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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Abstract

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

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

1. Introduction

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

In healthy phytoplankton cells, light absorption by chlorophyll creates an excited singlet state (^{1}Chl), which leads to the classical fast reactions of photosynthesis (Foote, 1976). The energy of this excited state is then transferred to various substrates, where it promotes photosynthetic reactions, while a relatively small proportion of ^{1}Chl (<0.1%) undergoes intersystem crossing (ISC) to form the longer-lived triplet state (^{3}Chl; Knox and Dodge, 1985) (Fig. 1). ^{3}Chl is not only potentially damaging in itself in Type I reactions (Knox and Dodge, 1985), but can also generate reactive singlet oxygen ($^1O_2$) by reaction with ground state oxygen ($^3O_2$) via Type II photoprocesses (Fig. 1) (Krieger-Liszkay, 2005). Despite the production of other Reactive Oxygen Species (ROS), it is generally considered that the photo-production of $^1O_2$ plays the major role in light-induced damage to plant cells (Triantaphylides et al., 2008).

In view of the susceptibility of plant cells to oxidative damage, there are many antioxidant protective mechanisms in chloroplasts. For example, carotenoids quench ^{3}Chl and $^1O_2$ by energy transfer mechanisms at very high rates (Fig. 1). Such antioxidants have a dual role: first, they limit $^1O_2$ formation, and second, they help remove any $^1O_2$ that does form (Foote, 1976; Tefler, 2002). Tocopherols and ascorbic acid are also efficient quenchers of $^1O_2$ (Halliwell, 1987; Havaux et al., 2005).

In senescent phototrophic organisms, the cessation of photosynthetic reactions results in an accelerated rate of formation of ^{3}Chl and ROS (mainly $^1O_2$) (Nelson, 1993; Triantaphylides et al., 2008). The rate of formation of these potentially damaging species then often exceeds the quenching capacity of the photoprotective system such that photodegradation of cell components can occur via the so-called photodynamic effect (Merzlyak and Hendry, 1994) (Fig. 1). Direct and irreversible reaction of ^{3}Chl with $^3O_2$ (photobleaching) gives photooxidation products (Harbour and Bolton, 1978) (Fig. 1), while $^1O_2$ reacts extremely rapidly with nearby biomolecules at near diffusion-controlled rates (photodynamic effect) (Knox and Dodge, 1985; Cadenas, 1989; Skovsen et al., 2005). The very high reactivity of $^1O_2$ with numerous cell components (unsaturated lipids, some amino acids, nucleic acids; Rontani, 2012, Devasagayam and Kamat, 2002) is a consequence of the loss of the spin restriction that normally hinders reaction of $^3O_2$ with these biomolecules (Zolla and Rinalducci, 2002). $^1O_2$ also reacts with the sensitizer (chlorophyll) inducing its photobleaching (Nelson, 1993; Rontani, 2012) (Fig. 1). It is important to note, however, that photobleaching of the sensitizer reduces $^1O_2$ production and is thus competitive with the photodynamic effect.

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

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

2. Experimental

2.1. Sample collection

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

123 *2.2. Sample treatment*

124 The whole material of the different samples was reduced with excess $NaBH_4$ 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 Na_2SO_4, 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 N_2, 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

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

2.4. Data treatment

2.4.1 Chlorophyll photooxidation estimates

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

2.4.1. Lipid photooxidation estimates

The extent of photooxidation (%) of sterols was estimated using the equation: Δ^5-sterol photooxidation % = (Δ^4-stera-6α/β-diols % × (1+0.3)/0.3) (Christodoulou et al., 2009).

Type II photosensitized oxidation of MUFAs was estimated after quantification of isomeric *trans* allylic hydroxyacids resulting from $NaBH_4$-reduction of the corresponding photochemically-produced hydroperoxides after subtraction of the amounts of these compounds arising from autoxidation (Marchand and Rontani, 2001).

2.4.3. Statistical analysis

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

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

3. Results and discussion

Since photodynamic processes and sensitizer photobleaching are competitive processes (Fig. 1), we used the ratio of the % photooxidation of membrane lipids to that of chlorophyll to estimate the efficiency of Type II photosensitized oxidation processes (the photodynamic effect in Fig. 1) in senescent phytoplankton at different latitudes. In the case of brassicasterol, a phytoplanktonic Δ^5-sterol widely distributed in the oceans (Volkman, 1986, 2003), values of this ratio obtained from previously published and unpublished data sets (Table 1) show a strong increase (albeit with high variability) in samples from the polar regions in comparison to samples collected from temperate and equatorial settings (Fig. 3). Such increases were found to be significant when the data from the temperate and equatorial settings were compared with those from the Arctic and Antarctic datasets (and the combined Arctic/Antarctic dataset), yet no significant difference was found between the high latitude datasets (Table S1). Low temperatures have previously been shown to reduce diffusion rate of $^1O_2$ through cell membranes (Ehrenberg et al., 1998), thus favouring the intra-cellular involvement of the photodynamic effect. More recently, Amiraux et al. (2016) confirmed these results in the case of the centric diatom *Chaetoceros neogracilis* (strain RCC2022) and observed an increase (3.0 ± 0.5 fold) of the ratio k_{camp}/k_{chl} (where k_{camp} is the first-order photodegradation rate of campesterol and k_{chl} this of chlorophyll) when the temperature decreased from 17 to 7°C. The characteristic low temperatures of the Arctic and Antarctic could thus be the cause of the high 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

released from the ice are generally concentrated into aggregates that become sinking particles (Riebesell et al., 1991). Moreover, sympagic diatoms exhibit a higher sensitivity towards light-induced stress than pelagic diatoms (Kvernvik et al., 2020). Such differences in sensitivity were attributed, in part, to the gradually changing and low amplitude irradiance typically experienced by sympagic algae (Hill et al., 2018), whereas pelagic cells in open water, in contrast, experience high amplitude changes in light intensity over much shorter timescales (MacIntyre et al., 2000). This interesting hypothesis is not supported, however, by: (i) the very low efficiency of the photodynamic effect observed in the bottom-most layer of sea ice (Table 2) and (ii) the lack of correlation between lipid photooxidation % and the concentration of the sea ice lipid biomarker IP_{25} (a well-known sea ice proxy, for reviews see Belt and Müller, 2013; Belt, 2018) in under ice traps ($R^2 < 0.008$).

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

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

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

4. Conclusions

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

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

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519

520 **Figure captions**

521

522 **Figure 1.** Potential pathways for chlorophyll (Chl) excitation energy in senescent
523 phytoplankton cells (simplified scheme limited to the formation of $^1O_2$ 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

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

Table captions

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

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.

Supplementary material

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.

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.

Table 1

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

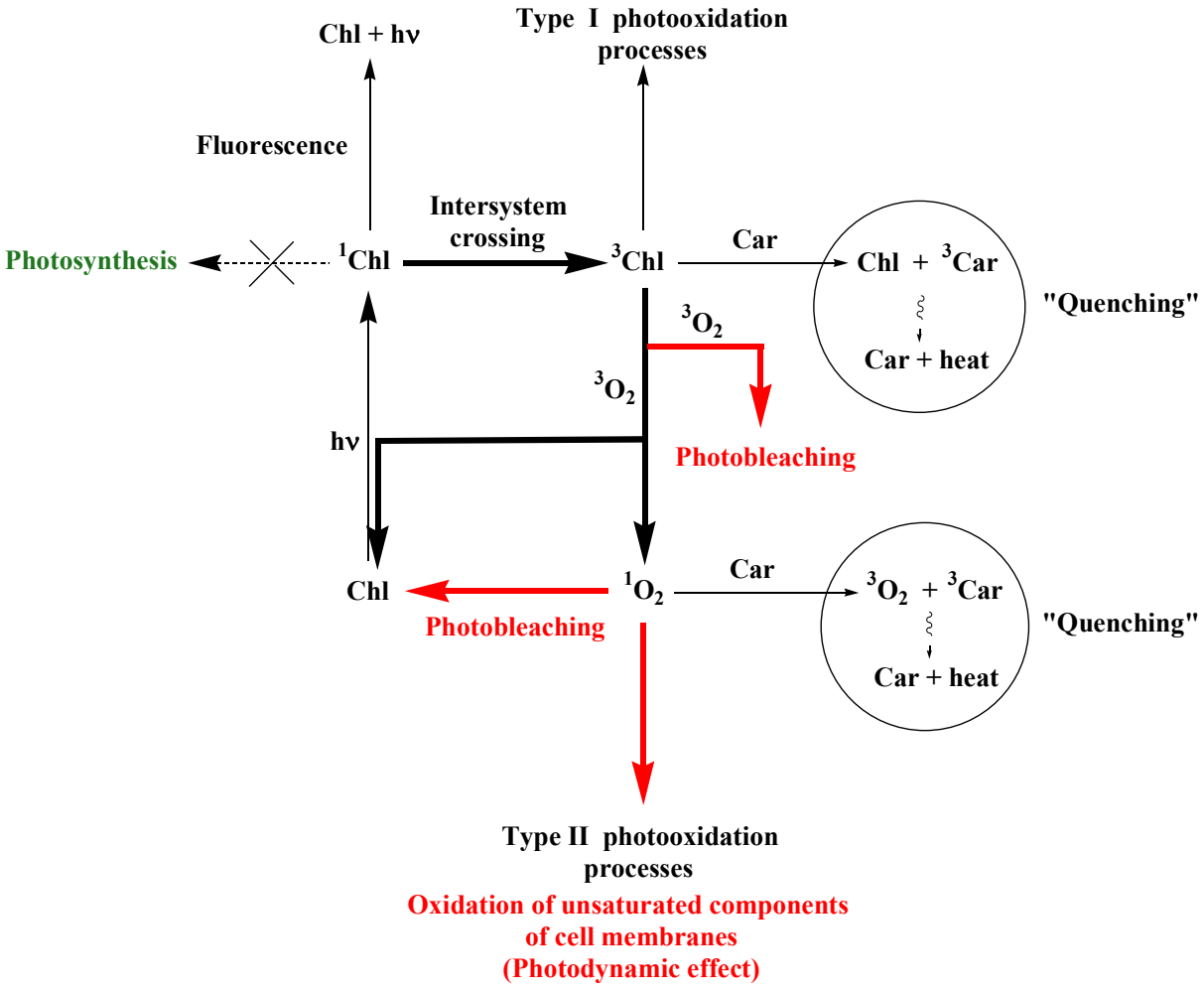
Latitude	Location	Nature of particles	n	Brassicasterol hν %/Chlorophyll hν %	References
71-74°N	Canadian Arctic	Suspended and sinking	46	0.77 ± 1.10	Rontani et al., 2012; 2016
50°N	English Channel	Suspended	24	0.02 ± 0.04	Rontani et al., 2021
43°N	Rhône Prodelta	Suspended	21	0.21 ± 0.11	Galeron et al., 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

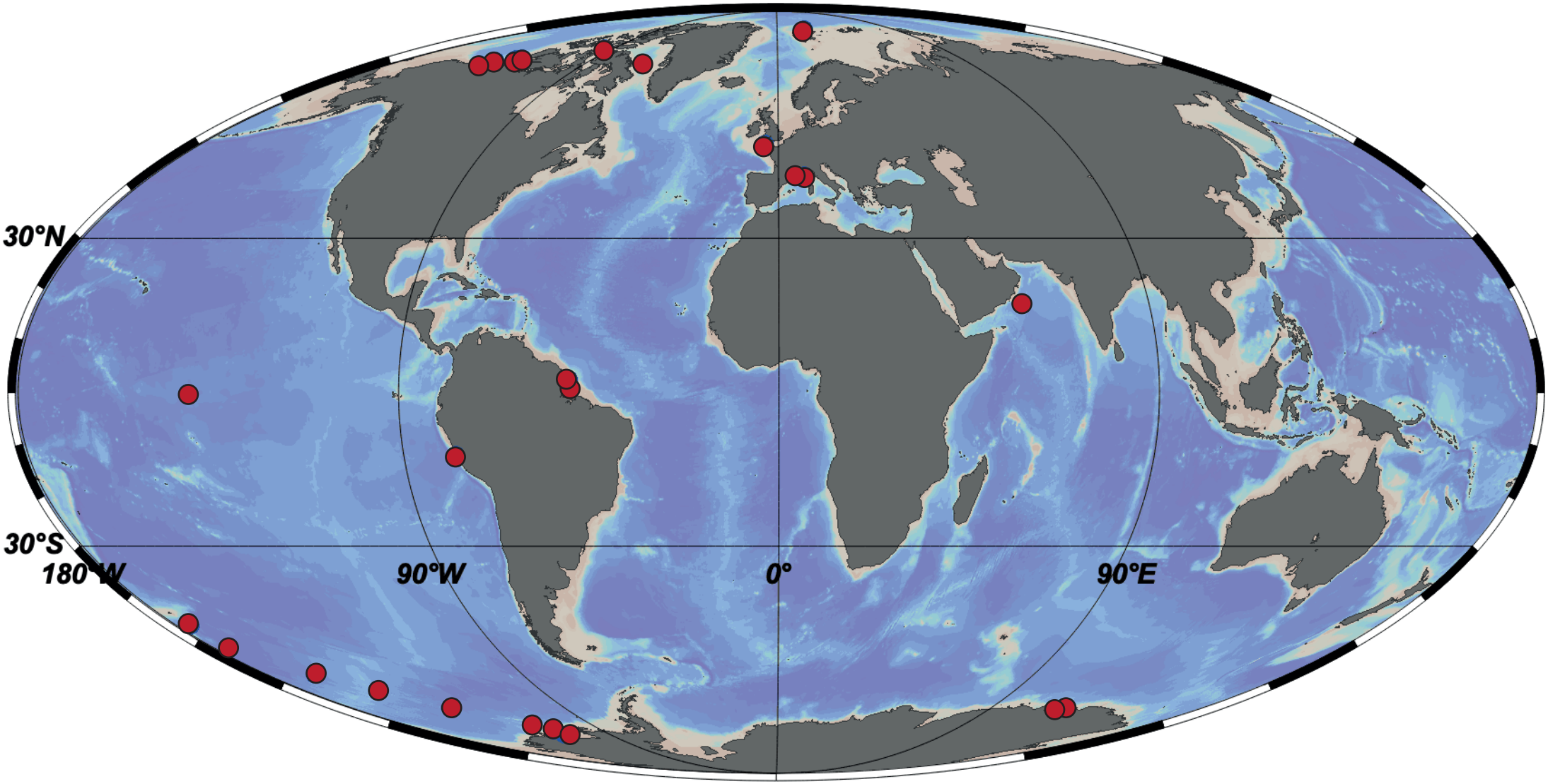
Table 2

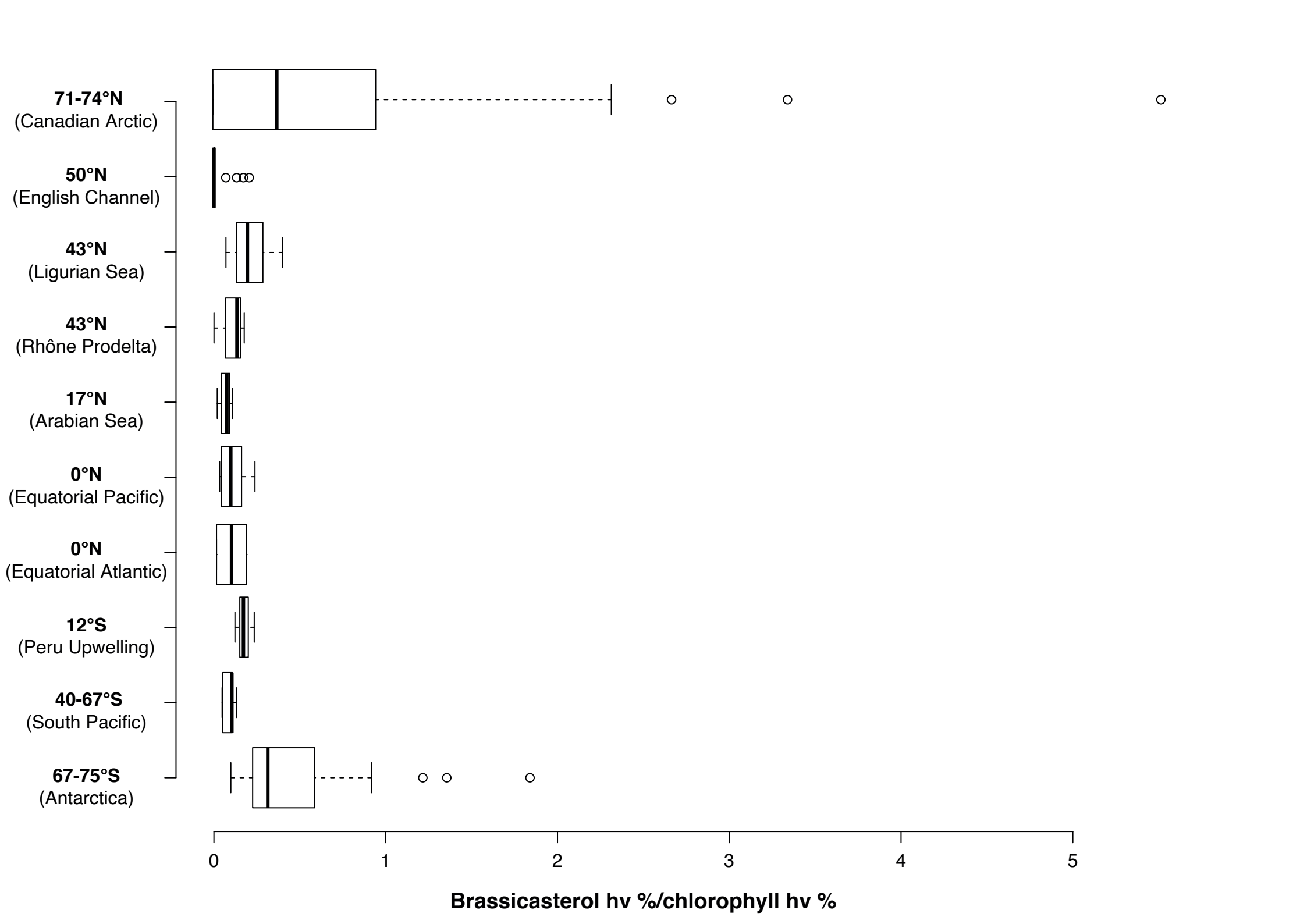
Photooxidation of chlorophyll, brassicasterol, 24-methylenecholesterol and palmitoleic acid in different sea ice, *M. arctica* and particulate matter samples collected in the Arctic.

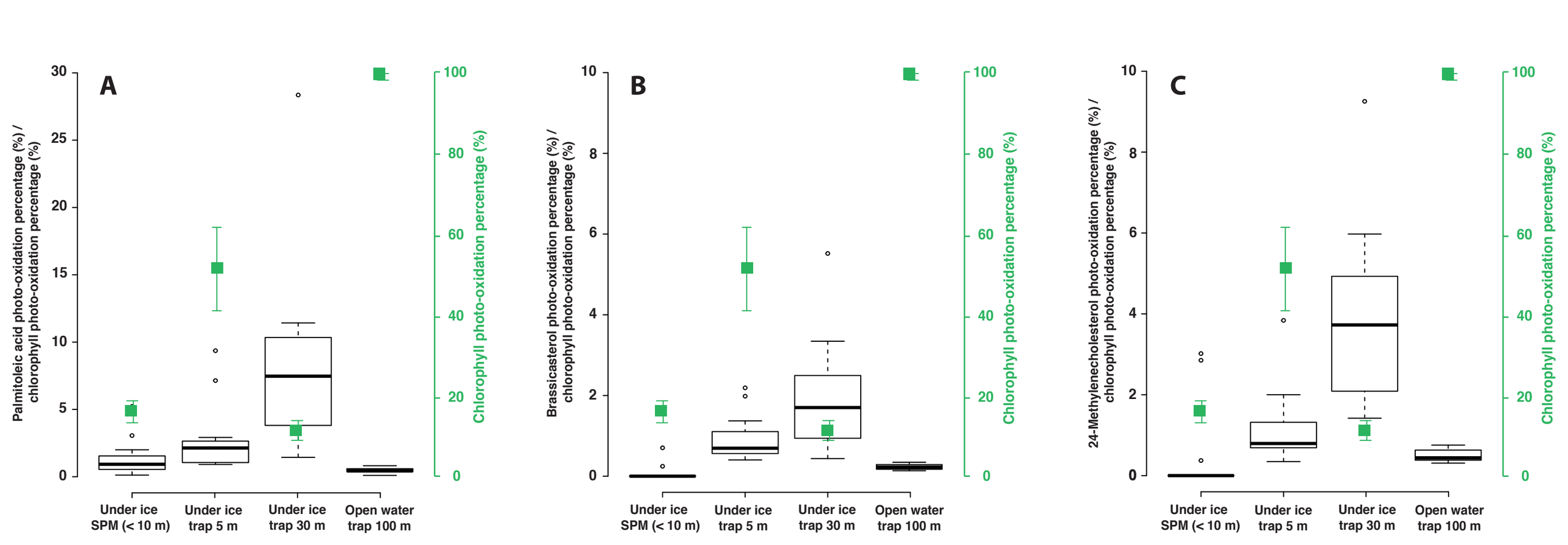
Samples	Location	n	Chlorophyll photooxidation %	Brassicasterol photooxidation %/ chlorophyll photooxidation %	24-Methylenecholesterol photooxidation %/ chlorophyll photooxidation %	Palmitoleic acid photooxidation %/ chlorophyll photooxidation %
Sea ice (0-3 cm)	Resolute Passage[a] and Davies Strait[b]	21	54.5 ± 38.4	0.02 ± 0.05	0.04 ± 0.10	0.05 ± 0.08
Melosira arctica	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

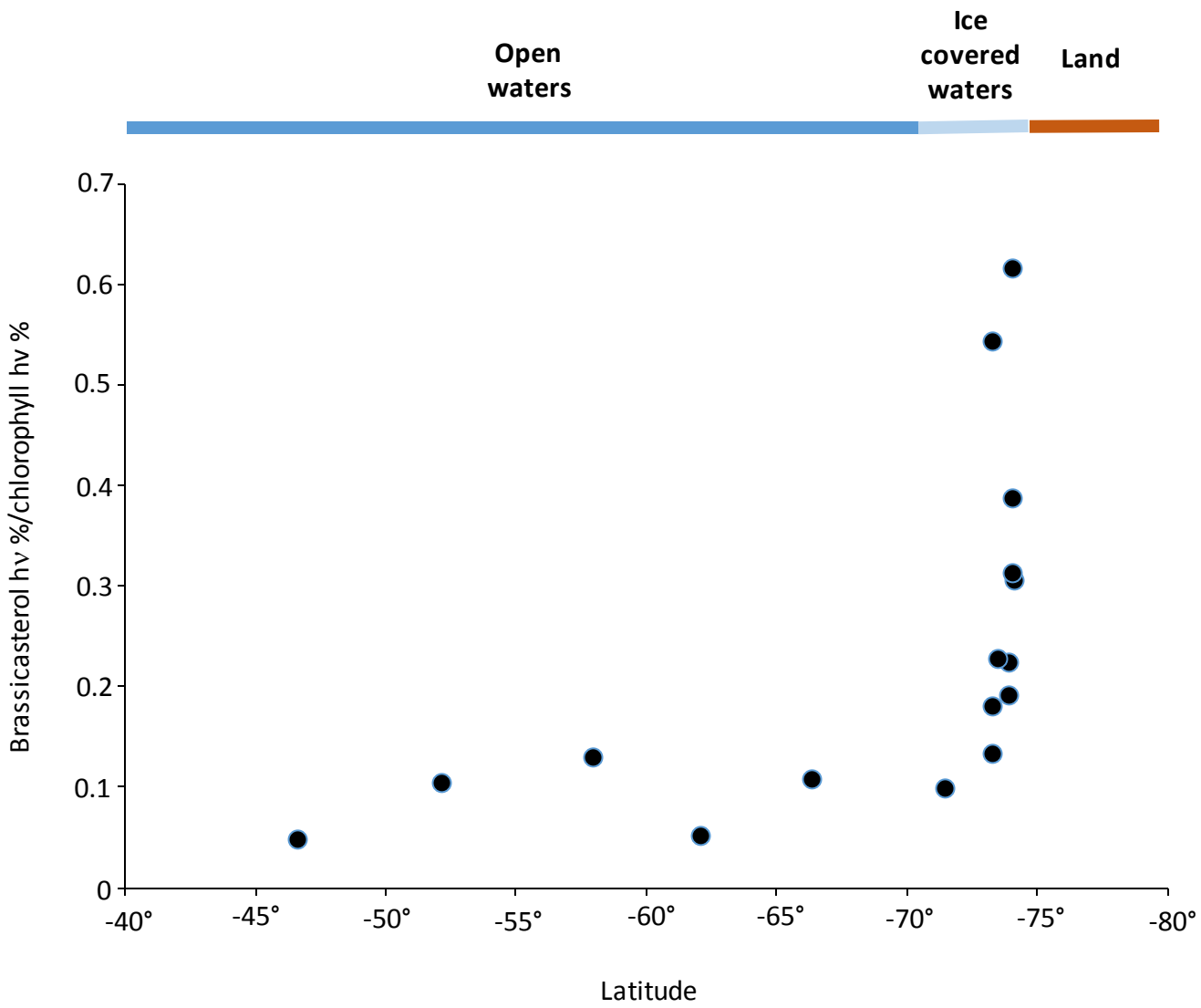
[a] Rontani et al., 2014
[b] Amiraux et al., 2017
[c] Rontani et al., 2016
[d] Rontani et al., 2012

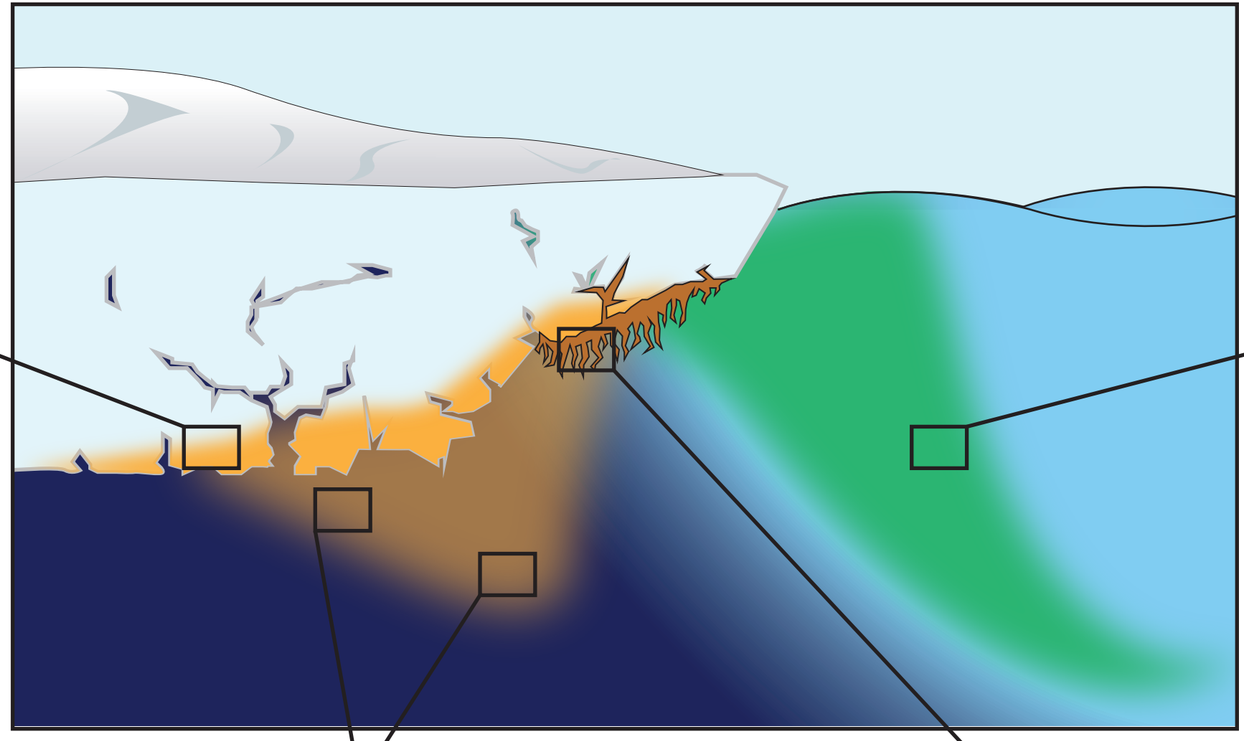

Chl + hν
Type I photooxidation processes
Fluorescence
Intersystem crossing
Photosynthesis
^{1}Chl
^{3}Chl
Car
Chl + ^{3}Car
Car + heat
"Quenching"
$^3O_2$
$^3O_2$
hν
Photobleaching
Chl
$^1O_2$
Car
$^3O_2$ + ^{3}Car
Car + heat
"Quenching"
Photobleaching
Type II photooxidation processes
Oxidation of unsaturated components of cell membranes (Photodynamic effect)


30°N
30°S
180°W
90°W
0°
90°E
Ocean Data View

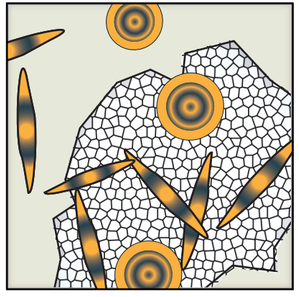

71-74°N
(Canadian Arctic)
50°N
(English Channel)
43°N
(Ligurian Sea)
43°N
(Rhône Prodelta)
17°N
(Arabian Sea)
0°N
(Equatorial Pacific)
0°N
(Equatorial Atlantic)
12°S
(Peru Upwelling)
40-67°S
(South Pacific)
67-75°S
(Antarctica)
0
1
2
3
4
5
Brassicasterol hv %/chlorophyll hv %

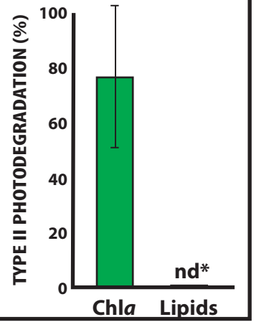

A
B
C
Palmitoleic acid photo-oxidation percentage (%) / chlorophyll photo-oxidation percentage (%)
Brassicasterol photo-oxidation percentage (%) / chlorophyll photo-oxidation percentage (%)
24-Methylenecholesterol photo-oxidation percentage (%) / chlorophyll photo-oxidation percentage (%)
Chlorophyll photo-oxidation percentage (%)
Under ice SPM (< 10 m)
Under ice trap 5 m
Under ice trap 30 m
Open water trap 100 m


Open waters
Ice covered waters
Land
Brassicasterol hv %/chlorophyll hv %
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-40°
-45°
-50°
-55°
-60°
-65°
-70°
-75°
-80°
Latitude

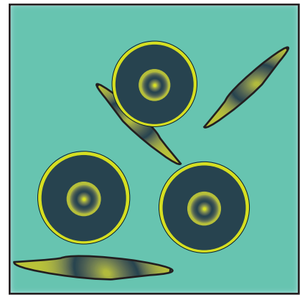


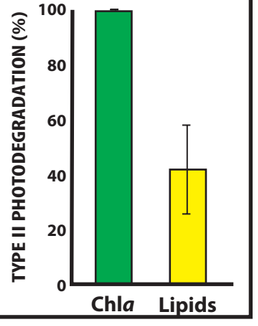
GROWING ICE ALGAE



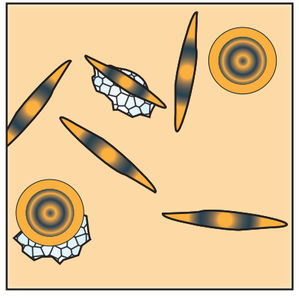


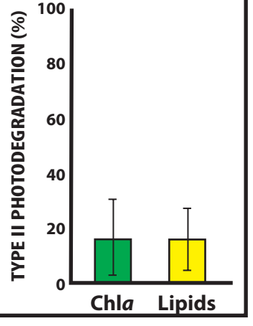
PHYTOPLANKTON



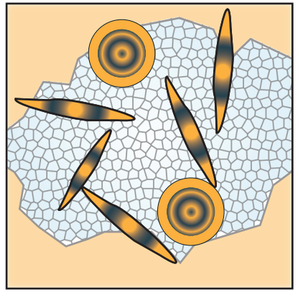


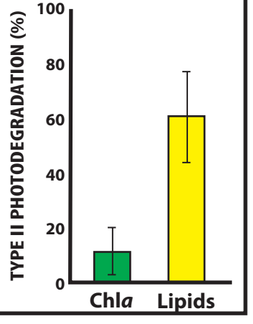
SUSPENDED GROWING ICE ALGAE



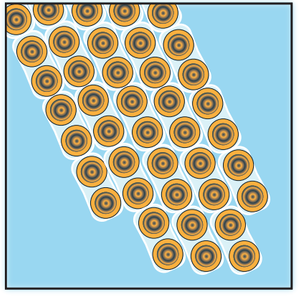


AGGLOMERATED SENESCENT SINKING ICE ALGAE





GROWING SUB-ICE COLONIAL *Melosira arctica*



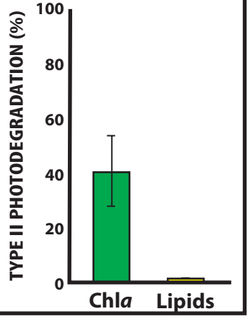


Table S1: Results of Mann – Whitney – Wilcoxon analysis testing the effect of the latitude on the brassicasterol photooxidation percentage : chlorophyll *a* photooxidation percentage ratio. Bold values are indicative of significance.

Source of variation	W	*p-value*
High latitudes[a] x low latitudes[b]	3861.5	$\mathbf{1 \times 10^{-7}}$
Arctic x Antarctic	583	0.71
Arctic x low latitudes	1107.5	$\mathbf{7 \times 10^{-4}}$
Antarctic x low latitudes	1513	$\mathbf{2 \times 10^{-9}}$

[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	*p-value*	W	*p-value*	W	*p-value*
Sea ice x SPM	180	0.4372	212.5	0.5858	4	**1.0×10^{-7}**
Sea ice x all traps	1	**3.0×10^{-10}**	2	**3.7×10^{-10}**	3	**7.2×10^{-10}**
SPM x all traps	78	**3.3×10^{-6}**	27	**2.0×10^{-8}**	242	**0.1034**
Surface[a] x Traps[b]	79	**5.6×10^{-12}**	29	**7.6×10^{-14}**	245	**1.4×10^{-6}**
Traps 5 m x Traps 30 m	10	**2.0×10^{-4}**	29	**0.0225**	19	**0.0028**
Traps 5 m x Traps 100 m	16	**2.3×10^{-3}**	0	**1.5×10^{-6}**	0	**1.5×10^{-6}**
Traps 30 m x Traps 100 m	0	**3.6×10^{-5}**	0	**7.4×10^{-7}**	0	**7.4×10^{-7}**

[a] Sum of sea ice and SPM

[b] Sum of traps