



## **Singlet oxygen-induced alteration of bacteria associated with phytodetritus: Effect of irradiance**

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**Singlet oxygen-induced alteration of bacteria associated  
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**Abstract.** Contrasting irradiation of senescent cells of the diatom *Thalassiosira* sp. in association with the bacterium *Pseudomonas stutzeri* showed the effect of intensity of irradiance on the transfer of singlet oxygen ( $^1\text{O}_2$ ) to bacteria attached to phytoplanktonic cells. Under low irradiances,  $^1\text{O}_2$  is produced slowly, favors the oxidation of algal unsaturated lipids (photodynamic effect) and limits  $^1\text{O}_2$  transfer to attached bacteria. However, high irradiances induce a rapid and intense production of  $^1\text{O}_2$ , which diffuses out of the chloroplasts and easily reaches the attached bacteria, where it efficiently oxidizes their unsaturated membrane components. Analysis of numerous sinking particle samples collected in different regions of the Canadian Arctic showed that the photooxidation state of attached bacteria increased from ice-covered areas to open water, in agreement with *in vitro* results. Photooxidation of bacteria appeared to be particularly intense in sea ice, where the sympagic algae–bacteria association is maintained at relatively high irradiances for long periods of time.

**Keywords.** Senescent phytoplankton; Attached bacteria; Type II photosensitized oxidation; Irradiance effect; Arctic; Sinking particulate matter; Sea ice.

## 1. Introduction

Type II photooxidation processes are light-induced indirect degradation reactions, that involve the action of a photosensitizer molecule (typically pigments or aromatic compounds) in its triplet state (Gollnick, 1968). Chlorophyll, which is an efficient photosensitizer (Foote, 1976), can trigger type II photooxidation processes in phytoplanktonic cells, especially in late bloom phases when they are senescent (Nelson, 1993). Indeed, in senescent cells, the cessation of photosynthetic reactions results in an accelerated rate of formation of  $^3\text{Chl}$  and reactive oxygen species (ROS), mainly singlet oxygen ( $^1\text{O}_2$ ) (Knox and Dodge, 1985; Nelson, 1993). The rate of formation of these potentially damaging species can then exceed the quenching capacity of the photoprotective system, thus enabling the photodegradation of cell components (photodynamic effect) to occur (Merzlyak and Hendry, 1994).  $^1\text{O}_2$  reacts with a broad range of cellular compounds but especially unsaturated lipids such as sterols and unsaturated fatty acids (Rontani and Belt, 2020), proteins (Morgan et al., 2004) and nucleic acids (Agnez-Lima et al., 1999; Ravanat et al., 2000). The very high reactivity of  $^1\text{O}_2$  with these biomolecules is due to the lack of spin restriction that normally prevents  $^3\text{O}_2$  from reacting with these compounds (Zolla and Rinalducci, 2002).

The  $^1\text{O}_2$  thus formed reacts not only with membrane components of phytoplankton but also with the monounsaturated fatty acids (MUFAs) of its neighboring attached bacteria (Rontani et al., 2003; Christodoulou et al., 2010, Petit et al., 2013, 2015). Indeed, in phototrophic cells, the radius of the sphere of activity of  $^1\text{O}_2$  from its point of production was estimated to be between 155 and 340 nm (Baier et al., 2005; Ogilby, 2010; Skovsen et al., 2005), which is a **sufficient** distance to allow it to cross the cellular membranes (Ogilby, 2010) and thus attack attached bacteria.

It has previously been demonstrated that low solar irradiance favors slow production and diffusion of  $^1\text{O}_2$  through the membranes and thus increases photooxidative damage of

the unsaturated algal lipids (Amiraux et al., 2016). However, the effects of intensity of solar irradiance on the photooxidation of bacteria attached to phytodetritus are totally unknown.

Here, to clarify this issue, we incubated senescent cells of the diatom *Thalassiosira* sp. (a phytoplankton genus widely distributed in oceans, Malviya et al., 2016) in association with the bacteria *Pseudomonas stutzeri* under contrasted artificial light irradiances. Bacteria of the *Pseudomonas* genus were selected because they are often associated with *Thalassiosira* cells (Bidle and Azam, 2001; Schaum, 2019). To validate the results, we compared the photooxidation state of diatoms and their attached bacteria in numerous samples of Arctic sea ice and sinking particulate matter. Samples were collected at different depths under open water, marginal ice zone and first-year ice).

## 2. Material and methods

### 2.1 Collection of in situ samples

Detailed descriptions of the Arctic marine particulate matter and sea ice sample collection processes (e.g. sampling dates, depths, volumes, etc.) can be found in Rontani et al. (2012, 2016, 2022) and Amiraux et al. (2020). Briefly, sinking particles were collected i) in Resolute Passage under first-year ice at 5 m and 30 m depth with Hydro-Bios MS12-model multi-sediment traps (Rontani et al., 2016), ii) in central Baffin Bay under the marginal ice zone at 25 m depth with a Technicap PPS4 drifting sediment trap (Rontani et al., 2022), and iii) in the Beaufort Sea in open water at 100 m depth with Technicap PPS traps (Rontani et al., 2012). Sea-ice samples were collected at GreenEdge Project landfast ice station located near Broughton Island in the Davis Strait using a Kovacs Mark V 14-cm-diameter corer and focusing on the bottommost 10 cm of sea ice (Amiraux et al., 2020) (Fig. 1).

## 2.2. Algal phytodetritus production

The non-axenic diatom *Thalassiosira* sp. RCC1714 was obtained from the Roscoff culture collection. Diatoms were grown in F/2 medium at 17°C in a constant-environment cabinet under an irradiance of 18 W.m<sup>-2</sup> (Osram, Lumilux 12:12h light/dark cycle). After two months of growth, cell density was measured by counting under microscope, and death of the algal cells was induced by sonication. *Thalassiosira* sp. cells were sonicated on ice using a Branson Sonifier 450 ultrasound generator equipped with a Branson S450A cell disruptor probe at 240 W for 10 minutes (duty cycle 50%). The sonicated cells were then sub-sampled in 50 mL Falcon tubes and stored at -20°C for later photooxidation experiments.

## 2.3. Culturing of *P. stutzeri*

Pre-culture of *P. stutzeri* ATCC 14405 was grown aerobically overnight on a rotary shaker in the dark at 17°C on marine broth medium (US Biological™) diluted 1:10 with sterilized artificial sea water (Kester et al., 1967) therefore not adding large amounts of assimilable organic matter from the inoculum in the further steps. The culture was inoculated with the aerobic pre-culture to obtain an initial OD<sub>620nm</sub>, about 0.020. At the mid growth exponential phase, the incubation was stopped and cells counted based on epifluorescence in the presence of fluorochrome (4P,6-diamidino-2P-phenylindole dihydrochloride, DAPI) as described in Otto (1990).

## 2.4. Photooxidation experiments

Phytodetritus and bacteria were mixed (ratio algal:bacterial cells = 1:5) in K medium (Keller et al., 1987) to obtain a final volume of 100 mL. The experiments were performed in

triplicate. After taking three 10 mL sub-samples (controls before irradiation) the reactional systems were exposed to high or low irradiance.

#### 2.4.1. *High irradiance experiments*

The high-irradiance experiments were carried out in sterilized quartz and glass tubes (100 mL) with an Atlas Suntest CPS + solar simulator equipped with a Xenon NXE 1500 lamp producing a high solar irradiance ( $500 \text{ W.m}^{-2}$ ) in the 300–800 nm range, i.e. close to that generally observed at noon at the surface of the Mediterranean Sea (Sarrazin et al., 2019) and not far from the one observed at the surface of Arctic waters in summer (up to  $350 \text{ W m}^{-2}$ , Horvat et al., 2020). To eliminate UV radiation, experiments were also performed in glass tubes reducing the irradiance to  $446 \text{ W.m}^{-2}$ . After irradiation with a light dose of  $1000 \text{ KJ.m}^{-2}$  (corresponding to an irradiation time of 0.5 and 15 h at the surface and at the deep chlorophyll maximum (DCM) of the Mediterranean Sea, respectively), 10 mL was collected. All the samples were filtered on  $0.8 \mu\text{m}$  glass fiber filters (GF/F) to concentrate bacteria attached on phytodetritus and stored at  $-20^\circ\text{C}$  until further lipid extraction.

Controls were also conducted in triplicate with no phytodetritus. Bacteria (*P. stutzeri*) were mixed with sterilized artificial sea water complemented with  $0.1 \text{ g.L}^{-1}$  of lactate/acetate (50:50) as carbon source, in 100 mL sterilized quartz or glass tubes and exposed to light in the solar simulator for the same duration as the tubes containing phytodetritus and bacteria. After irradiation, 50 mL was sampled and bacteria were concentrated by centrifugation (Beckman & Coulter Allegra X-22 centrifuge at  $20,000 \text{ g}$  for 30 min). The irradiated bacterial cells were then stored at  $-20^\circ\text{C}$  until further lipid extraction.

#### 2.4.2. *Low irradiance experiments*



Low-irradiance photosynthetically active radiation (PAR) ( $18 \text{ W.m}^{-2}$ ) in the range 400–750 nm, i.e. comparable to that observed at the DCM in the Mediterranean Sea (Marañón et al., 2020), was obtained with a Binder incubator equipped with Osram Lumilux lamps. The vials were exposed to a light dose of  $1000 \text{ KJ.m}^{-2}$  in the incubator at  $17^\circ\text{C}$ . After irradiation, 10 mL samples were collected, filtered on  $0.8 \mu\text{m}$  GF/F and stored at  $-20^\circ\text{C}$  until further lipid extraction. Control experiments without phytodetritus were also carried out as described above.

### 2.5. Lipid extraction and derivatization

Samples (GF/F filters or bacterial pellets) were reduced with excess  $\text{NaBH}_4$  after adding MeOH (25 mL, 30 min) to reduce labile hydroperoxides (resulting from photooxidation) to alcohols, which are more amenable to gas chromatography-mass spectrometry (GC-MS) analysis. Water (25 mL) and KOH (2.8 g) were then added and the resulting mixture was saponified by refluxing (2 h), then cooled, acidified ( $\text{HCl}$ , 2 N) to pH 1, and extracted with dichloromethane ( $3 \times 20 \text{ mL}$ ). The combined extracts were then concentrated by rotary evaporation at  $40^\circ\text{C}$  to give total lipid extracts (TLEs).

Dry TLEs were derivatized by dissolving them in 300  $\mu\text{L}$  of a mixture of pyridine/bis-(trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v/v) and silylated in a heating block ( $50^\circ\text{C}$ , 1 h). After evaporation to dryness under a stream of  $\text{N}_2$ , the derivatized residue was dissolved in ethyl acetate/BSTFA (to avoid desilylation) and analyzed by GC-MS/MS.

### 2.6. Gas chromatography-tandem mass spectrometry (GC-MS/MS)

GC-MS/MS analyses were performed on an Agilent 7890A/7010A tandem-quadrupole gas chromatograph system (Agilent Technologies, Les Ulis, France) using a cross-linked 5% phenyl-methylpolysiloxane (Agilent; HP-5MS ultra inert,  $30 \text{ m} \times 0.25 \text{ mm}$ ,  $0.25 \mu\text{m}$  film

thickness) capillary column. Analyses were performed with an injector operating in pulsed splitless mode set at 270°C. Oven temperature was ramped from 70°C to 130°C at 20°C.min<sup>-1</sup>, then to 250°C at 5°C.min<sup>-1</sup> and finally to 300°C at 3°C.min<sup>-1</sup>. Pressure of the carrier gas (He) was maintained at  $0.69 \times 10^5$  Pa until the end of the temperature program, then ramped from  $0.69 \times 10^5$  Pa to  $1.49 \times 10^5$  Pa at  $0.04 \times 10^5$  Pa.min<sup>-1</sup>. The following mass spectrometer conditions were used: electron energy 70 eV, source temperature 230°C, quadrupole 1 temperature 150°C, quadrupole 2 temperature 150°C, collision gas (N<sub>2</sub>) flow 1.5 mL.min<sup>-1</sup>, quench gas (He) flow 2.25 mL.min<sup>-1</sup>, mass range 50–700 Daltons, cycle time 313 ms. Vaccenic acid photooxidation products were quantified in multiple reaction monitoring (MRM) mode using the transitions  $m/z$  339 → 131 for the parent vaccenic acid and  $m/z$  199 → 129,  $m/z$  213 → 129,  $m/z$  357 → 129 and  $m/z$  371 → 129 for its oxidation products (Rontani, 2021). Precursor ions were selected from the most intense ions and specific fragmentations observed in electron ionization (EI) mass spectra. Collision-induced dissociation (CID) was optimized by using collision energies at 5, 10, 15 and 20 eV. Quantification involved peak integration and determination of individual response factors using standard compounds and Mass Hunter software (Agilent Technologies, Les Ulis, France).

## 2.7. Standard compounds

Vaccenic and palmitoleic acids were obtained from Sigma-Aldrich. Vaccenic acid oxidation was achieved using Fe<sup>2+</sup>/ascorbate (Loidl-Stahlhofen and Spiteller, 1994). Subsequent reduction of the resulting hydroperoxides in methanol with excess NaBH<sub>4</sub> afforded the corresponding hydroxyacids.

## 2.8. Statistical analysis

Results of statistical tests were considered to be significant at a confidence level of 95% ( $\alpha = 0.05$ ). All tests were performed using XL-Stat Statistics software.

### 3. Results and Discussion

#### 3.1. *In vitro* experiments

To determine the effect of solar irradiance on the efficiency of transfer of  $^1\text{O}_2$  from phytodetritus to their attached bacteria, senescent *Thalassiosira* sp. cells associated with *P. stutzeri* were irradiated by a light dose of  $1000 \text{ KJ.m}^{-2}$  under contrasting irradiances, i.e. 18 (PAR), 446 (PAR) and 500 (UV+PAR)  $\text{W.m}^{-2}$ . The efficiency of  $^1\text{O}_2$  transfer to bacteria was estimated based on the measured concentration of photooxidation products of vaccenic acid ( $\text{pmol.L}^{-1}$ ). Vaccenic acid was present in high proportion in *P. stutzeri* (Rainey et al., 1994) but only in weak amount in the unknown bacterial community associated with the non-axenic strain of *Thalassiosira* sp. employed (amount estimated to be more than one order of magnitude lesser than this present in the cells of *P. stutzeri* added during the different experiments).

Type-II photosensitized oxidation of vaccenic acid involves the addition of  $^1\text{O}_2$  to the two carbon atoms of its  $\Delta^{11}$  double bond, and leads to the formation of 11-hydroperoxyoctadec-12(*trans*)-enoic and 12-hydroperoxyoctadec-10(*trans*)-enoic acids (Rontani, 2021). These hydroperoxides can subsequently undergo stereoselective radical allylic rearrangement to afford 13-hydroperoxyoctadec-11(*trans*)-enoic and 10-hydroperoxyoctadec-11(*trans*)-enoic acids, respectively (Porter et al., 1995). *Trans* allylic hydroxy acids arising from  $\text{NaBH}_4$  reduction of these hydroperoxyacids are sufficiently stable for use as tracers of type-II photosensitized oxidation processes (Marchand and Rontani, 2001).

218 Interestingly, we detected only trace amounts of vaccenic acid photooxidation  
219 products before irradiation (under the detection limit) and in the different controls carried  
220 out without algae (Table 1, Fig. 2). Significant increases of vaccenic acid photooxidation  
221 products were observed with algae amendment after 0.5 and 15H for low and high irradiance  
222 respectively (Wilcoxon test,  $n=6$ ,  $p=0.031<0.05$ ). As previously observed (Rontani et al.,  
223 2003; Petit et al., 2015), photooxidation of heterotrophic bacteria membranes requires the  
224 presence of senescent phytoplankton cells. Our results showed a strong effect of intensity of  
225 irradiance on the photooxidation of the bacterial membranes (Table 1, Fig. 2). Indeed, the  
226 concentration of vaccenic acid photooxidation products reached  $2741 \pm 21 \text{ nmol.L}^{-1}$  under  
227 high PAR irradiance but only  $464 \pm 190 \text{ nmol.L}^{-1}$  under low irradiance (Fig. 2). The highest  
228 concentration of vaccenic acid oxidation products ( $3998 \pm 1010 \text{ nmol.L}^{-1}$ ) was observed  
229 under high UV+PAR irradiance (Table 1, Fig. 2) and may be attributed to the presence of  
230 additional UV radiations. In phytodetritus, chlorophyll can act as photosensitizer not only  
231 under PAR (Nelson, 1993) but also under UV (Ying He and Häder, 2002), since they absorb  
232 in the UV range (Queseda and Vincent, 1997; Ehling-Schulz and Scherer, 1999). This  
233 assumption is well supported by the profile of photooxidation products obtained under these  
234 conditions, showing the presence of a high proportion of allylic 11- and 12-hydroxyacids  
235 with a cis double bond (Fig. S1) typical of the UV-induced photooxidation of MUFAs  
236 (Christodoulou et al., 2010).

237 Amiraux et al. (2016) previously showed in senescent diatom cells that low irradiances  
238 induce a slow but long-lasting production of  $^1\text{O}_2$  that strongly oxidizes algal unsaturated  
239 lipids and sterols, through a process called “photodynamic effect” (Knox and Dodge, 1985;  
240 Skovsen et al., 2005), whereas high irradiances lead to stronger but shorter production of  $^1\text{O}_2$   
241 that strongly photooxidizes the sensitizer (chlorophyll) through a process called  
242 “photobleaching” but with only a weak photodynamic effect (Amiraux et al., 2016; Rontani

et al., 2021). This effect of the intensity of solar irradiance on the efficiency of the photodynamic effect in senescent phytoplankton cells was then confirmed *in situ* (Rontani et al., 2021).

The effect of irradiance on the efficiency of photooxidation of attached bacteria thus appears to be exactly the opposite of the effect on phytoplankton. Under low irradiance, the low flux of  $^1\text{O}_2$  produced reacts with the unsaturated membrane components of phytodetritus and thus gets quenched before it reaches attached bacteria (Fig. 3). In contrast, under strong irradiance, a higher proportion of  $^1\text{O}_2$  is efficiently transferred to the attached bacteria, strongly oxidizing their unsaturated lipids (Fig. 3). This new concept opens interesting perspectives in the study of phytoplankton-bacteria relationships.

### 3.2. Confirmation of the results obtained *in vitro* in samples collected *in situ*

To confirm the enhancement of the efficiency of photooxidation processes on bacteria attached to phytoplankton cells, we analyzed a variety (n=58) of sinking particulate matter and sea ice samples collected in the Arctic (Fig. 1), where irradiance at the sea ice–water interface and in the water column varies strongly according to the albedo of snow and ice and to snow and ice thickness (Chresten Lund-Hansen et al., 2021). Sinking particulate matter samples were collected: (i) in summer at 100 m in open water in the Beaufort Sea (Rontani et al., 2012), (ii) in summer at 25 m in the marginal ice zone of central Baffin Bay (Rontani et al., 2022), and (iii) in spring at 5 m and 30 m in ice-covered Resolute Passage (Rontani et al., 2016). Sea-ice samples (0–10 cm) were collected in spring during the GreenEdge campaign at Qikiqtarjuaq (Baffin Bay, Arctic Ocean; Amiraux et al., 2020). To compare the efficiency of type-II photooxidation processes in algal and bacterial material, we used the ratio of % vaccenic acid photooxidation to % palmitoleic acid photooxidation. Vaccenic acid is generally considered to be specific to bacteria (Lambert and Moss, 1983;

Sicre et al., 1988), whereas palmitoleic acid is the main fatty acid component of sympagic diatoms (Fahl and Kattner, 1993; Falk-Petersen et al., 1998; Leu et al., 2010). Although palmitoleic acid is also present in several bacteria (e.g. de Carvalho and Caramujo, 2014), the contribution of bacteria to palmitoleic acid in the samples analyzed (dominated by diatoms) is negligible relative to the contribution of sympagic algae.

The results obtained show higher % vaccenic acid photooxidation/% palmitoleic photooxidation ratios in sinking particles collected in open-water Beaufort Sea than in ice-covered Resolute Passage (Fig. 4A). This difference may be attributed to the mean PAR irradiance in the mixed surface layer, which is considerably higher in open water than in ice-covered zones (e.g.  $365 \pm 62$  and  $10.9 \pm 2.7 \mu\text{mol photons.m}^{-2}.\text{s}^{-1}$  during the spring-summer transition in Beaufort Sea, respectively; Alou-Font et al., 2016). The ratios observed in the Baffin Bay marginal ice zone (where ice concentration ranges from 15% to 80%) were logically intermediate (Fig. 4A). The decrease in the ratio observed between 5 and 30 m in the Resolute Passage (Fig. 4A) could be attributed to the presence in the deeper trap of highly aggregated senescent sea-ice algae settling sufficiently rapidly out of the euphotic zone to avoid significant photooxidation (Rontani et al., 2016), however these differences **were not significant** (p-value > 0.05, see Fig. 4A, Table S1).

Very high ratios were found in the bottommost 10 cm of sea ice collected at the GreenEdge ice camp in 2016 (Fig. 4B). Under 75 cm of sea ice, irradiance can reach  $105.9 \mu\text{mol photons m}^{-2}.\text{s}^{-1}$  without snow cover and decrease to  $51.9 \mu\text{mol photons m}^{-2}.\text{s}^{-1}$  with a snow cover of 1 cm (Lund-Hansen et al., 2021). In this solid habitat, the bacteria-sympagic algae association may thus be maintained at relatively high irradiances during long periods, these conditions strongly favoring the photooxidation of bacteria. It was previously demonstrated that during the early stages of ice melt, sympagic bacteria undergo an intense osmotic stress in hypersaline ice brines (Amiraux et al., 2017) and are affected later in the

season by the release of bactericidal free palmitoleic acid by sympagic algae under the effect of light stress (Amiriaux et al., 2020). Our results show that these organisms may also undergo a strong photooxidative stress in the ice resulting from a strong and efficient transfer of  $^1\text{O}_2$  from senescent sympagic algae. These different stresses are thought to strongly decrease the mineralization potential of bacteria attached to ice algae and thus favor the preservation of sympagic material in Arctic sediments (Amiriaux et al., 2021; Rontani et al., 2022).

#### 4- Conclusion

Incubation of senescent cells of the diatom *Thalassiosira* sp. associated with the bacteria *P. stutzeri* under contrasting artificial light irradiances made it possible to demonstrate that high irradiances strongly favor photooxidation of the unsaturated membrane components of bacteria attached to senescent phytoplankton cells. Under these conditions, only a small part of  $^1\text{O}_2$  produced in chloroplasts reacts with membrane components of senescent algae, and so the remainder is efficiently transferred to their attached bacteria, inducing strong oxidative damage. Conversely, low irradiances favor photooxidation of the unsaturated algal lipids rather than attached bacteria. Indeed,  $^1\text{O}_2$  slowly generated under these conditions reacts with unsaturated lipids of the algal cells and is thus quenched before it can reach bacterial membranes. These findings were also confirmed *in situ*, where we observed the same tendencies in a variety of Arctic environmental samples (sea ice and sinking particulate matter). The transfer of  $^1\text{O}_2$  from senescent algae to their attached bacteria appeared to be particularly efficient in sea ice where the sympagic algae–bacteria association is maintained at relatively high irradiances during long periods of time.

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## FIGURE CAPTIONS

**Fig. 1.** Map showing the location of the different stations investigated. Sinking particles were collected in open water, first-year ice, and marginal ice zones in Beaufort Sea, Resolute Passage and central Baffin Bay, respectively. Sea ice samples originated from Davis Strait.

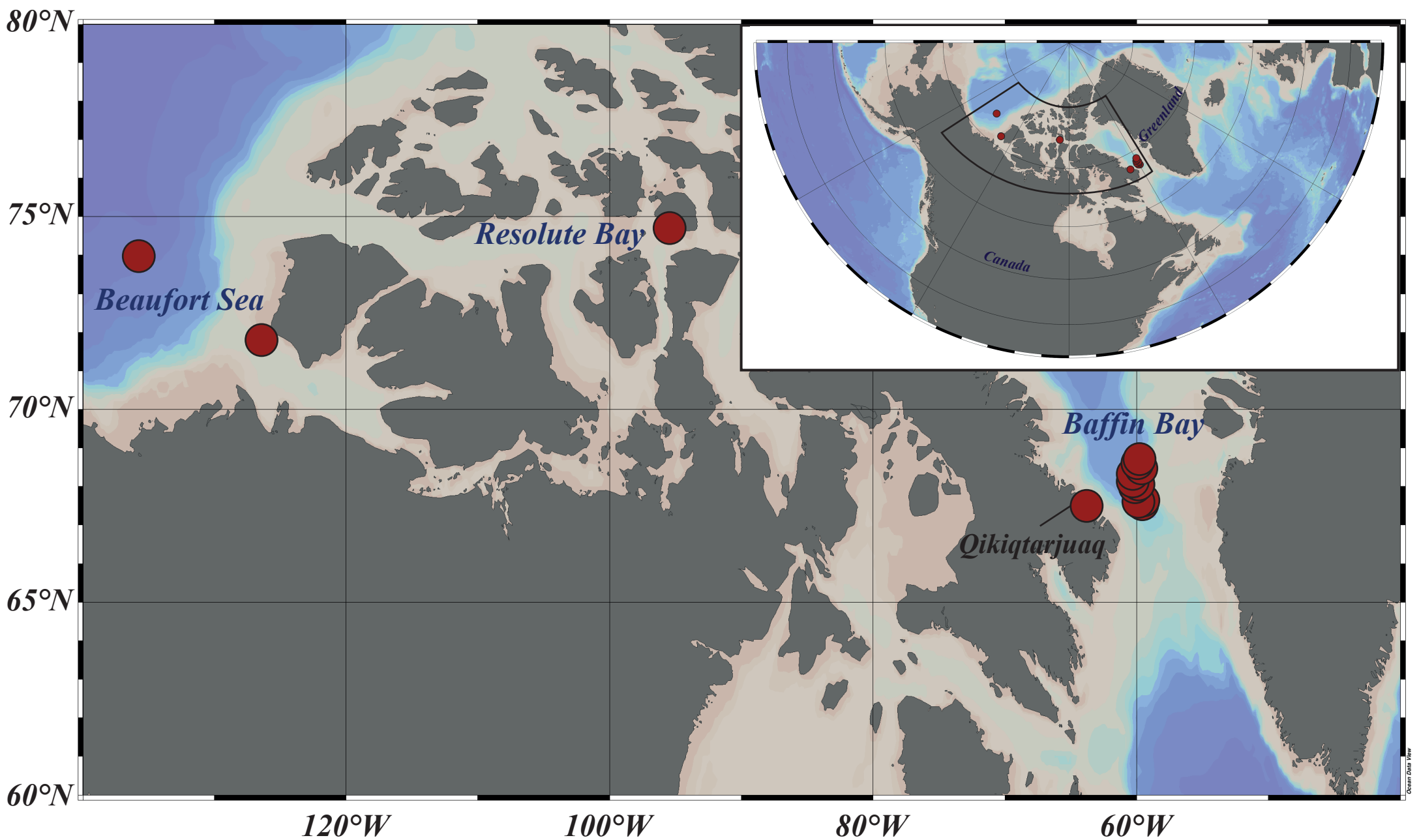
**Fig. 2.** Measurement of vaccenic acid photooxidation products in *P. stutzeri* cultures with and without addition of *Thalassiosira* sp. cells after irradiation (1000 KJ.m<sup>-2</sup>) under low PAR, high PAR and high PAR+UV irradiances (n=3).

**Fig. 3.** Conceptual scheme of the effect of <sup>1</sup>O<sub>2</sub> on bacteria attached to senescent phytoplankton cells under low or high irradiance.

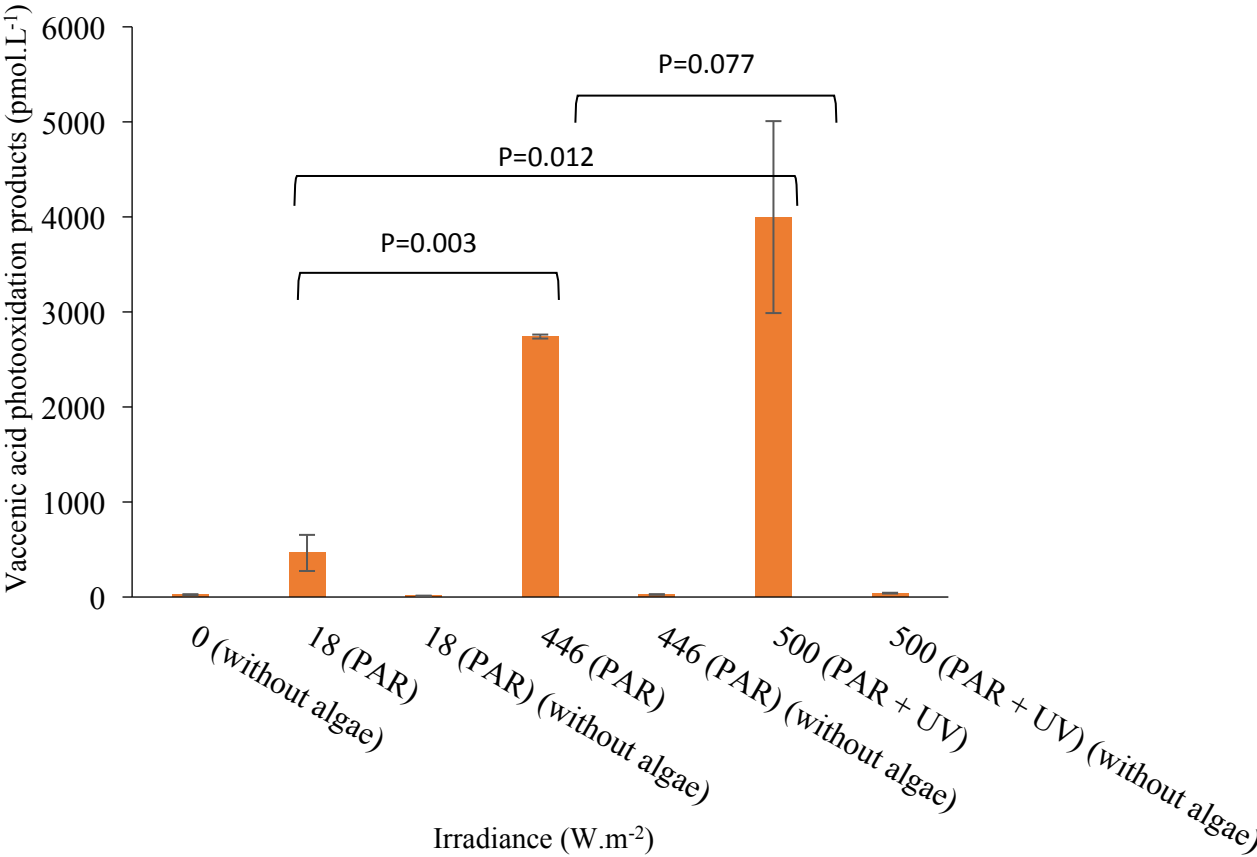
**Fig. 4.** Values of the ratio of % vaccenic acid photooxidation to % palmitoleic acid photooxidation in particulate matter samples collected in the Arctic under different irradiance conditions (A) and in sea-ice samples collected at the GreenEdge 2016 ice camp (B). Kruskal-Wallis test,

p-values : 0 < "\*\*\*\*" < 0.001 < "\*\*\*" < 0.01 < "\*" < 0.05 < " "

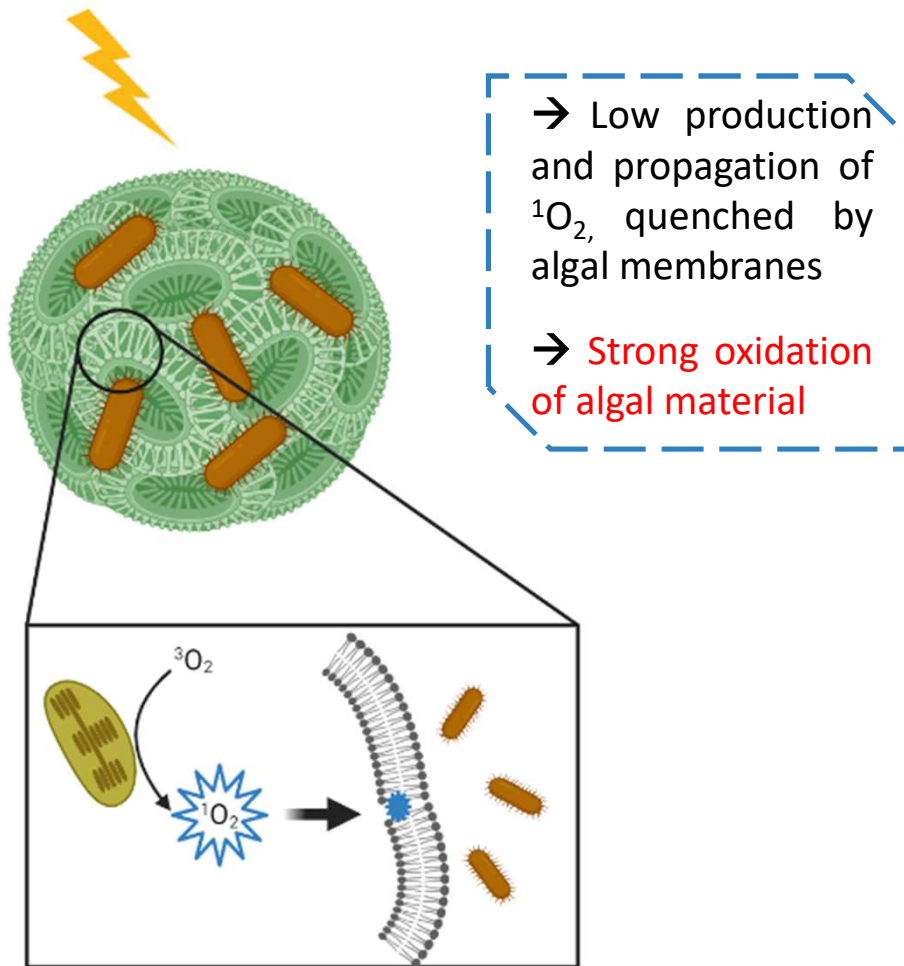
**Fig. S1.** MRM chromatograms (with the transitions  $m/z$  357 → 129 and  $m/z$  199 → 129) showing the production of significant proportions of 12-hydroxyoctadec-10(*cis*)-enoic and 11-hydroxyoctadec-12(*cis*)-enoic acids (indicative of an effect of UV radiation, Christodoulou et al., 2010), respectively, after irradiation of *Thalassiosira* sp. cells associated with *P. stutzeri* under high solar irradiance (500 W.m<sup>-2</sup>) for 3h 30.



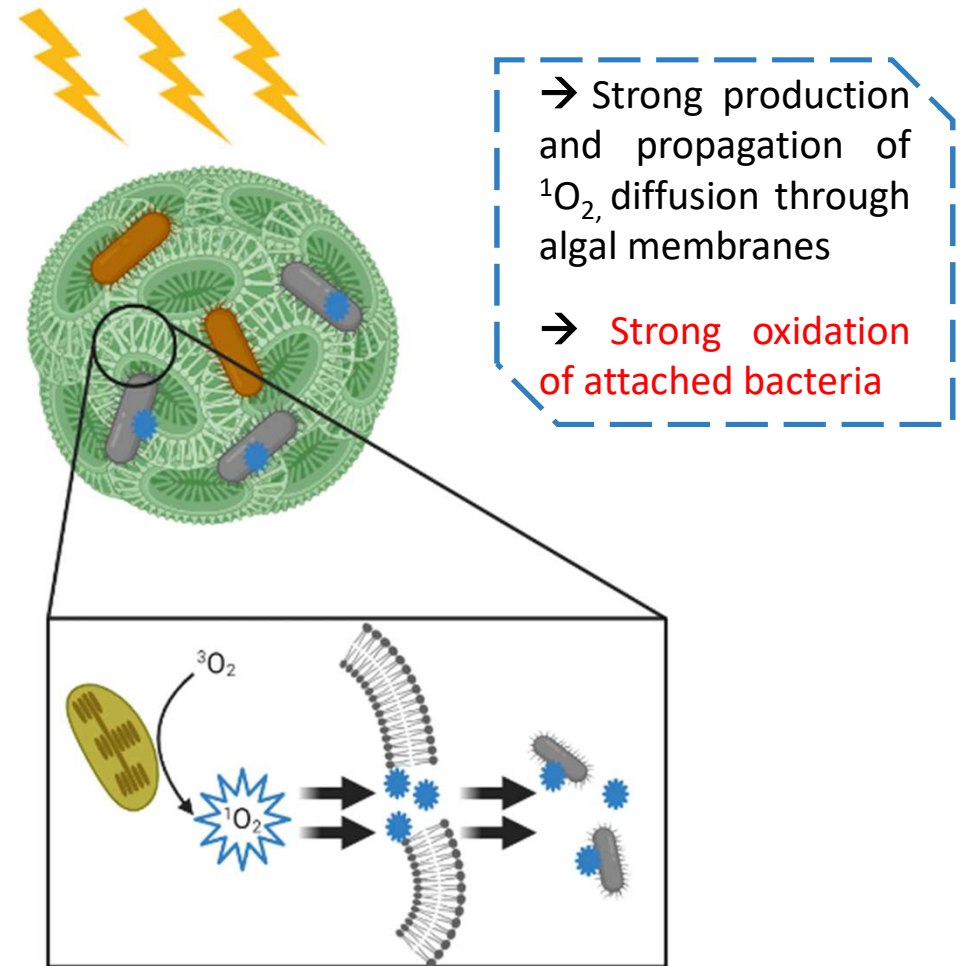




### Low irradiance



### High irradiance



Algal cell



Healthy bacteria



Lipid membrane

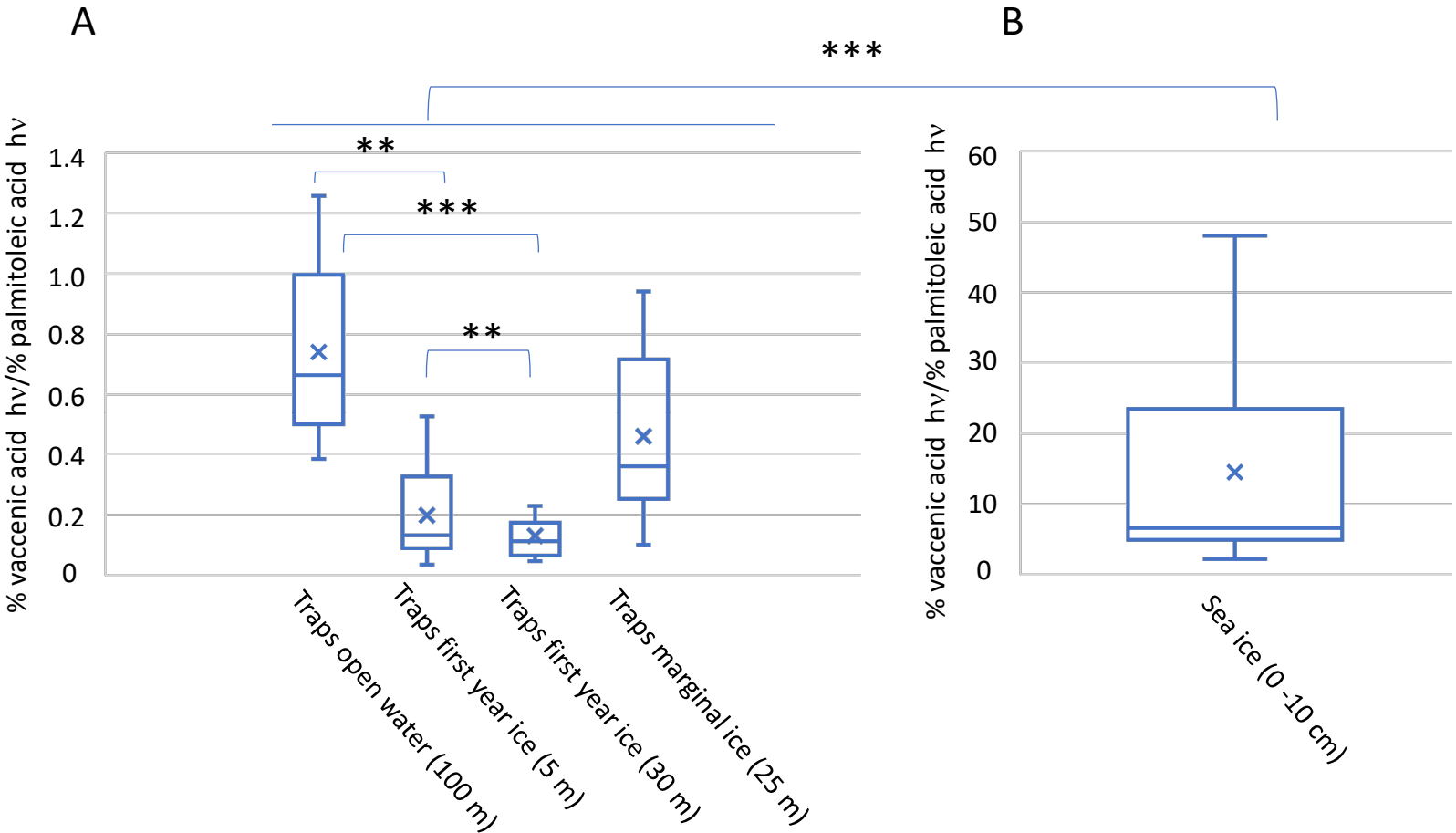


Chloroplast



Singlet oxygen

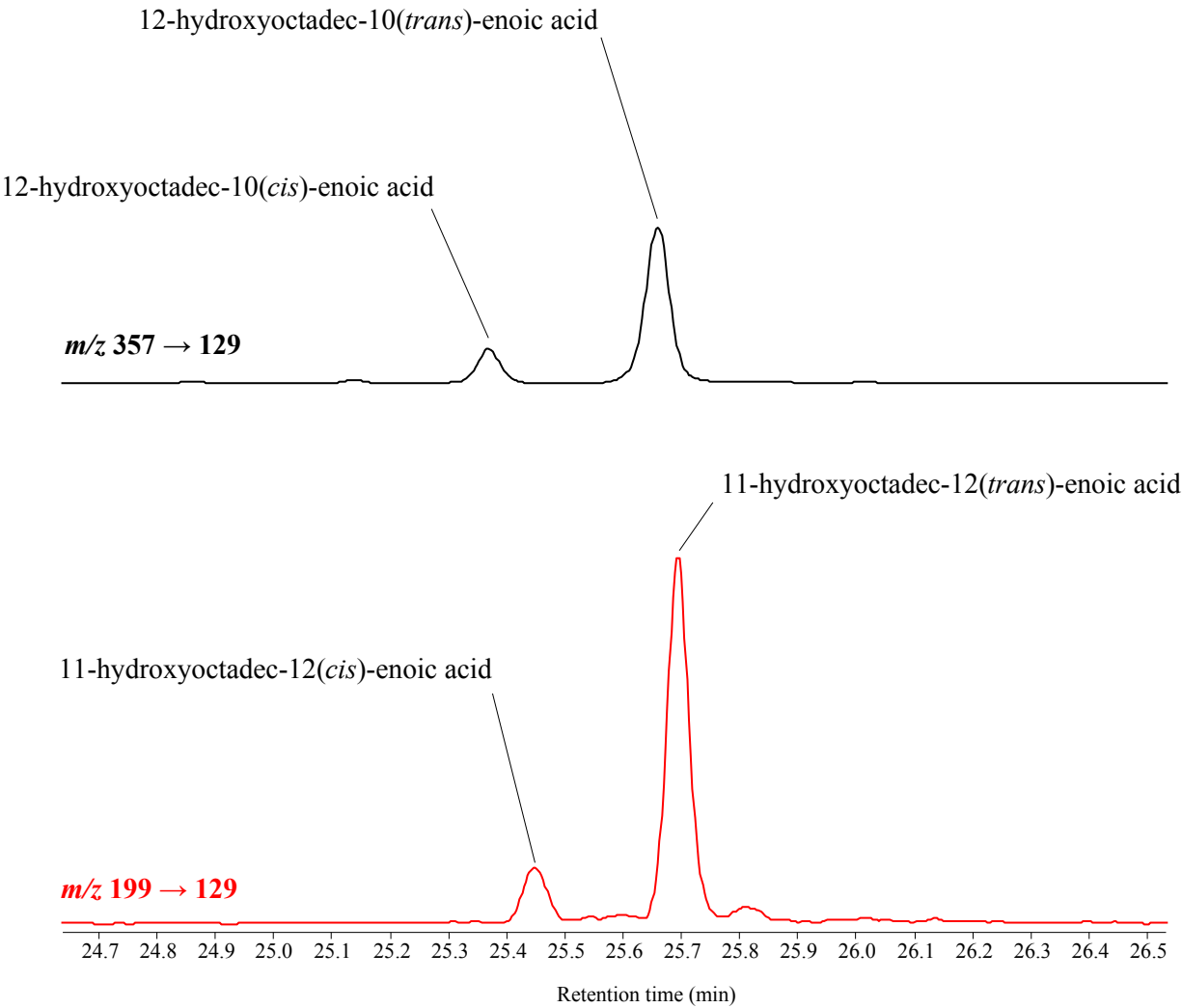
Bacteria damaged by  $^1\text{O}_2$



**Table 1.** Concentration of vaccenic acid photooxidation products in *P. stutzeri* cultures with and without addition of *Thalassiosira* sp. cells after irradiation (1000 KJ.m<sup>-2</sup>) under low PAR, high PAR and high PAR+UV irradiances (n=3).

Irradiance (W m <sup>-2</sup> )	Vaccenic acid hv (pmol.L <sup>-1</sup> ) <sup>a</sup>	Standard deviation
0 (without algae)	24	6
18 (PAR)	464	190
18 (PAR) (without algae)	13	0
446 (PAR)	2741	21
446 (PAR) (without algae)	27	3
500 (PAR + UV)	3998	1010
500 (PAR + UV) (without algae)	41	4

<sup>a</sup> Mean values.



**Table S1:** Significant differences between % vaccenic acid photooxidation to % palmitoleic acid photooxidation ratios measured in the Arctic under different irradiances (P-Values, n = 3, KW test)

	Traps under open water (100 m) Malina	Traps under first year ice (5 m) (Resolute Passage)	Traps under first year ice (30 m) Resolute passage	Traps under marginal ice zone (30 m) Baffin Bay	Sea ice
Traps under open water (100 m) Malina	1	0,005	0,000	0,109	0,001
Traps under first year ice (5 m) (Resolute Passage)	0,005	1	0,997	0,111	0,002
Traps under first year ice (30 m) Resolute passage	0,000	0,997	1	0,004	0,001
Traps under marginal ice zone (30 m) Baffin Bay	0,109	0,111	0,004	1	0,001
Sea ice	0,001	0,002	0,001	0,001	1