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Type II photosensitized oxidation in senescent microalgal cells at different latitudes: Does low under-ice irradiance in polar regions enhance efficiency?

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4 regions enhance efficiency?
5

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30

31

32 **Abstract**

33 Comparison of Type II photosensitized oxidation of lipids (the photodynamic effect) and
34 photodegradation of chlorophyll (sensitizer photobleaching) in samples of particulate matter
35 collected previously from locations representing a diverse range of latitudes reveals an
36 enhancement of the photooxidation of lipids at the expense of chlorophyll photodegradation in
37 the polar regions. The efficiency of the photodynamic effect appears to be particularly high in
38 sinking particles collected under sea ice and is attributed to the rapid settling of highly
39 aggregated sympagic algae to depths of low light transmission favouring the photodynamic
40 effect at the expense of photobleaching of the sensitizer. Paradoxically, the low efficiency of
41 Type II photosensitized oxidation of lipids observed in temperate and equatorial regions is
42 associated with high solar irradiances in these regions. Type II photosensitized oxidation of
43 lipids in senescent phytoplankton seems thus to be strongly dependent of the intensity of solar
44 irradiance.

45

46 **Keywords:** Photodynamic effect; Senescent phytoplankton; Latitude; Polar regions; Solar
47 irradiance.

48 **1. Introduction**

49 Reconstructions of sedimentary palaeoenvironments are essential to place the current global
50 warming trends into the context of natural and long-term climate variability. Lipid biomarkers
51 preserved in sediments are often used for this purpose since they are key indicators of organic
52 matter (OM) sources (Volkman et al., 1998; Wakeham et al., 1997). Maximizing the reliability
53 of these reconstructions requires careful consideration of the processes that affect the fate of
54 OM – notably OM degradation and/or preservation – during its transport down the water
55 column from the euphotic zone to the seafloor. Degradation may be biotic (i.e. induced by
56 zooplankton and bacteria, Harvey et al., 1987; Grossart et al., 2007) or abiotic (i.e. induced by
57 light or radicals, Rontani, 2012). Photooxidation (which has generally received little attention
58 until now in the literature) that destroys most of the unsaturated components of biogenic OM
59 initially present in the settling material (for a recent review see Rontani and Belt, 2020) can
60 strongly alter the lipid signature of OM reaching the seafloor. It is thus essential to take into
61 account the potential effects of abiotic degradation when making palaeoenvironmental
62 reconstructions from sedimentary OM.

63 In healthy phytoplankton cells, light absorption by chlorophyll creates an excited singlet
64 state (^1Chl), which leads to the classical fast reactions of photosynthesis (Foote, 1976). The
65 energy of this excited state is then transferred to various substrates, where it promotes
66 photosynthetic reactions, while a relatively small proportion of ^1Chl (<0.1%) undergoes
67 intersystem crossing (ISC) to form the longer-lived triplet state (^3Chl ; Knox and Dodge, 1985)
68 (Fig. 1). ^3Chl is not only potentially damaging in itself in Type I reactions (Knox and Dodge,
69 1985), but can also generate reactive singlet oxygen ($^1\text{O}_2$) by reaction with ground state oxygen
70 ($^3\text{O}_2$) via Type II photoprocesses (Fig. 1) (Krieger-Liszkay, 2005). Despite the production of
71 other Reactive Oxygen Species (ROS), it is generally considered that the photo-production of
72 $^1\text{O}_2$ plays the major role in light-induced damage to plant cells (Triantaphylides et al., 2008).

73 In view of the susceptibility of plant cells to oxidative damage, there are many antioxidant
74 protective mechanisms in chloroplasts. For example, carotenoids quench ^3Chl and $^1\text{O}_2$ by
75 energy transfer mechanisms at very high rates (Fig. 1). Such antioxidants have a dual role: first,
76 they limit $^1\text{O}_2$ formation, and second, they help remove any $^1\text{O}_2$ that does form (Foote, 1976;
77 Tefler, 2002). Tocopherols and ascorbic acid are also efficient quenchers of $^1\text{O}_2$ (Halliwell,
78 1987; Havaux et al., 2005).

79 In senescent phototrophic organisms, the cessation of photosynthetic reactions results in
80 an accelerated rate of formation of ^3Chl and ROS (mainly $^1\text{O}_2$) (Nelson, 1993; Triantaphylides
81 et al., 2008). The rate of formation of these potentially damaging species then often exceeds the
82 quenching capacity of the photoprotective system such that photodegradation of cell
83 components can occur via the so-called photodynamic effect (Merzlyak and Hendry, 1994)
84 (Fig. 1). Direct and irreversible reaction of ^3Chl with $^3\text{O}_2$ (photobleaching) gives photooxidation
85 products (Harbour and Bolton, 1978) (Fig. 1), while $^1\text{O}_2$ reacts extremely rapidly with nearby
86 biomolecules at near diffusion-controlled rates (photodynamic effect) (Knox and Dodge, 1985;
87 Cadenas, 1989; Skovsen et al., 2005). The very high reactivity of $^1\text{O}_2$ with numerous cell
88 components (unsaturated lipids, some amino acids, nucleic acids; Rontani, 2012, Devasagayam
89 and Kamat, 2002) is a consequence of the loss of the spin restriction that normally hinders
90 reaction of $^3\text{O}_2$ with these biomolecules (Zolla and Rinalducci, 2002). $^1\text{O}_2$ also reacts with the
91 sensitizer (chlorophyll) inducing its photobleaching (Nelson, 1993; Rontani, 2012) (Fig. 1). It
92 is important to note, however, that photobleaching of the sensitizer reduces $^1\text{O}_2$ production and
93 is thus competitive with the photodynamic effect.

94 In this study, we investigated the photooxidation of chlorophyll (photobleaching) and
95 some common algal unsaturated lipids (Δ^5 -sterols and monounsaturated fatty acids (MUFAs))
96 (photodynamic effect) in marine particulate matter from locations representing a diverse range
97 of latitudes, from the Arctic to the Antarctic. In order to try to explain an increased, yet highly

98 variable, efficiency of the photodynamic effect observed in material from the polar regions,
99 particular attention was given to samples from the Canadian Arctic representing sea ice, the
100 water column under the ice, and regions of open water.

101

102 **2. Experimental**

103

104 *2.1. Sample collection*

105 Detailed descriptions (e.g. sampling dates, depths, volumes, etc) of the collection of samples of
106 marine particulate matter from the Arctic, English Channel, Mediterranean Sea, Arabian Sea,
107 Equatorial Pacific, Equatorial Atlantic, Peru upwelling and East Antarctica (Fig. 2) has been
108 described previously (see references in Tables 1 and 2). Briefly, suspended particulate matter
109 (SPM) samples were collected with Niskin bottles or an in situ multiple-unit large-volume
110 filtration system (MULVFS), while sinking particles were collected with floating or fixed
111 mooring sediment traps. Sub-samples for lipid analysis were then filtered onto GF/F filters and
112 stored frozen ($-80\text{ }^{\circ}\text{C}$). Sympagic algae were obtained from the bottom-most layer of sea ice
113 (0-10 cm) from Resolute Passage (Canadian Arctic) (Rontani et al., 2014). Samples of the sub-
114 ice colonial diatom, *Melosira arctica*, which colonises the underside of sea ice and is widely
115 distributed across the Arctic (Boetius et al., 2013), were collected from the Canadian icebreaker
116 CCGS Amundsen under the ice ($49 \pm 4\text{ cm}$) in Baffin Bay ($70^{\circ}28'32''\text{N}$, $64^{\circ}0'37''\text{W}$) in June
117 2016 (GreenEdge Campaign)) and on board of R/V Lance ($81^{\circ}14'22''\text{N}$, $21^{\circ}54'50''\text{E}$) in
118 August 2017 as part of an oceanographic transect north of Svalbard from Rijpfjorden towards
119 the Nansen Basin. Near-surface ($<10\text{ m}$) water column samples (ca. 1 – 4 l) were collected
120 along a N-S transect terminating in the Amundsen Sea (Antarctica) and filtered (GF/F) on board
121 the Korean Icebreaker RV Araon in January/February 2016.

122

123 *2.2. Sample treatment*

124 The whole material of the different samples was reduced with excess NaBH₄ in MeOH (25 ml;
125 30 min) to reduce labile hydroperoxides (resulting from Type II photooxidation) to their
126 corresponding alcohols, which are more amenable to analysis using gas
127 chromatography/electron ionization mass spectrometry (GC-EIMS), gas
128 chromatography/electron ionization tandem mass spectrometry (GC-EIMS/MS) and gas
129 chromatography/electron ionization quadrupole time of flight mass spectrometry (GC-QTOF).
130 Water (25 ml) and KOH (2.8 g) were then added and the resulting mixture saponified by
131 refluxing (2 h). After cooling, the mixture was acidified (HCl, 2 N) to pH 1 and extracted with
132 dichloromethane (DCM; 3 x 20 ml). The combined DCM extracts were dried over anhydrous
133 Na₂SO₄, filtered and concentrated via rotary evaporation at 40 °C to give total lipid extracts
134 (TLEs). All the solvents (pesticide/glass distilled grade) and reagents (Puriss grade) were
135 obtained from Rathburn and Sigma-Aldrich, respectively. TLEs were derivatized by dissolving
136 them in 300 µL pyridine/bis-(trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v/v) and
137 silylated (50 °C, 1 h). After evaporation to dryness under a stream of N₂, the derivatized residue
138 was dissolved in hexane/BSTFA (to avoid desilylation) and analysed by the aforementioned
139 mass spectrometric methods.

140

141 *2.3. Assignment and quantification of lipids and their degradation products*

142 Lipids and their degradation products were identified by comparison of retention times and
143 mass spectra with those of standards and quantified using GC-EIMS, GC-EIMS/MS and GC-
144 QTOF based on calibrations with external standards. Operating conditions employed during
145 these analyses were as per those described previously (Rontani et al, 2019 and references
146 therein). Standards of phytol, palmitoleic acid, 24-methylcholesta-5,22-dien-3β-ol
147 (brassicasterol) and 24-methylcholesta-5,(24/28)-dien-3β-ol (24-methylenecholesterol) were

148 obtained from Sigma-Aldrich. Standard oxidation products of these compounds were produced
149 according to previously described procedures (Rontani and Marchand 2000; Marchand and
150 Rontani 2001; Rontani and Aubert, 2005).

151

152 2.4. Data treatment

153

154 2.4.1 Chlorophyll photooxidation estimates

155 The molar ratio 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol (phytyldiol):phytol
156 (Chlorophyll Phytyl side-chain Photodegradation Index, CPPI) has been previously proposed
157 to estimate the extent of photodegradation of chlorophylls possessing a phytyl side-chain in
158 natural marine samples through use of the empirical equation: chlorophyll photodegradation %
159 = $(1 - [\text{CPPI} + 1]^{-18.5}) \times 100$ (Cuny et al., 1999).

160

161 2.4.1. Lipid photooxidation estimates

162 The extent of photooxidation (%) of sterols was estimated using the equation: Δ^5 -sterol
163 photooxidation % = $(\Delta^4\text{-stera-}6\alpha/\beta\text{-diols \%} \times (1+0.3)/0.3)$ (Christodoulou et al., 2009).

164 Type II photosensitized oxidation of MUFAs was estimated after quantification of
165 isomeric *trans* allylic hydroxyacids resulting from NaBH₄-reduction of the corresponding
166 photochemically-produced hydroperoxides after subtraction of the amounts of these
167 compounds arising from autoxidation (Marchand and Rontani, 2001).

168

169 2.4.3. Statistical analysis

170 Mann – Whitney – Wilcoxon tests were performed to identify any significant differences in: (i)
171 the ratio of brassicasterol photo-oxidation percentage / chlorophyll photo-oxidation percentage
172 with latitude (Table S1), and (ii) the ratios of 24-methylenecholesterol photooxidation

173 percentage / chlorophyll photooxidation percentage, palmitoleic acid photooxidation
174 percentage / chlorophyll photooxidation percentage and brassicasterol photooxidation
175 percentage / chlorophyll photooxidation percentage between different sample types (i.e. sea ice
176 POM, SPM and sediment traps) (Table S2).

177 **3. Results and discussion**

178 Since photodynamic processes and sensitizer photobleaching are competitive processes (Fig.
179 1), we used the ratio of the % photooxidation of membrane lipids to that of chlorophyll to
180 estimate the efficiency of Type II photosensitized oxidation processes (the photodynamic effect
181 in Fig. 1) in senescent phytoplankton at different latitudes. In the case of brassicasterol, a
182 phytoplanktonic Δ^5 -sterol widely distributed in the oceans (Volkman, 1986, 2003), values of
183 this ratio obtained from previously published and unpublished data sets (Table 1) show a strong
184 increase (albeit with high variability) in samples from the polar regions in comparison to
185 samples collected from temperate and equatorial settings (Fig. 3). Such increases were found
186 to be significant when the data from the temperate and equatorial settings were compared with
187 those from the Arctic and Antarctic datasets (and the combined Arctic/Antarctic dataset), yet
188 no significant difference was found between the high latitude datasets (Table S1). Low
189 temperatures have previously been shown to reduce diffusion rate of $^1\text{O}_2$ through cell
190 membranes (Ehrenberg et al., 1998), thus favouring the intra-cellular involvement of the
191 photodynamic effect. More recently, Amiraux et al. (2016) confirmed these results in the case
192 of the centric diatom *Chaetoceros neogracilis* (strain RCC2022) and observed an increase (3.0
193 ± 0.5 fold) of the ratio $k_{\text{camp}}/k_{\text{chl}}$ (where k_{camp} is the first-order photodegradation rate of
194 campesterol and k_{chl} this of chlorophyll) when the temperature decreased from 17 to 7°C. The
195 characteristic low temperatures of the Arctic and Antarctic could thus be the cause of the high
196 values of the ratio % photooxidation brassicasterol / % photooxidation chlorophyll measured in

197 samples from these regions. However, low temperatures alone cannot explain the very high
198 variability of this ratio observed within these samples (Fig. 3).

199 In an effort to explain this strong variability, we examined, more closely, Arctic samples
200 collected from sea ice, under the ice (suspended and sinking particles) and from open water
201 conditions (sinking particles), which are all dominated by diatoms. The % photooxidation of
202 the common diatom lipids brassicasterol, 24-methylenecholesterol and palmitoleic acid to that
203 of chlorophyll are summarized in Table 2 and Fig. 4. Strong differences of photodynamic effect
204 efficiency were observed between these different kinds of particles. These differences were
205 found to be significant between surface samples (sea ice and SPM) and traps and between under
206 ice traps and open water traps (Table S2). These different samples having been collected at very
207 close temperatures (ranging from -1 to -2 °C in surface waters of Arctic), it is clear that the low
208 temperatures do not represent the main driver for the enhancement of photodynamic efficiency
209 in polar regions.

210 Riebesell et al. (1991) previously suggested that growing cells released by sea ice remain
211 largely unaggregated (i.e. mainly in suspension). The very low photooxidation state of lipids
212 and chlorophyll observed in SPM collected under the ice (Fig. 4) could thus result from the
213 healthy state of the algal cells present in these samples (Rontani et al., 2016), which are largely
214 unaffected by photooxidative damage. Indeed, in healthy cells, the greater part of the
215 photoexcited chlorophyll singlet state is used in the fast photochemical reactions of
216 photosynthesis.

217 The efficiency of the photodynamic effect appears to be considerably higher in material
218 collected in sediment traps in spring from under sea ice compared to those collected in summer
219 from open water (Fig. 4, Table S2), which is likely attributable to the respective contributions
220 of sympagic (i.e. living within ice) vs pelagic algae. Indeed, in contrast to healthy and largely
221 unaggregated sympagic algal cells (see above), less metabolically-active sea ice algae that are

222 released from the ice are generally concentrated into aggregates that become sinking particles
223 (Riebesell et al., 1991). Moreover, sympagic diatoms exhibit a higher sensitivity towards light-
224 induced stress than pelagic diatoms (Kvernvik et al., 2020). Such differences in sensitivity were
225 attributed, in part, to the gradually changing and low amplitude irradiance typically experienced
226 by sympagic algae (Hill et al., 2018), whereas pelagic cells in open water, in contrast,
227 experience high amplitude changes in light intensity over much shorter timescales (MacIntyre
228 et al., 2000). This interesting hypothesis is not supported, however, by: (i) the very low
229 efficiency of the photodynamic effect observed in the bottom-most layer of sea ice (Table 2)
230 and (ii) the lack of correlation between lipid photooxidation % and the concentration of the sea
231 ice lipid biomarker IP₂₅ (a well-known sea ice proxy, for reviews see Belt and Müller, 2013;
232 Belt, 2018) in under ice traps ($R^2 < 0.008$).

233 During in vitro experiments carried out on senescent cells of the centric diatom
234 *Chaetoceros neogracilis* (strain RCC2022), Type II photosensitized oxidation of lipids was also
235 observed to be strongly enhanced by low irradiance levels, whereas the opposite was true for
236 the photodegradation of chlorophyll (Amiriaux et al., 2016). The ratio k_{camp}/k_{chl} thus increased
237 4.2 ± 0.8 fold when irradiance decreased from 2038 to 165 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$. In the Arctic,
238 the mean PAR (Photosynthetically Active Radiation) irradiance in the surface mixed layer is
239 considerably higher in open water than in ice-covered zones (365 ± 62 and $10.9 \pm 2.7 \mu\text{mol}$
240 $\text{photons m}^{-2} \text{s}^{-1}$, respectively, Alou-Font et al., 2016). The intensity of solar irradiance may thus
241 be at the origin of the contrasting efficiency of the photodynamic effect observed in sinking
242 particles collected under sea ice compared to those from open water (Fig. 4). Further, the
243 increase of this efficiency with depth in under ice samples (Fig.4, Table S2) could result from
244 enhanced aggregation of senescent sympagic algae as they sink to deeper traps (Riebesell et al.,
245 1991; Rontani et al., 2016) where light transmission is lower. In contrast, the relatively high
246 irradiance observed at the ice-water interface (up to ca. 100 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ in Davis

247 Strait, Galindo et al., 2017) could explain the greatly diminished photodynamic effect in
248 sympagic algae inhabiting the bottom-most layer of sea ice and in *Melosira arctica* (Table 2)
249 (Fig. 6). Examination of near-surface (<10 m) SPM samples collected along a N-S transect
250 terminating in the Amundsen Sea (Antarctica) in open water and seasonally ice covered zones
251 further confirmed the increase of photodynamic efficiency in regions of sea ice cover (Fig. 5)
252 ($W = 52$, $p\text{-value} = 0.003205$). In addition, the relatively higher photooxidation state of these
253 suspended particles compared to those collected in the Arctic (Fig. 4, Table 2) may be attributed
254 to the low contribution (typically 0.5 to 2%) of sympagic algae to primary production in
255 January-February in the Antarctic (Lizotte, 2001).

256 Due to their strong aggregation capability (Macdonald et al., 1998; Ambrose et al., 2001,
257 2005) and the low remineralizing potential of their associated bacteria (Amiriaux et al., 2017,
258 2020), sympagic algae seem to contribute more significantly than open water phytoplankton to
259 the export of carbon to Arctic sediments, providing an early season food source for benthic
260 fauna (Macdonald et al., 1998; Mincks et al., 2005). Episodic massive falls of *M. arctica* can
261 sink to the seafloor (Ambrose et al., 2005; Boetius et al., 2013; Lalande et al., 2019). The
262 polyunsaturated fatty acid (PUFA) content in algal biomass that reached the seafloor is essential
263 for growth and reproduction of benthic fauna (Brett and Müller-Navarra, 1997; McMahon et
264 al., 2006). Due to the high photosensitized oxidation of MUFAs observed in samples sinking
265 under sea ice cover (Fig. 4), and the well-known increasing photooxidation rates of fatty acids
266 with their degree of unsaturation (Frankel, 1998; Rontani et al., 1998), the PUFA content of
267 sympagic material reaching the sediment would thus be greatly reduced. *Melosira* strands that
268 are weakly affected by abiotic degradation processes under the ice (ratio C_{20:5} acid vs
269 palmitoleic acid ranging from 0.25 to 0.47), despite a significant photooxidation of chlorophyll
270 (Table 2), and that sink very quickly to the seafloor (Syvertsen, 1991) in massive falls (Ambrose

271 et al., 2005; Boetius et al., 2013; Lalande et al., 2019) may be an important source of fresh
272 material rich in OM (i.e., PUFAs) for the benthos.

273 Further, the expected reduction of sea ice cover resulting from increased global warming
274 may result in a shift in the relative contributions of ice-associated vs pelagic algae (Carroll and
275 Carroll, 2003) to the seafloor. The high flux of fast-sinking aggregates of strongly abiotically-
276 altered sympagic algae and fast sinking well preserved *M. arctica* reaching Arctic sediments
277 could thus be replaced, progressively, by a lower flux of weakly abiotically altered pelagic
278 biomass. Such a shift should thus strongly impact the quality and quantity of food reaching
279 benthic communities, as previously proposed by Sun et al. (2007), and could significantly alter
280 the community structure and spatial distribution of the benthos.

281

282 **4. Conclusions**

283 During this work, Type II photosensitized oxidation of lipids (photodynamic effect) and
284 photodegradation of chlorophyll (photobleaching) were compared in several samples of
285 particulate matter from locations ranging from the Arctic to the Antarctic. The results obtained
286 clearly showed an enhancement of the photooxidation of lipids at the expense of chlorophyll
287 photodegradation in polar regions compared to temperate and equatorial regions. Careful
288 examination of different samples of sympagic and epiphytic algae, suspended and sinking
289 particles collected in Arctic allowed to show that the efficiency of photodynamic effect was
290 particularly high in sinking particles collected under the ice (Fig. 6). This high efficiency was
291 attributed to the rapid settling of highly aggregated sympagic algae to depths of low light
292 transmission favouring photodynamic effect at the expense of photobleaching of the sensitizer.
293 In contrast, in the case of samples exposed to relatively high solar irradiances - sympagic and
294 epiphytic algae collected in the bottommost layer of ice or at the underside of ice, respectively,
295 and particles collected from open waters - the efficiency of photodynamic effect appeared to be

296 relatively weak (Fig. 6). The low efficiency of Type II photosensitized oxidation of lipids
297 observed in temperate and equatorial regions could, perhaps paradoxically, thus be attributed
298 to the high solar irradiances received in these regions. The intensity of solar irradiance seems
299 thus to be a key parameter during the Type II photosensitized oxidation of lipids in senescent
300 phytoplankton.

301

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333

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519

Figure captions

520

521

522 **Figure 1.** Potential pathways for chlorophyll (Chl) excitation energy in senescent
523 phytoplankton cells (simplified scheme limited to the formation of $^1\text{O}_2$ and photoprotective role
524 of carotenoids (Car)).

525

526 **Figure 2.** Sampling locations.

527

528 **Figure 3.** Values of the ratio brassicasterol photooxidation %/chlorophyll photooxidation % in
529 particulate matter samples collected at different latitudes.

530

531 **Figure 4.** Values of the ratios brassicasterol photooxidation %/chlorophyll photooxidation %,
532 24-methylenecholesterol photooxidation %/chlorophyll photooxidation % and palmitoleic acid
533 photooxidation %/chlorophyll photooxidation % in particulate matter samples collected in
534 Arctic ice-covered and open water zones.

535

536 **Figure 5.** Values of the ratio brassicasterol photooxidation %/chlorophyll photooxidation % in
537 SPM samples collected in open and ice-covered zones along a N-S transect terminating in the
538 Amundsen Sea (Antarctica).

539

540 **Figure 6.** Conceptual scheme summarizing the efficiency of photodynamic effect in sympagic,
541 epiphytic and pelagic algae in polar regions. (To simplify the scheme only the Type II
542 photosensitized oxidation of palmitoleic acid is shown) (nd = not detected).

543

544 **Table captions**

545

546 **Table 1.** Variation of the ratio brassicasterol photooxidation %/chlorophyll photooxidation %
547 in particulate matter samples according to the latitude.

548

549 **Table 2.** Photooxidation of chlorophyll, brassicasterol, 24-methylenecholesterol and
550 palmitoleic acid in different sea ice, *M. arctica* and particulate matter samples collected in the
551 Arctic.

552

553 **Supplementary material**

554

555 **Table S1.** Results of Mann – Whitney – Wilcoxon analysis testing the effect of the latitude on
556 the brassicasterol photooxidation percentage : chlorophyll a photooxidation percentage ratio.
557 Bold values are indicative of significance.

558

559 **Table S2.** Results of Mann – Whitney – Wilcoxon analysis testing the effect of the sample type
560 on the 24-methylenecholesterol photo-oxidation percentage / chlorophyll photo-oxidation
561 percentage, palmitoleic acid photo-oxidation percentage / chlorophyll photo-oxidation
562 percentage and brassicasterol photo-oxidation percentage / chlorophyll photo-oxidation
563 percentage ratios. Bold values are indicative of significance.

Table 1

Variation of the ratio brassicasterol photooxidation %/chlorophyll photooxidation % in particulate matter samples according to the latitude.

Latitude	Location	Nature of particles	n	Brassicasterol hv %/Chlorophyll hv %	References
71-74°N	Canadian Arctic	Suspended and sinking	46	0.77 ± 1.10	Rontani et al., 2012; 2016
50°N	English Channel	Suspended	24	0.02 ± 0.04	Rontani et al., 2021
43°N	Rhône Prodelta	Suspended	21	0.21 ± 0.11	Galeron et al., 2018
43°N	Ligurian Sea	Sinking	12	0.21 ± 0.10	Christodoulou et al., 2009
17°N	Arabian Sea	Suspended and sinking	7	0.07 ± 0.04	Wakeham et al., 2002
0°	Equatorial Atlantic	Suspended	2	0.10 ± 0.12	Galeron et al., 2018
0°	Equatorial Pacific	Suspended and sinking	11	0.11 ± 0.07	Wakeham et al., 2002; Rontani et al., 2011
12°S	Peru Upwelling	Sinking	10	0.18 ± 0.04	Bretagnon et al., 2018
40-67°S	South Pacific	Suspended	5	0.09 ± 0.04	
67-75°S	Antarctica	Suspended	23	0.50 ± 0.45	Rontani et al., 2019

Table 2

Photooxidation of chlorophyll, brassicasterol, 24-methylenecholesterol and palmitoleic acid in different sea ice, *M. arctica* and particulate matter samples collected in the Arctic.

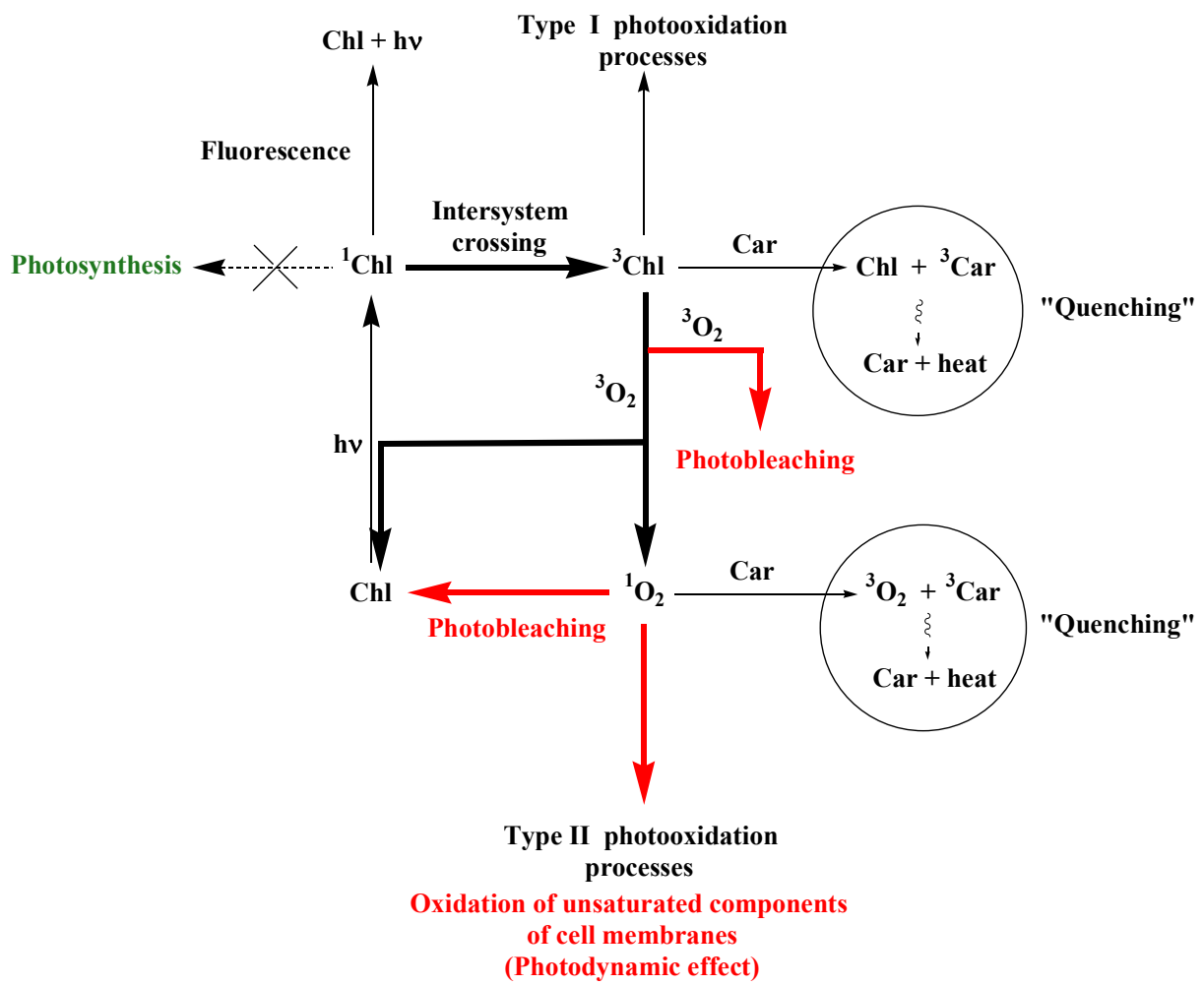
Samples	Location	n	Chlorophyll photooxidation %	Brassicasterol photooxidation %/ chlorophyll photooxidation %	24-Methylenecholesterol photooxidation %/ chlorophyll photooxidation %	Palmitoleic acid photooxidation %/ chlorophyll photooxidation %
Sea ice (0-3 cm)	Resolute Passage ^a and Davies Strait ^b	21	54.5 ± 38.4	0.02 ± 0.05	0.04 ± 0.10	0.05 ± 0.08
<i>Melosira arctica</i>	Baffin Bay and North of Svalbard	6	40.2 ± 12.8	-	-	0.03 ± 0.03
Under ice spm (<10 m)	Resolute Passage ^c	20	16.3 ± 13.9	0.05 ± 0.17	0.42 ± 0.96	1.00 ± 1.60
Under ice trap (5 m)	Resolute Passage ^c	11	55.7 ± 34.1	1.10 ± 0.62	1.22 ± 0.98	2.87 ± 2.78
Under ice trap (30 m)	Resolute Passage ^c	11	11.5 ± 8.6	2.00 ± 1.39	3.97 ± 2.22	8.39 ± 7.15
Open water trap (100 m)	Beaufort Sea ^d	12	99.8 ± 0.2	0.23 ± 0.07	0.48 ± 0.14	0.47 ± 0.19

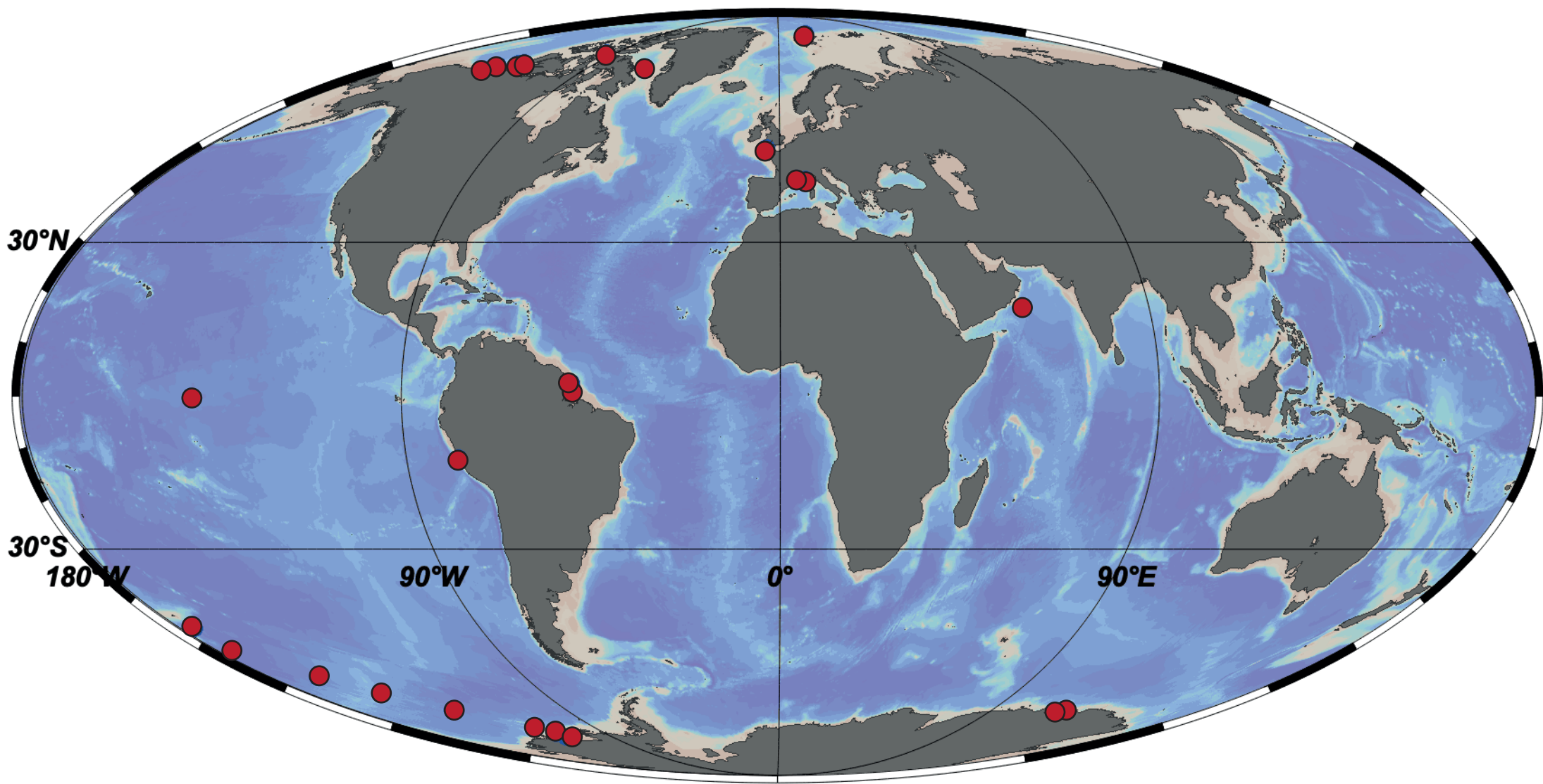
^a Rontani et al., 2014

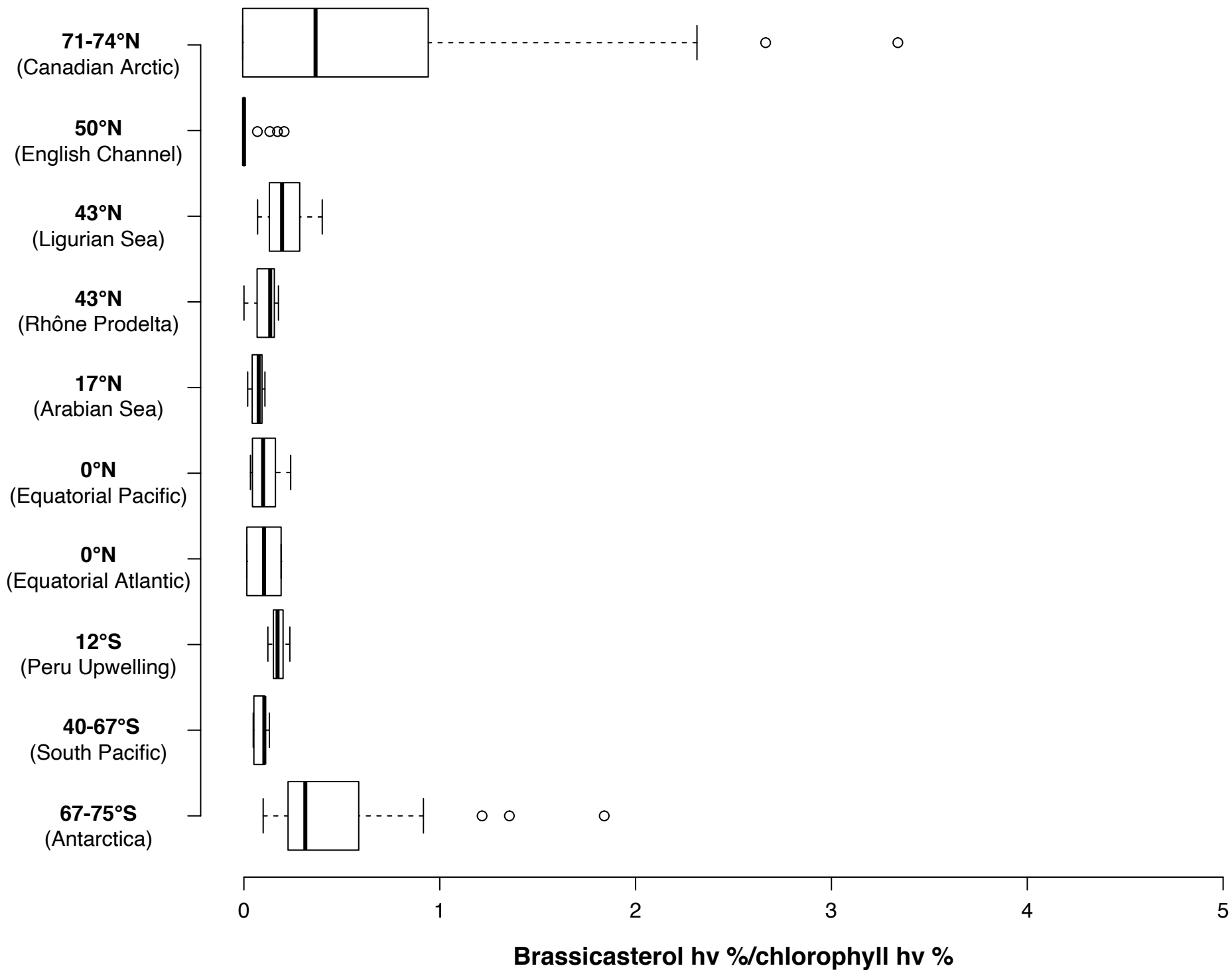
^b Amiraux et al., 2017

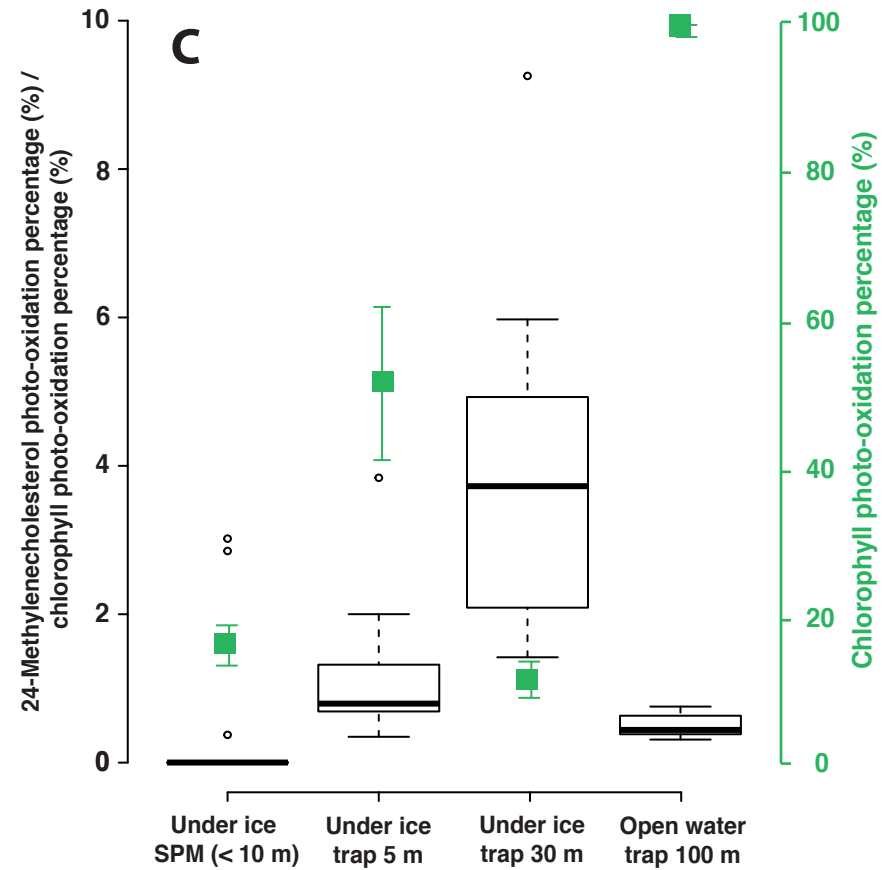
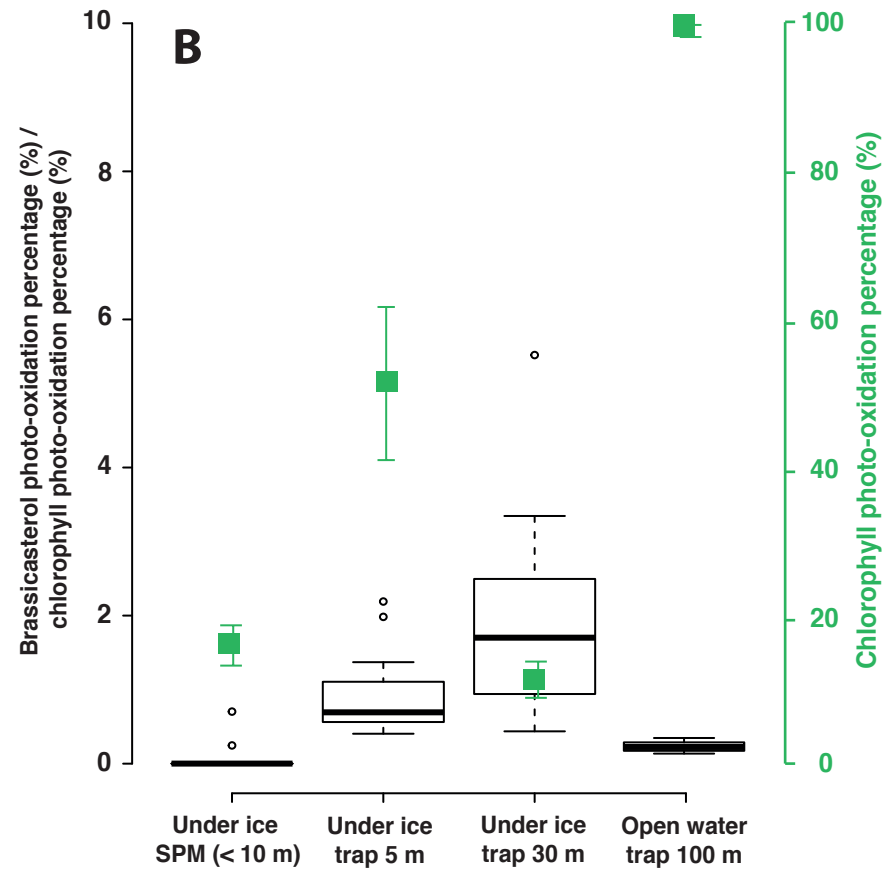
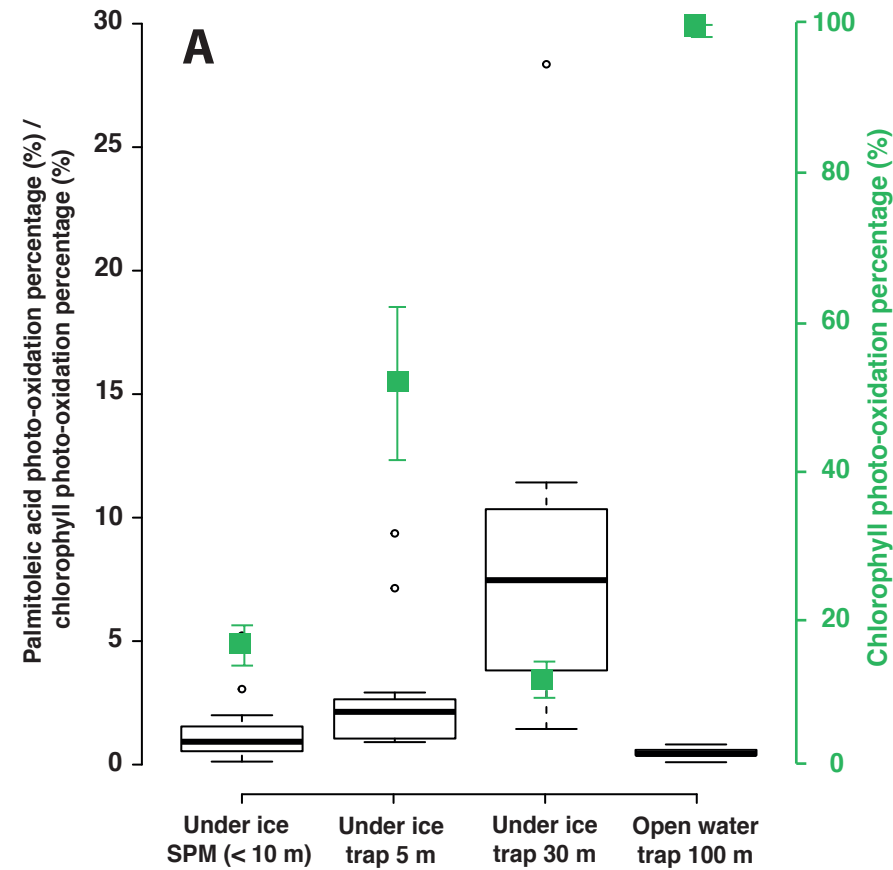
^c Rontani et al., 2016

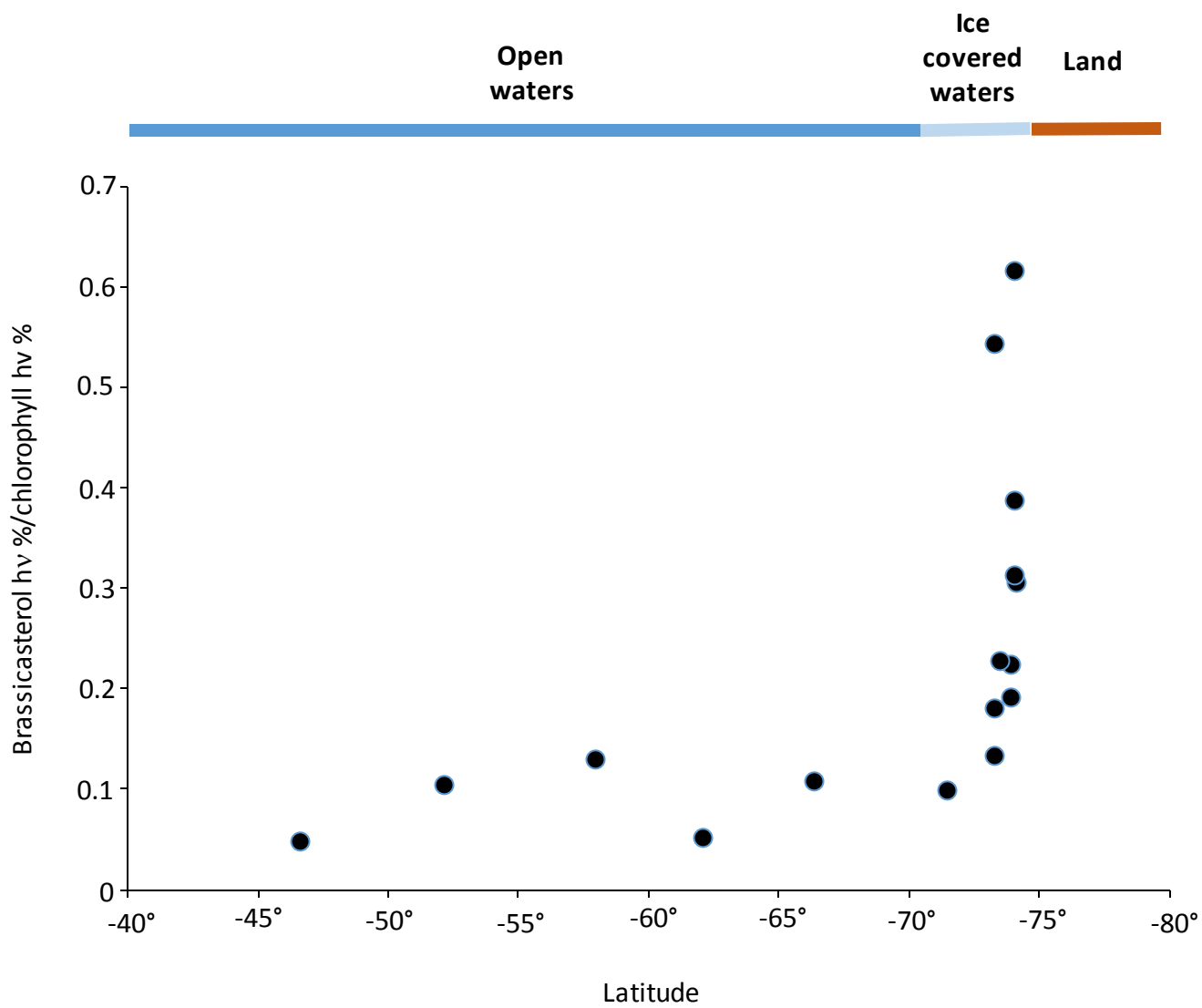
^d Rontani et al., 2012











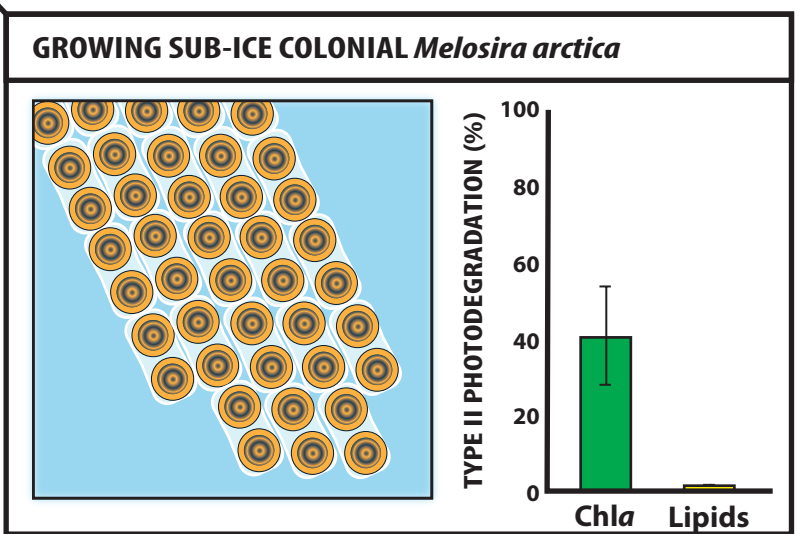
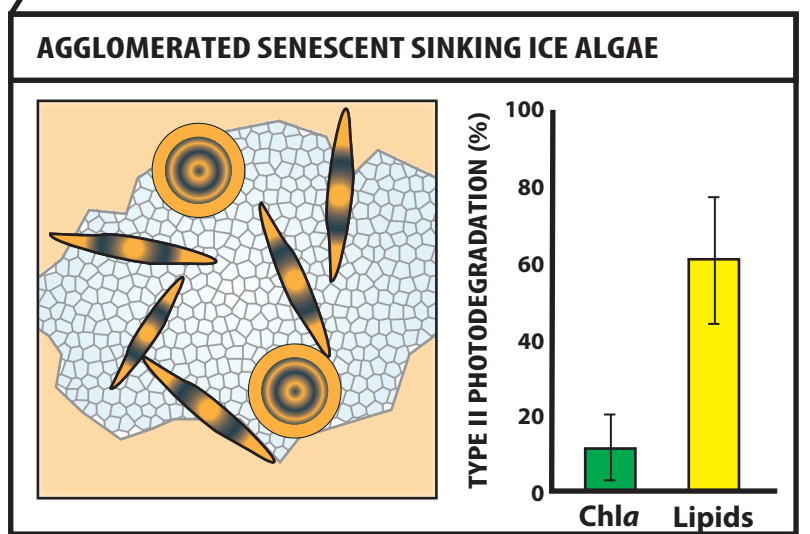
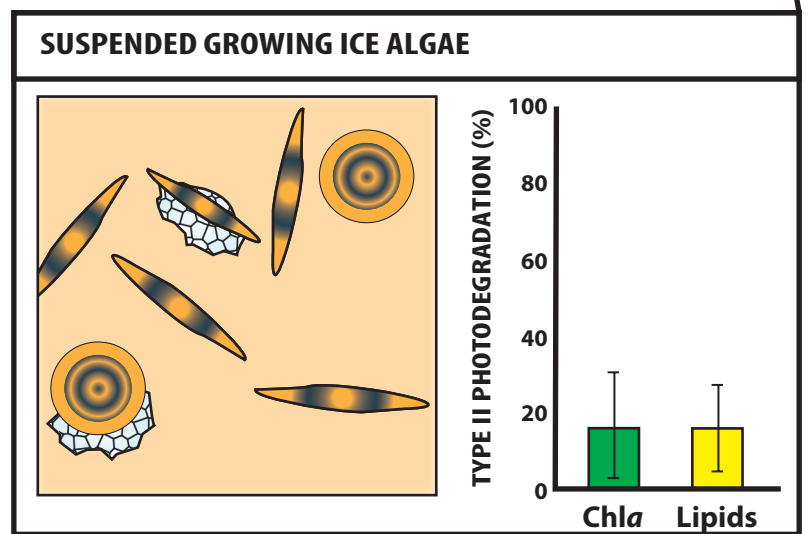
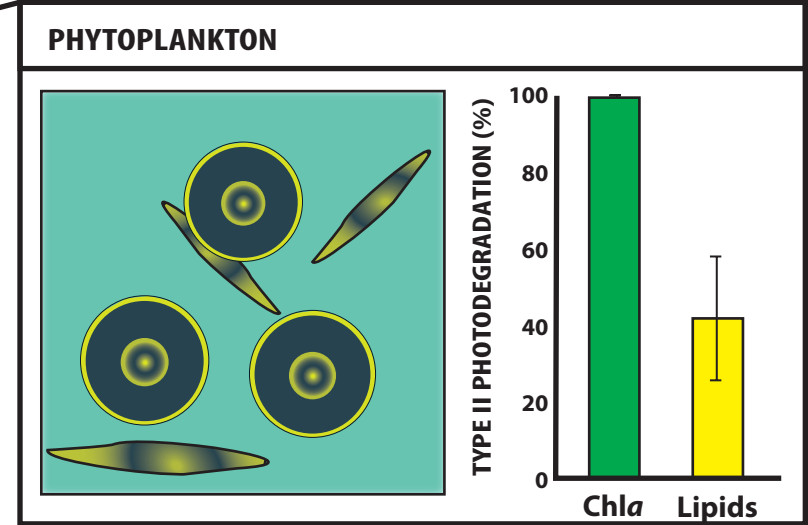
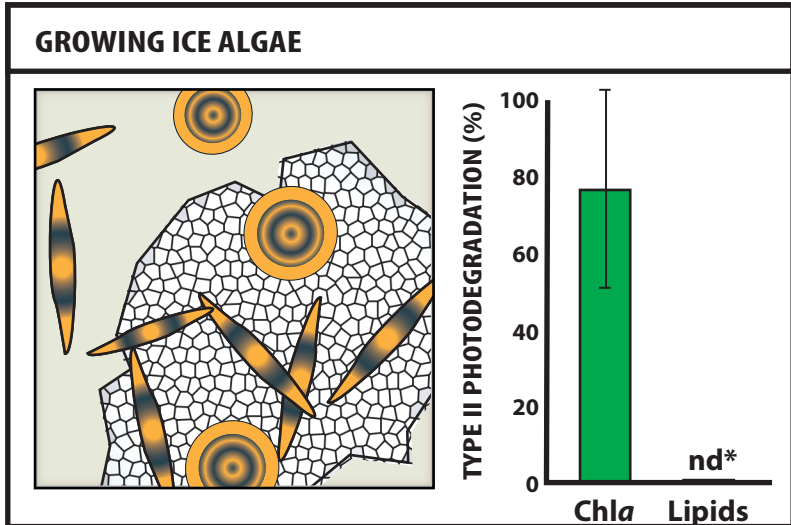
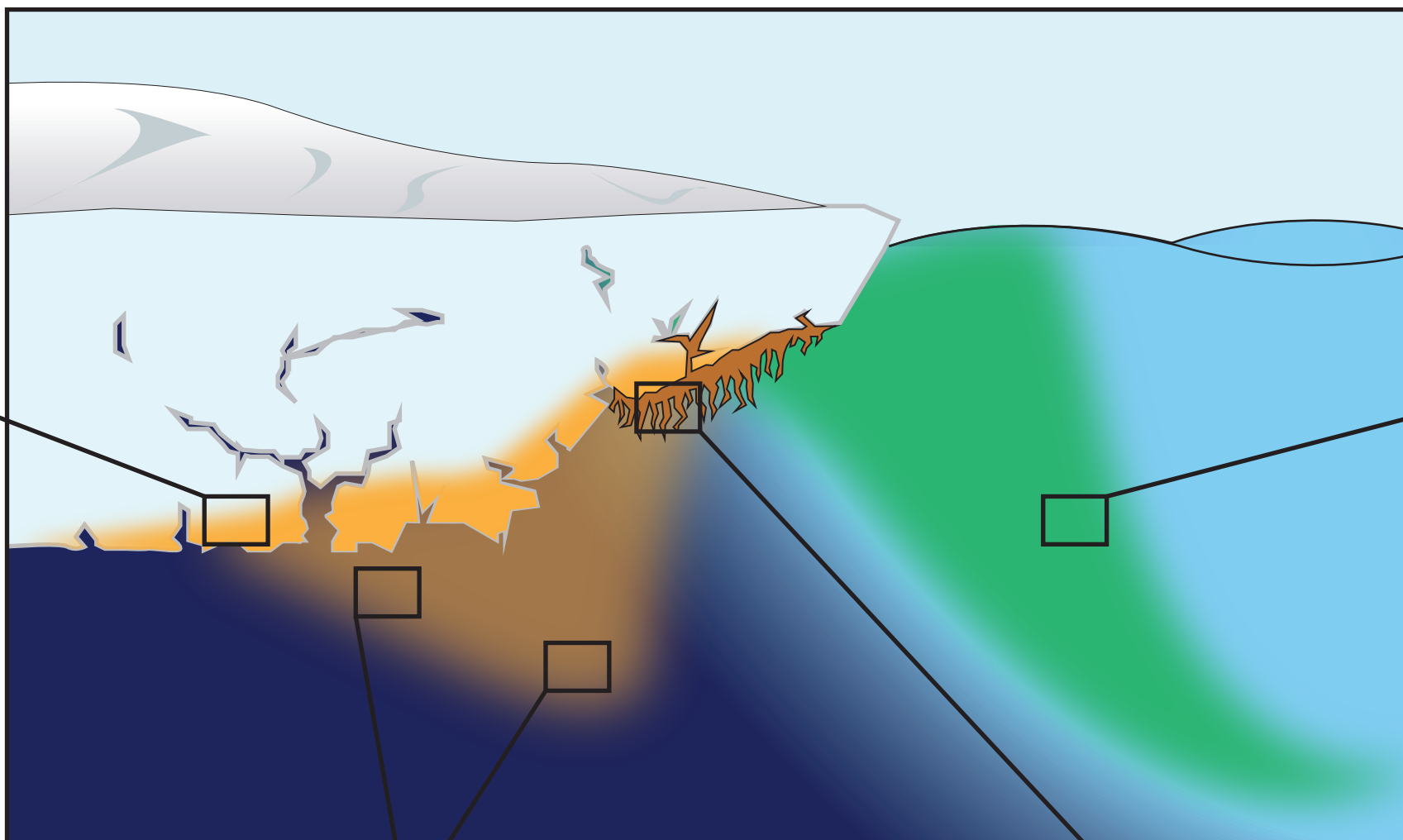


Table S1: Results of Mann – Whitney – Wilcoxon analysis testing the effect of the latitude on the brassicasterol photooxidation percentage : chlorophyll *a* photooxidation percentage ratio. Bold values are indicative of significance.

Source of variation	W	<i>p</i> -value
High latitudes ^a x low latitudes ^b	3861.5	1×10^{-7}
Arctic x Antarctic	583	0.71
Arctic x low latitudes	1107.5	7×10^{-4}
Antarctic x low latitudes	1513	2×10^{-9}

^a Sum of Arctic and Antarctic values

^b Sum of low latitude values (between 67°S and 50°N)

Table S2: Results of Mann – Whitney – Wilcoxon analysis testing the effect of the sample type on the 24-methylenecholesterol photo-oxidation percentage / chlorophyll photo-oxidation percentage, palmitoleic acid photo-oxidation percentage / chlorophyll photo-oxidation percentage and brassicasterol photo-oxidation percentage / chlorophyll photo-oxidation percentage ratios. Bold values are indicative of significance.

Source of variation	24-Me-cholesterol		Brassicasterol		Palmitoleic acid	
	W	<i>p-value</i>	W	<i>p-value</i>	W	<i>p-value</i>
Sea ice x SPM	180	0.4372	212.5	0.5858	4	1.0 x 10⁻⁷
Sea ice x all traps	1	3.0 x 10⁻¹⁰	2	3.7 x 10⁻¹⁰	3	7.2 x 10⁻¹⁰
SPM x all traps	78	3.3 x 10⁻⁶	27	2.0 x 10⁻⁸	242	0.1034
Surface ^a x Traps ^b	79	5.6 x 10⁻¹²	29	7.6 x 10⁻¹⁴	245	1.4 x 10⁻⁶
Traps 5 m x Traps 30 m	10	2.0 x 10⁻⁴	29	0.0225	19	0.0028
Traps 5 m x Traps 100 m	16	2.3 x 10⁻³	0	1.5 x 10⁻⁶	0	1.5 x 10⁻⁶
Traps 30 m x Traps 100 m	0	3.6 x 10⁻⁵	0	7.4 x 10⁻⁷	0	7.4 x 10⁻⁷

^a Sum of sea ice and SPM

^b Sum of traps