (Table 3) clearly showed
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49 338 that hydroperoxyacids accounted for a substantial share of the palmitoleic acid and its oxidation
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339 products at the stations strongly affected by autoxidation ($\approx 30\%$ at station 605). Note that
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2 340 hydroperoxyacids also accounted for a substantial share of vaccenic acid oxidation products at
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4 341 this same station (Table 3). Deleterious hydroperoxides are thus present in significant
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7 342 proportions not only in sympagic algal material but also in its associated bacteria in some
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9 343 sediments of central and eastern Baffin Bay.

14 345 *3.2. Impact of copepod grazing on the preservation of sympagic material*

17 346 We posited that sympagic material would be better preserved if (i) herbivorous
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20 347 copepods (*Calanus spp.*) were in low numbers and if (ii) the feeding activity of the surface
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22 348 copepods is low. On Figure 2, the 9 stations of interest are labelled and coloured in yellow,
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25 349 orange and red according to their transect. The objective was to compare stations with high
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27 350 sympagic material preservation (409, 605 and 707) against stations with low sympagic material
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29 351 preservation (403, 418, 600, 615, 719 and 713). Copepod concentrations and activities are also
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32 352 shown for all other stations sampled for zooplankton (grey points) in order to see whether the
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34 353 9 stations of interest are effectively representative (Fig. 2A). Figures 2B and 2D plot copepod
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37 354 numbers according to open water days (OWD), a variable that represents the number of days a
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39 355 location has been free of ice (positive values) or conversely the number of days until the location
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42 356 thaws (negative values) (Randelhoff et al. 2019). Finally, Figure 6C presents a feeding activity
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44 357 index for the surface copepod community by station, inferred from copepod position on images
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47 358 (see section 2.8).

49 359 Figures 2B and 2D show that copepod concentrations were low and homogenous before
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51 360 ice melt ($\text{OWD} < -10$), and that two clouds of points emerged after the start of ice melt. One
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54 361 group of stations contains high copepod numbers ($> 10 \text{ individuals.m}^{-3}$) and the other has much
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56 362 lower concentrations ($< 10 \text{ individuals.m}^{-3}$). Copepod concentrations were relatively low and
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59 363 homogenous in all stations sampled for sediment analyses except for the ice-free station 418

364 (Fig. 2B and 2D). Station 409 presented copepod concentrations typical of stations with
365 negative OWD. Stations 605 and 707 had low copepod concentrations despite the beginning of
366 ice melt. Copepods distribution is known to be patchy (as demonstrated for *Calanus*
367 *finmarchicus*, Basedow et al., 2019). This pattern could reflect the good conditions that
368 individuals may find in some specific stations (few predators, high algae growth), or could be
369 simply a consequence of a random transport by currents. Another hypothesis is that copepods
370 regroup in swarms as a predator avoidance strategy (Basedow et al., 2019), but such behaviour
371 has still to be proven.

372 Community feeding activities (Fig. 2C) varied widely among the stations of interest.
373 Feeding activity index at station 409 was again typical of other ice-covered stations, whereas
374 feeding activity index in stations 615 and 707 was particularly low (below the first quartile),
375 especially compared to other stations from the ‘transition zone’ at the ice edge. Feeding activity
376 was consistently low in the 3 CTD-UVP casts in stations 605 and 707, which means that feeding
377 activity appears to be weak in those stations whatever the time of the day, which was not the
378 case for other stations (e.g. stations 403 or 418).

379 Given that between-station variations in copepod abundance were very low and
380 decoupled from material preservation in the 9 stations of interest, we can conclude that copepod
381 abundance is not a ‘game-changer’ for sympagic material preservation. However, copepod
382 concentrations in stations 605 and 707 were still really low and their communities also showed
383 low feeding activity despite the beginning of ice melt and resulting ice-algae release in the water
384 column. It thus appears that copepod grazing pressure was limited in stations 605 and 707 and
385 may thus have helped preserve—or at least not eroded—the sympagic material.

387 3.3. Sinking particles

388 The strong autoxidation of sympagic algae and their attached bacteria observed in some
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2 389 of the sediments investigated likely results from the decomposition (homolytic cleavage) of
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4 390 hydroperoxides photochemically produced in ice or the water column (Girotti, 1998; Rontani,
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6 391 2021). To confirm this hypothesis, we examined the lipid content of a time-series of sinking
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8 392 particulate material collected at 25 m by the ‘Crosby’ drifting sediment trap (Fig. 1). Diatom
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10 393 and Chl *a* fluxes (Fig. 7) were very high from 5 to 7 July, suggesting the presence of large
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12 394 amounts of algae sinking during this sampling period. The H-print % (pelagic HBI III /
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14 395 (sympagic IP₂₅ and IPSO₂₅ + pelagic HBI III) × 100) (Brown et al., 2014; Brown and Belt,
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16 396 2017) measured in the hydrocarbon fraction of this sample was close to 0%, thus confirming
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18 397 the presence of a material strongly dominated by sympagic algae. Algal cells collected from 15
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20 398 June to 9 July indicated a continuous export of ice-associated diatoms during the drift, while
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22 399 the export of a large colony of *Navicula* spp. cells between 5 and 7 July mainly contributed to
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24 400 the elevated diatom and Chl *a* fluxes (Fig. 7).

31 401 MUFAs and their oxidation products in these different samples confirmed the presence
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33 402 of an intense flux of sympagic algae in early July through the prominence of palmitoleic acid
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35 403 concentration during this period (Fig. 8A). The particles exported at that time also exhibited a
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37 404 relatively low vaccenic acid/palmitoleic acid ratio (0.012) compared to all the other samples
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39 405 (vaccenic acid/palmitoleic acid ratio ranging from 0.026 to 0.162), which points to low bacterial
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41 406 colonization. The intense flux of aggregated sympagic algae sinking in the water column in the
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43 407 vicinity of station 409 (Fig. 1) appeared to be strongly affected by type II-photosensitized
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45 408 oxidation processes (Figs. 5B and 8A). The strong photooxidation state of bacteria associated
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47 409 with this algal material (Fig. 8B) explains its relatively weak bacterial colonization. Indeed, it
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49 410 is now well known that singlet oxygen produced in senescent algae (Nelson, 1993) is transferred
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51 411 efficiently to their attached bacteria, inducing oxidative damage in bacterial membranes
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53 412 (Rontani et al., 2003; Petit et al., 2015). It was recently shown that high irradiances strongly
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413 favour photooxidation of bacteria associated to algal cells, notably in the bottommost layer of
414 sea ice (Burot, 2022) where the sympagic algae-bacteria association is maintained at relatively
415 high irradiances (up to 105.9 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ after snow melt; Lund-Hansen et al., 2021)
416 during long periods. Homolytic decomposition of the hydroperoxides resulting from this
417 intense photodegradation can thus drive strong autoxidation of sympagic algae and bacteria
418 observed in sediments of this zone (Girotti, 1998; Rontani, 2021).

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420 *3.4. Considerations surrounding the preservation of ice algae in Arctic sediments*

421 Active benthic bacteria are generally considered as better adapted to the deep-sea
422 environment than surface-derived bacteria (Tamburini et al., 2013). In the Arctic, these benthic
423 bacteria are dominated by members of the *Roseobacter* clade (Rapp et al., 2018), which contain
424 large proportions of vaccenic acid (Kim et al., 2010, 2016; Yang et al., 2014) and quickly
425 colonize the deposited algal aggregates (Rapp et al., 2018). Members of the
426 alphaproteobacterial *Roseobacter* clade, which are well adapted to the utilization of deposited
427 algal detritus (Emil Ruff et al., 2014), probably played an important role in the degradation of
428 the ice algal material at stations 403, 600, 719 and 713 that presented very low palmitoleic acid
429 concentrations and bacteria weakly affected by oxidation (Figs. 2A and 3). On the other hand,
430 the strong oxidation state of bacterial MUFAs (and notably of vaccenic acid) observed at
431 stations 409, 605 and 707 (Fig. 3), likely resulting from a transfer of $^1\text{O}_2$ from senescent ice
432 algae to their attached bacteria and subsequent induction of radical chain oxidation by
433 homolysis of the hydroperoxides thus formed (Fig. 9), points to a lack of colonization of
434 deposited ice algal aggregates by active benthic bacteria. The evidence suggests that this lack
435 of colonization is due to the deleterious properties of hydroperoxides contained in the ice algal
436 material. Note that FFAs excreted by sympagic algae can also induce the death of bacteria by:
437 (i) disrupting the electron transport chain, (ii) uncoupling oxidative phosphorylation, (iii)

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2 438 disrupting membrane enzyme activity and (iv) permeabilizing and disrupting bacterial
3 439 membranes (Jung et al., 2015; Yoon et al., 2018; Pretorius et al., 2021). Furthermore, the
4 440 incorporation of oxidized FFAs in bacterial membranes (Pretorius et al., 2021) can also play a
5 441 role in the induction of autoxidation processes in bacteria (Fig. 9). FFAs and hydroperoxyacids
6 442 present in high proportions at these stations (Tables 2 and 3) therefore appear to have a very
7 443 strong deleterious effect on benthic bacteria and may thus contribute to the preservation of sea
8 444 ice material in Arctic surficial sediments.

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20 446 **4. Conclusion**

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23 447 High amounts of ice algae have been observed in various Arctic sediments (Koch et al.,
24 448 2020; Yunda-Guarin et al., 2020; Amiraux et al., 2021; this work). The timing of the sea ice
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26 449 retreat and the match or mismatch between zooplankton activity and ice algal release appears
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28 450 to dictate the timing of this contribution (Nadaï et al., 2021; Kitamura et al., 2017). The ice
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30 451 algae released at the beginning of the ice melt period thus predominantly contribute to the
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32 452 sediments of the Beaufort Sea and western Baffin Bay (Amiraux et al., 2021), whereas the ice
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34 453 algae released at the end of the ice melt predominantly contribute to the sediments of the
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36 454 Chukchi Sea (Koch et al., 2020) and central and eastern Baffin Bay (this work). The good
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38 455 preservation of ice algal material in Arctic sediments results from: (i) its strong aggregation-
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40 456 enhancing rates of sinking to the seafloor (Riebesell et al., 1991), (ii) the non-growing and/or
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42 457 dead state of its attached bacteria resulting from in-ice osmotic (Amiraux et al., 2017), chemical
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44 458 (Amiraux et al., 2020) and oxidative (Burot, 2022) stresses limiting the efficiency of
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46 459 biodegradation processes, and (iii) its high content of bactericidal compounds (FFAs and
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48 460 hydroperoxides) (Amiraux et al., 2020; This work) that shield against colonization by active
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58 461 pelagic and benthic bacteria.

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687 **FIGURE CAPTIONS**

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6 689 **Figure 1.** Map of the study area showing the location of the sediment stations and the positions
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9 690 of the drifting sediment trap.

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15 692 **Figure 2.** Copepod concentrations and feeding activities from net sampling and *in situ*
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17 693 quantitative imagery. A – Each grey point is a sampling station where the Underwater Vision
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19 694 Profiler 5 (UVP5) was deployed, with point shapes representing ice conditions: ICW = ice-
20 695 covered waters, TZ = transition zone, OW = open waters (defined in Vilgrain et al., 2021). In
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22 696 stations marked with a black dot, net sampling of zooplankton was also performed. The nine
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24 697 stations analysed for sympagic material are colored in yellow, orange and red for transects 400,
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26 698 600 and 700 respectively. The three stations with well-preserved sympagic material in
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28 699 sediments are labelled in bold. B – Integrated concentrations of *Calanus* feeding stages (third
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30 700 stage nauplii to adults) estimated by microscope counts after net sampling, according to Open
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32 701 Water Days (see text). C – Inferred feeding activity estimated from copepod position on images
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34 702 in the three ice conditions. D – Integrated concentrations of copepods in a surface layer (<80
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36 703 m) calculated from UVP images according to Open Water Days.

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48 705 **Figure 3.** (A) Concentrations and (B) relative abundance of C_{16:1ω7} (palmitoleic) acid and its
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50 706 oxidation products at the different sediment stations investigated.

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57 708 **Figure 4.** Map showing the photooxidation and autooxidation percentages of bacterial (A) C_{18:1ω7}
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59 709 (vaccenic) and (B) C_{16:1ω5} acids at the different sediment stations investigated.

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3 711 **Figure 5.** Partial ion chromatograms (m/z 199.1518, 213.1675, 329.1918 and 343.2125)
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5 712 showing (A) the presence of palmitoleic acid autoxidation products in silylated TLE of
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8 713 sediments from station 605 and (B) palmitoleic acid photooxidation products (characterized by
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10 714 the lack of *cis*-oxidation products; Marchand & Rontani, 2001) in sinking particles collected
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13 715 with the ‘Crosby’ drifting sediment trap between 05 and the 07 July 2016.

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19 717 **Figure 6.** Proposed mechanisms for vaccenic acid autoxidation involving hydrogen abstraction
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21 718 at C-13 (Adapted from Porter et al., 1995). Similar mechanisms occur when a hydrogen atom
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24 719 is abstracted at C-10.

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30 721 **Figure 7.** Diatom (histograms) and chlorophyll (dashed line) fluxes during the period of
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32 722 sampling by the Crosby drifting trap.

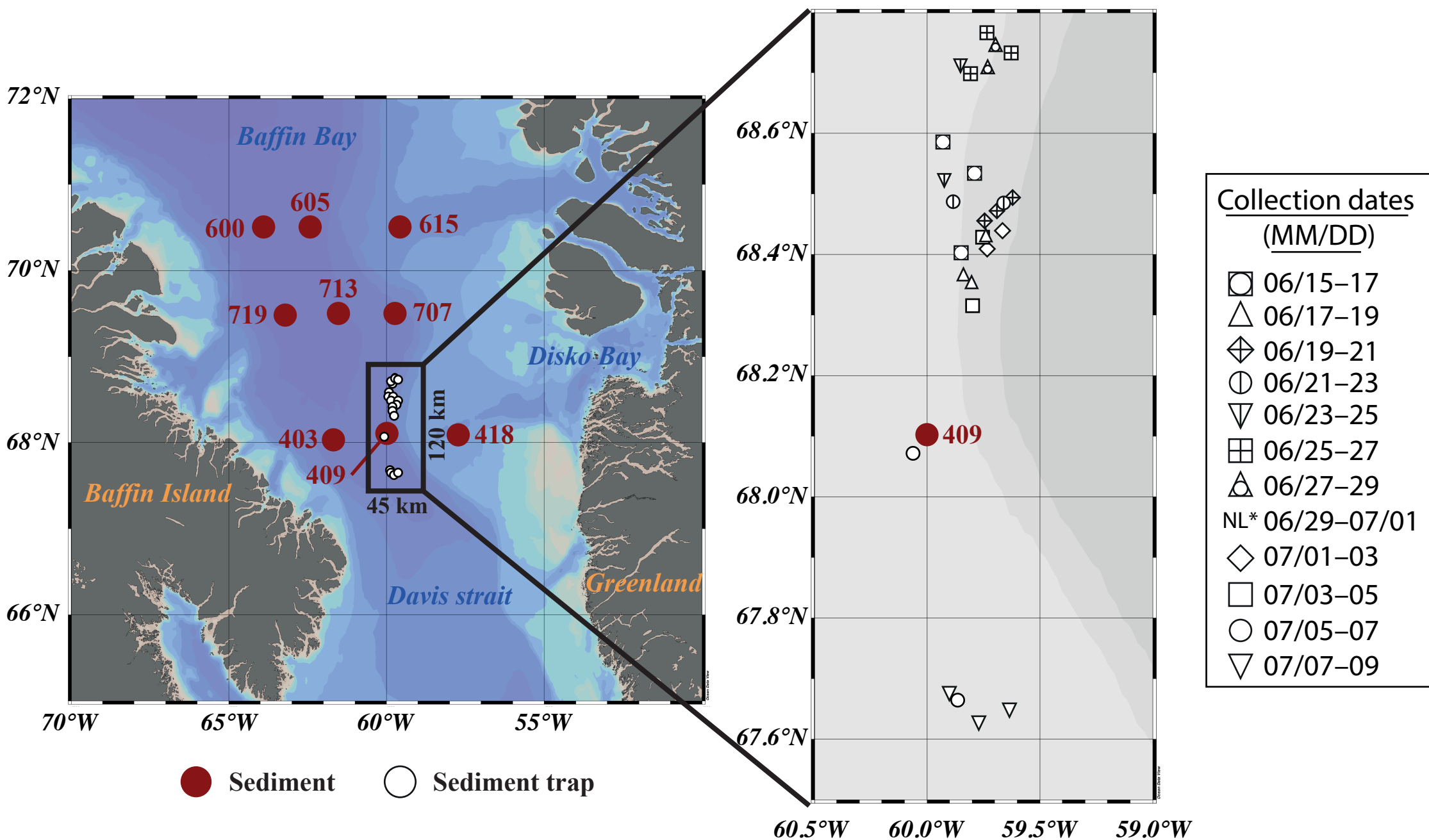
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39 724 **Figure 8.** Fluxes of (A) palmitoleic and (B) vaccenic acids and their oxidation products during
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41 725 the period of sampling by the Crosby drifting trap.

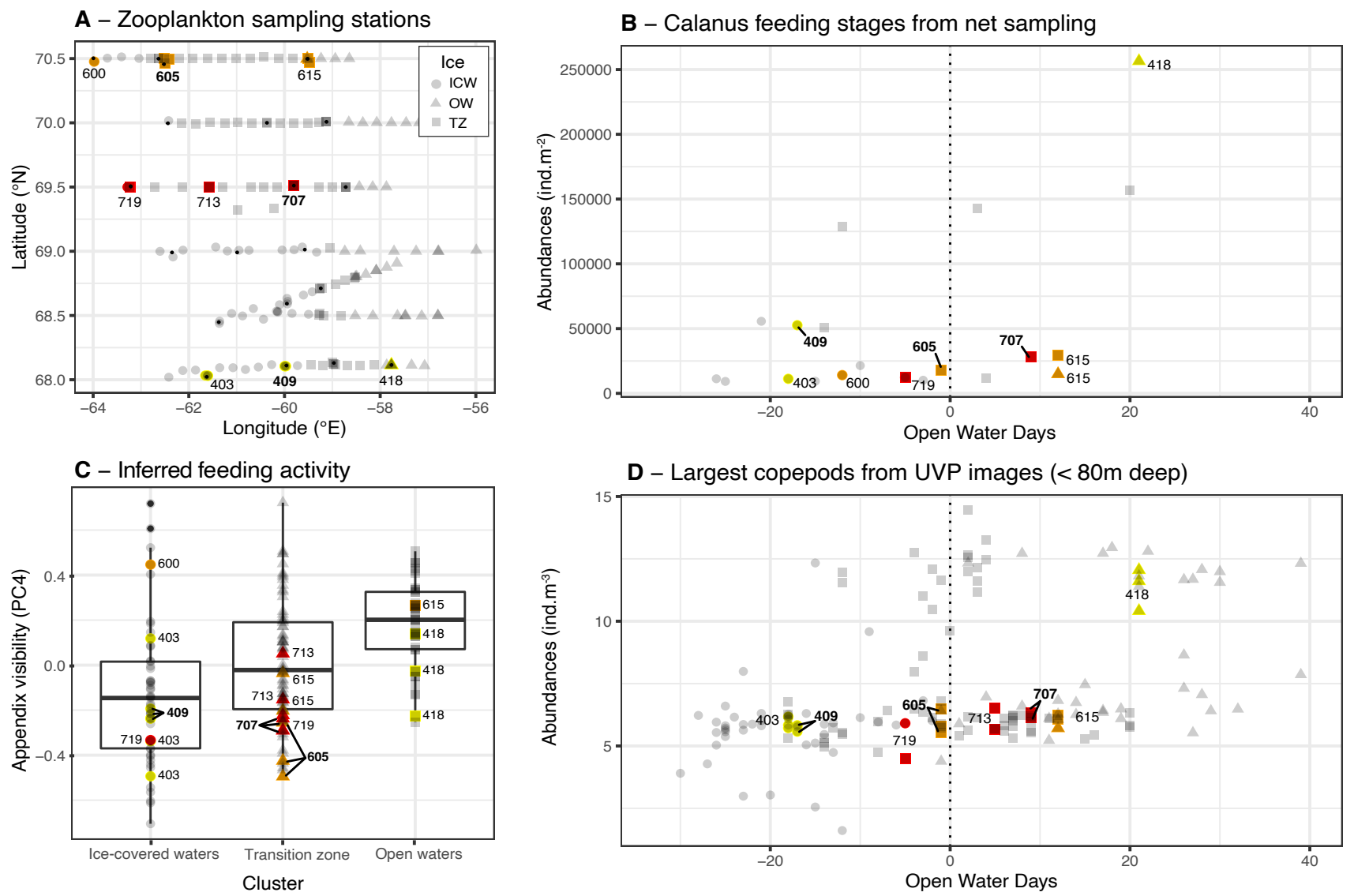
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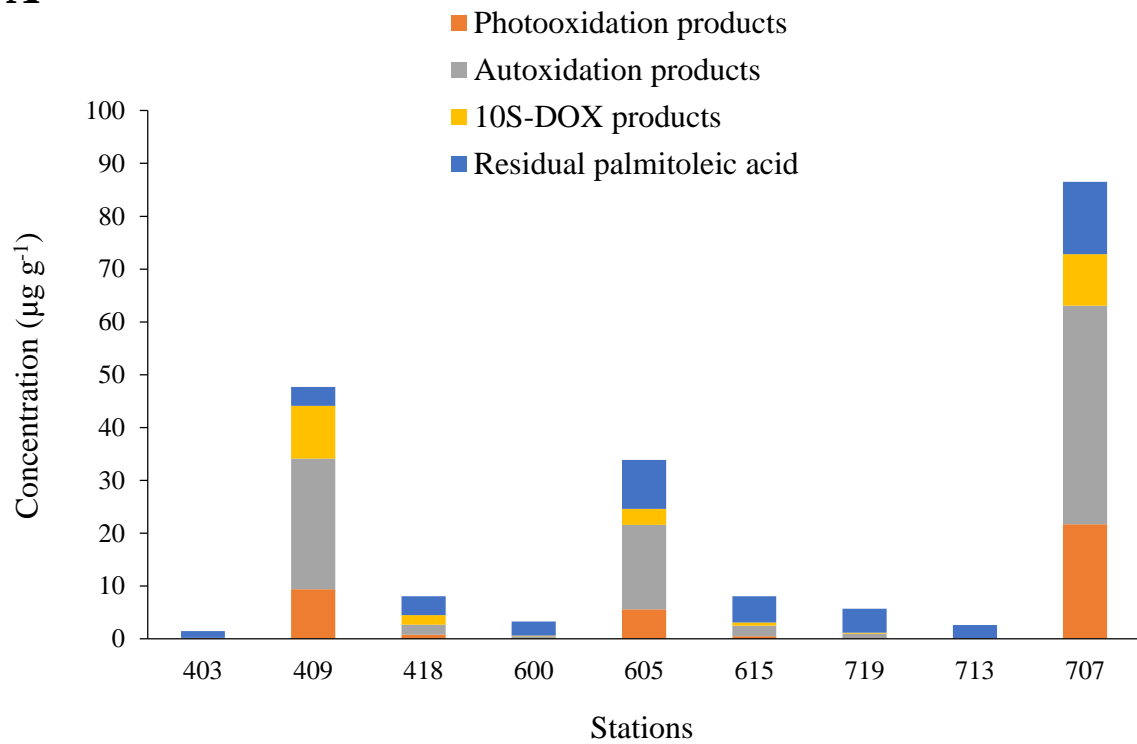
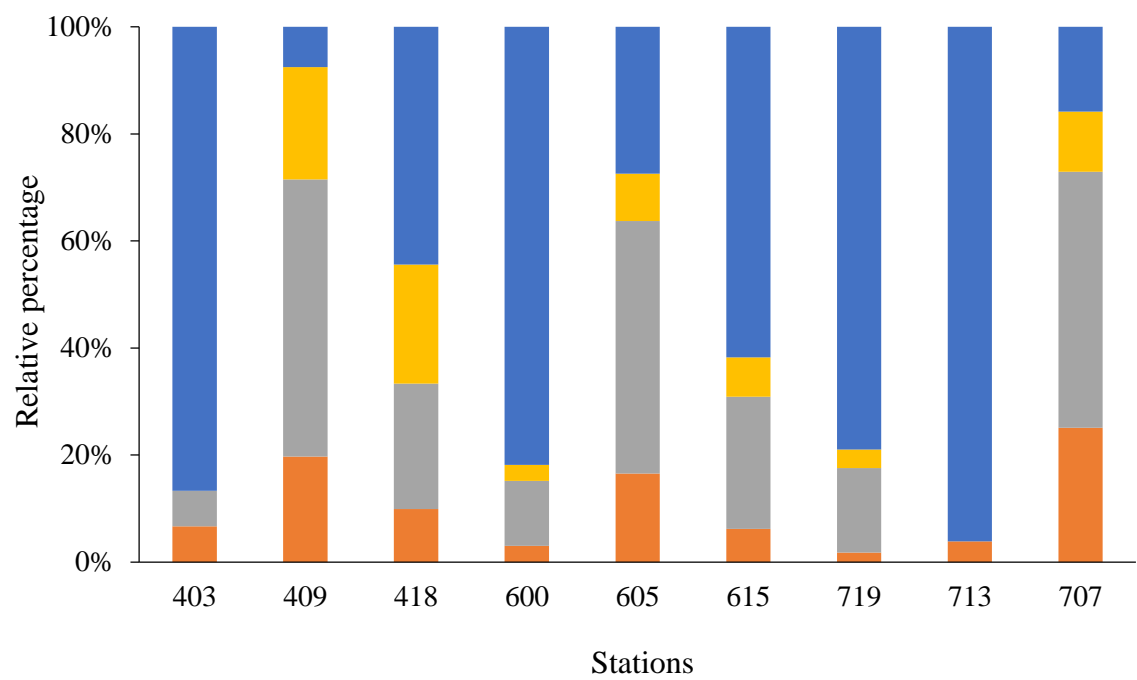
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47 727 **Figure 9.** Conceptual scheme showing how autoxidative alterations are induced in the
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50 728 membranes of bacteria associated to senescent ice algae.

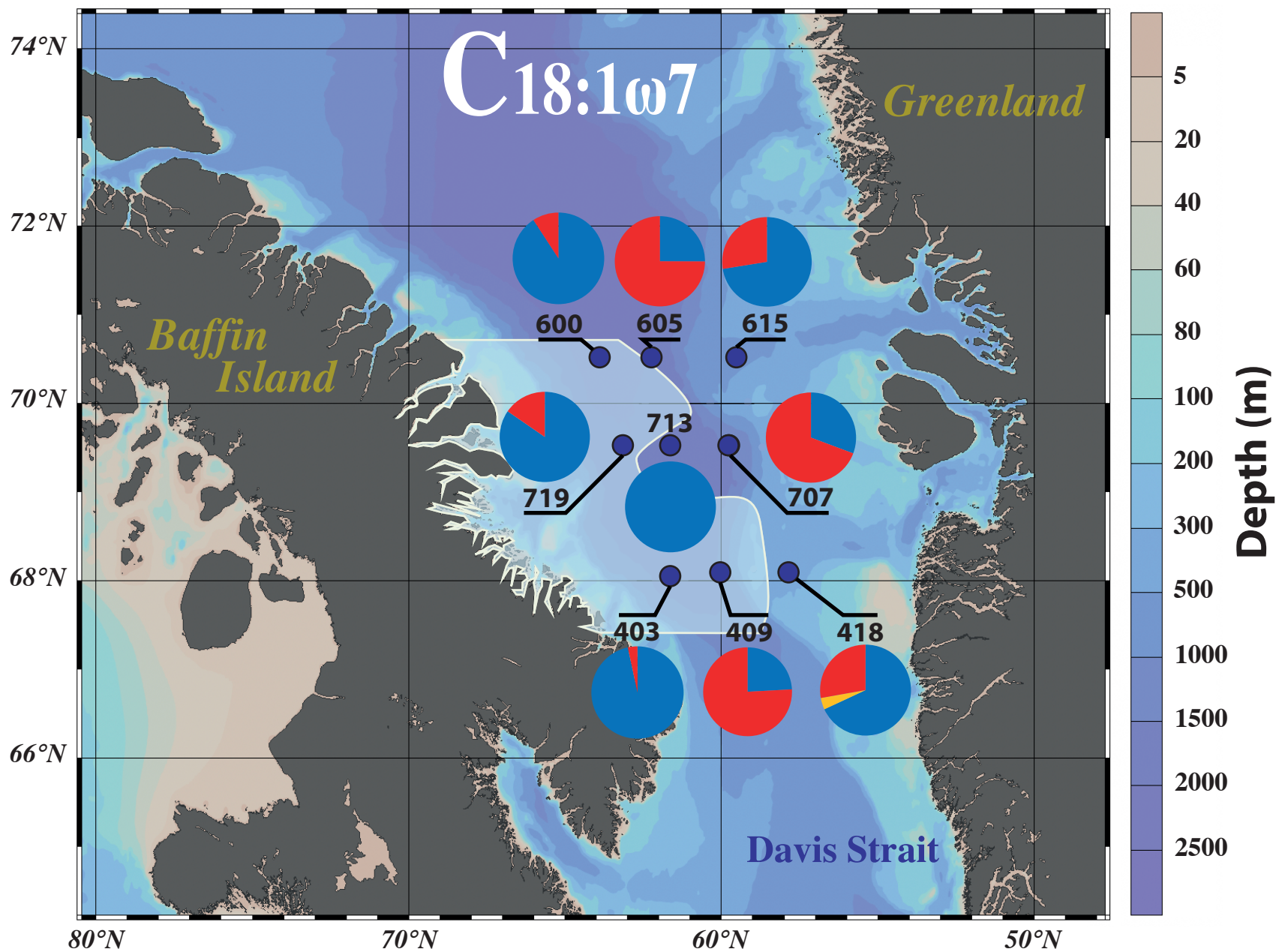
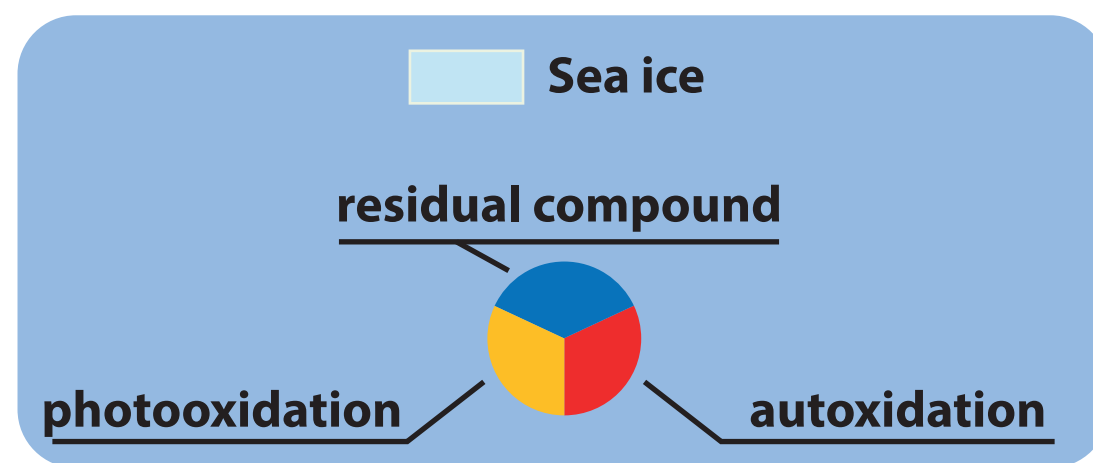
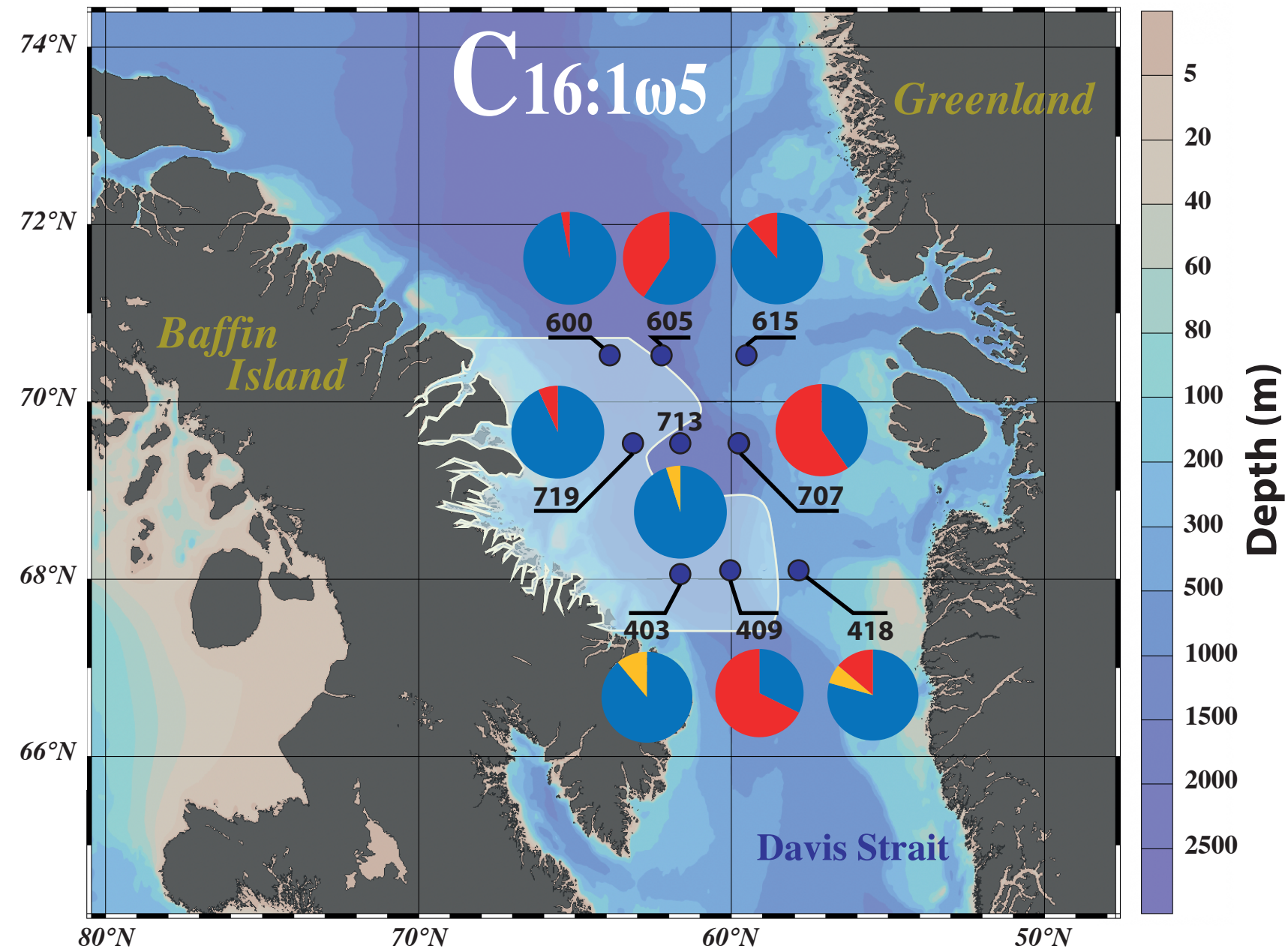
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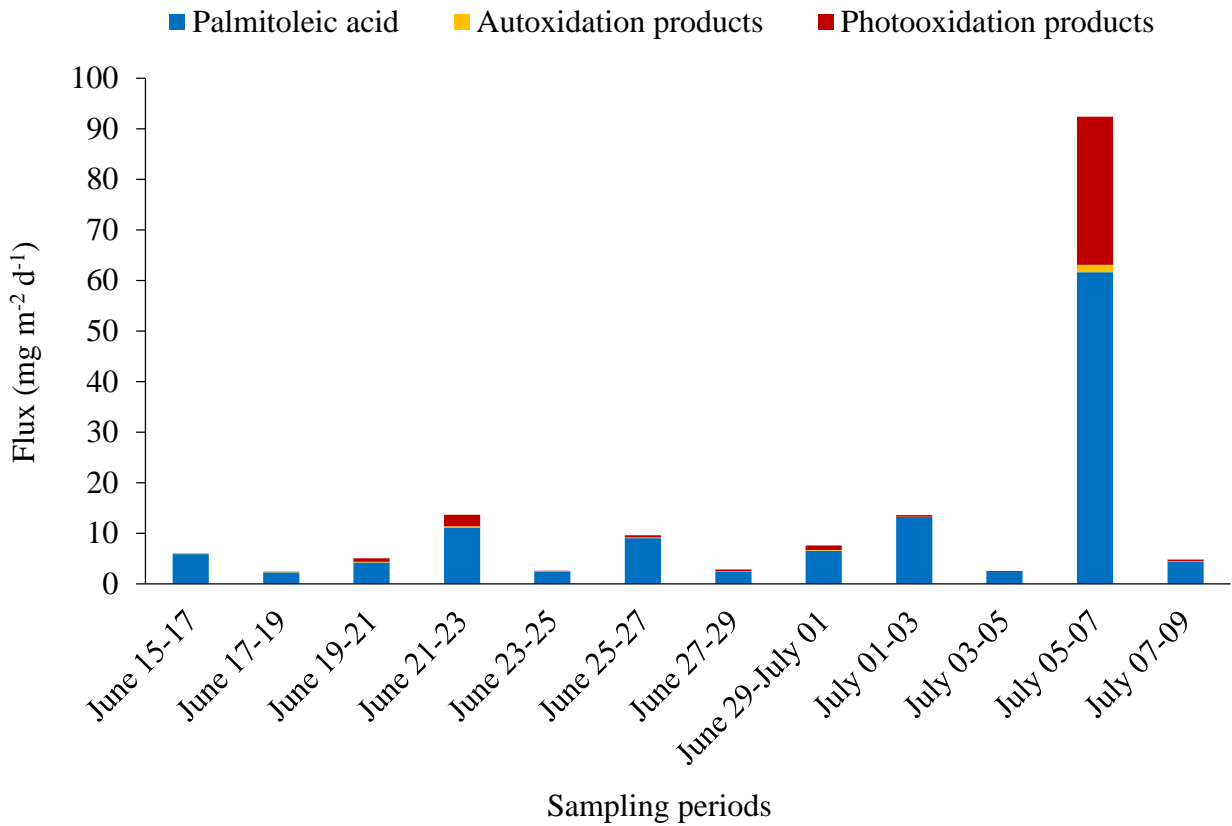
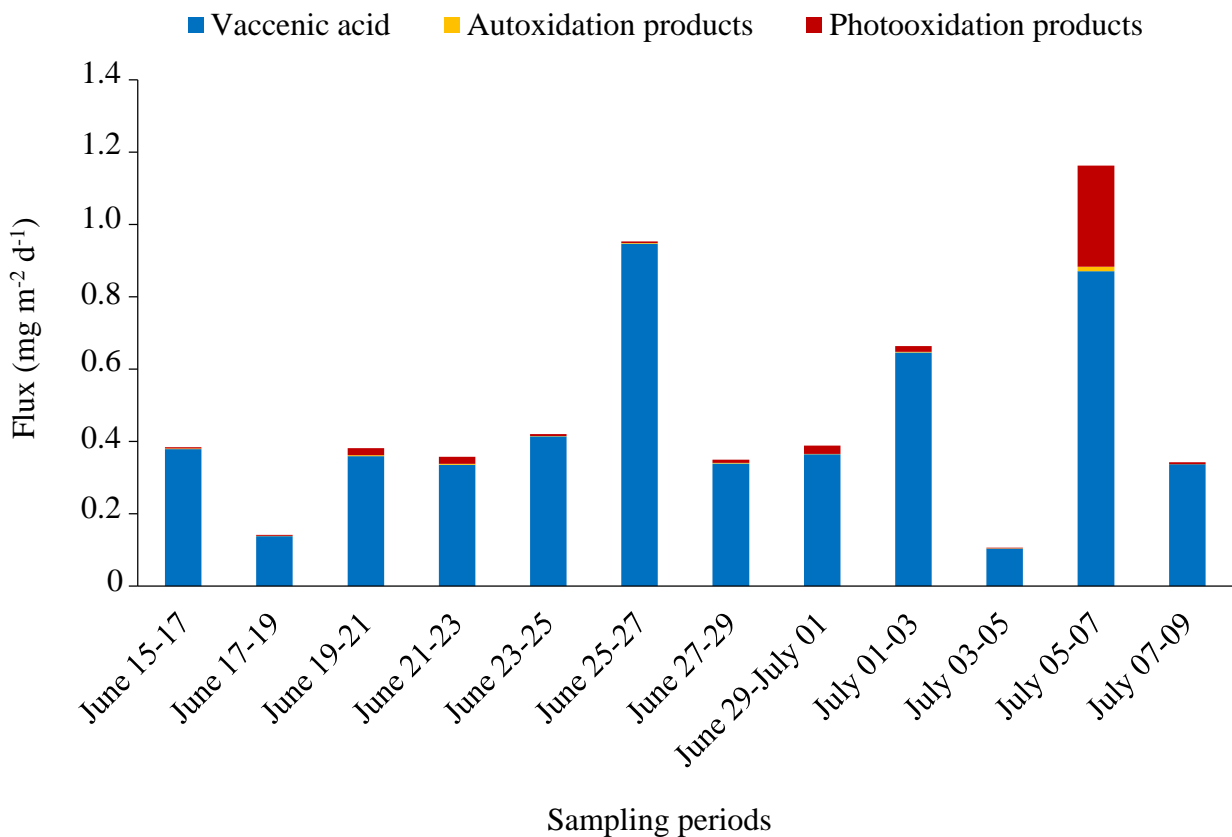


NL*: not located



A**B**

A**B**

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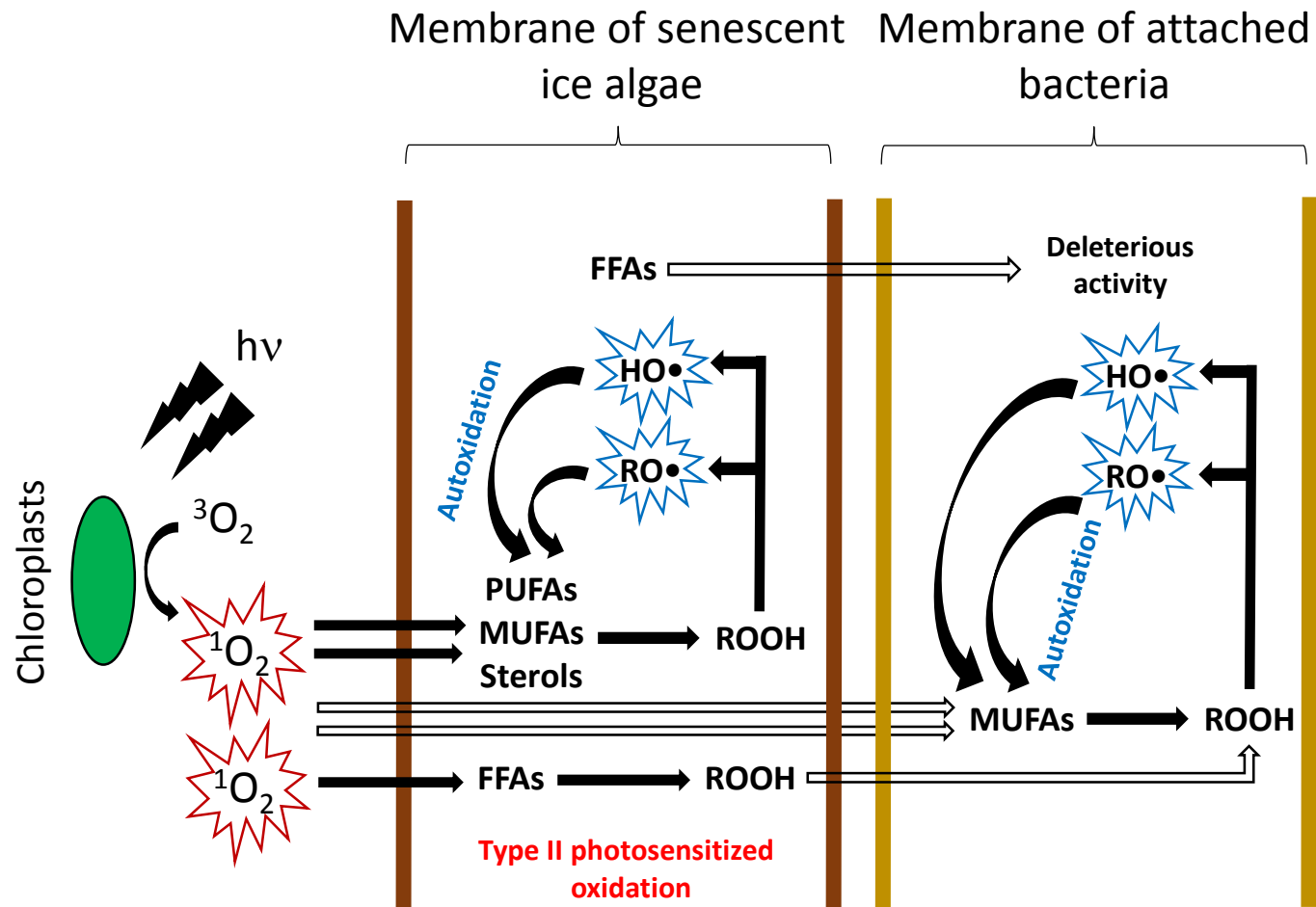


Table 1: Concentrations of C_{16:1ω7}, C_{18:1ω7} and C_{16:1ω5} acids and their oxidation products in the different sediment samples (μg g⁻¹).

Station	C _{16:1ω7}					C _{18:1ω7}			C _{16:1ω5}		
	Residual compound	photooxidation products	autoxidation products	10S-DOX products	Total	Residual compound	photooxidation products	autoxidation products	Residual compound	photooxidation products	autoxidation products
403	1.3	0.1	0.1	-	1.5	0.2	-	-	0.1	-	-
409	3.6	9.4	24.7	10	47.7	2.1	-	6.5	1.1	-	2.3
418	3.6	0.8	1.9	1.8	8.1	0.6	0.1	0.3	0.3	-	0.1
600	2.7	0.1	0.4	0.1	3.3	1	-	0.1	0.4	-	-
605	9.3	5.6	16	3	33.9	1.4	-	4.3	1.1	-	0.8
615	5	0.5	2	0.6	8.1	1.3	-	0.5	0.6	-	0.1
719	4.5	0.1	0.9	0.2	5.7	0.9	-	0.2	0.3	-	-
713	2.5	0.1	- ^a	-	2.6	3.7	-	-	0.2	-	-
707	13.7	21.7	41.4	9.7	86.5	2.7	-	6.1	1.7	-	2.5

^a Not shown (concentration < 0.1 μg g⁻¹)

Table 2. Concentrations and percentages of total and free palmitoleic acid in sediments from the two contrasted stations 403 and 605.

Station	C _{16:1ω7}		
	Free ($\mu\text{g g}^{-1}$)	Total ($\mu\text{g g}^{-1}$)	free/total (%)
403	0.08 \pm 0.01	1.25 \pm 0.05	6.4
605	2.05 \pm 0.05	9.30 \pm 0.10	22.0

Table 3. Relative percentages of oxidation products of palmitoleic and vaccenic acids in sediments of stations 403 and 605.

Station	MUFA	Residual acid (%)	Hydroperoxyacid (%)	Hydroxyacid (%)	Oxoacid (%)
403	Palmitoleic acid	86.7	4.4	3.8	5.1
	Vaccenic acid	96.0	1.1	1.1	1.8
605	Palmitoleic acid	27.4	29.5	13.1	30.0
	Vaccenic acid	43.4	20.4	10.1	26.0