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Inventory of UV-absorbing mycosporine-like amino acids in polar macroalgae and factors controlling their content

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ABSTRACT

In the Arctic and Antarctic, a quantitative survey of mycosporine-like amino acids (MAAs) in benthic macroalgal species based on their vertical distribution was performed. Differerences in MAA concentrations were related to the distinct habitats and to the underwater radiation climate which was measured, in addition to the atmospheric irradiance at both field stations. Red algae from the eulittoral generally contained higher MAA concentrations than those of the lower and upper sublittoral. The dependency of MAA synthesis on radiation conditions was also found in induction experiments in algae of both regions. The presence and type of trigger mechanisms for MAA biosynthesis is discussed as well as the possible photoprotective role of MAAs.

KEYWORDS

macroalgae • irradiance • mycosporine-like amino acids • UVR • vertical distribution

INTRODUCTION

The Antarctic and Arctic are polar regions exhibiting both similarities and differences. The Arctic Ocean, an almost enclosed ocean basin, is characterized by limited water exchange with the Atlantic and Pacific Oceans. There is large freshwater input from river systems, including large input of soils and clays, and it is often nutrient limited, especially with respect to inorganic nutrients (Wängberg *et al.* 1996). In contrast, the Southern Ocean is connected to the adjacent seas. The sediments are formed from a mosaic of muds, sands, and boulders of glacial origin. In addition, the Southern Ocean generally has higher nutrient levels and is colder as compared to the Nordic waters (Wängberg *et al.* 1996, references therein).

However, these two polar regions also share similarities, particularly with respect to ice cover and irradiance trends. Solar radiation reaches the extremes of 24 h daylength in summer and 24 h darkness in winter within the polar circles, resulting in a large seasonal variability. Ozone depletion in the stratosphere has also been reported in both polar regions (Holm-Hansen *et al.* 1993, Groß *et al.* 2001). Although reduction in ozone

levels in the Arctic atmosphere is less than reported for Antarctica, the depletion is still high enough to cause an increase in deleterious UVB radiation (320 – 280 nm) in this region. Both terrestrial, as well as marine environments are affected, as ultraviolet radiation (UVR, 400 – 280 nm) can penetrate the water column in clear Antarctic waters even down to 60 – 70 m (Smith *et al.* 1992).

UVB can cause many negative effects on marine organisms, such as genetic damage (Vincent & Neale 2000), inhibition of photosynthesis (Hanelt *et al.* 1997), and reduction of growth, reproduction and productivity (Aguilera *et al.* 1999, Wiencke *et al.* 2000). Therefore, it is vital, particularly for benthic organisms to develop strategies to cope with increased UVR in order to reduce UV-induced damage. This includes DNA and protein repair at the molecular level, or physiological and biochemical counteracting strategies such as the expression of detoxifiying enzymes to protect against UV-induced reactive oxygen compounds (Dunlap & Yamamoto 1995). The synthesis of UV-absorbing sunscreen compounds is also an important mechanism to reduce potential damage (Cockell 2001). In particular, mycosporine-like amino acids (MAAs), with their absorbance maxima ranging from 309 to 360 nm, are postulated to have a photoprotective role against damaging UVR in the cells (Dunlap & Shick 1998). These passive sunscreens have been detected in vertebrates, invertebrates, coral reef organisms, bacteria, and algae throughout the oceans of the world (Cockell & Knowland 1999, references therein). To date, 19 distinct molecular structures of MAAs have been identified. They are made up of free amino acids either, with a cyclohexenone or cyclohexenimine chromophore, conjugated with a nitrogen substitution of an amino acid (Dunlap & Shick 1998). It has been suggested that MAAs are synthesized via the shikimate pathway, which is found only in microorganisms and plants, but not in animals (Shick *et al.* 1999). Animals, therefore, must aquire MAAs through diet or symbiotic associations with microorganisms or microalgae (Carroll & Shick 1996). MAA-containing macroalgae may be an important food resource for herbivores and detrivores not only as a nutritional source but also for protection against UVB damage (Adams & Shick 2001). In all studies conducted in different geographical regions it has been demonstrated, that MAAs are found mainly in red algae. Only few green algae contain MAAs, whereas in most brown algae, these compounds are completely absent (McClintock & Karentz 1997, Karsten *et al.* 1998, Hoyer *et al.* 2001).

The aim of our study was to detect possible differences in the MAA content of macroalgal species from the Antarctic and the Arctic, and relate these to the habitat-

specific UVR conditions. Finally, irradiance as a possible primary abiotic factor inducing MAA formation was studied under controlled conditions, in an attempt to elucidate the trigger for MAA biosynthesis in species from both polar regions.

MATERIALS AND METHODS

Study sites and algal material

The samples of macroalgae were collected from different habitats by SCUBA diving from the sublittoral and the eulittoral in Antarctica at Potter Cove, King George Island, South Shetlands (Jubany Station, Dallmann Laboratory, 62°14´S, 58°40´W) during the austral summer of 1997/98 and in the Arctic at Kongsfjord, Ny-Ålesund, Spitsbergen (78°55´N, 11°55´E) during several summers (details of sample locations and collecting dates are listed in Table 1).

Red algae were isolated for culture purposes from Potter Cove 1994 and established as permanent growth culture in the laboratory. The light regime was varied between 5 h (winter) and 20 h (summer), simulating fluctuating Antarctic daylengths (Wiencke 1990).

Table 1: Investigated field macroalgae with details of sampling location and date.

Species	Sample location (depth)	Sampling date
RHODOPHYCEAE	**Potter Cove, King George Island, Antarctica**	
Curdiea racovitzae Hariot (Gracilariales)	eulittoral, inner fjord	28.01.1998
Georgiella confluens (Reinsch) Kylin (Ceramiales)	eulittoral, inner fjord; sublittoral, outer fjord (-7 m, -15 m)	01.01.1998, 29.12.1997, 05.01.1998
Gigartina skottsbergii Setchell & Gardner (Gigartinales)	outer fjord, (-9 m)	20.01.1998, 24.12.1997
Gymnogongrus antarcticus Skottsberg (Gigartinales)	inner fjord (-1-0 m)	01.12.1997
Hymenocladiopsis crustigena Moe (Rhodymeniales)	outer fjord (-15 m)	05.01.1998
Iridaea cordata (Turner) Bory de Saint Vincent (Gigartinales)	eulittoral, inner fjord, outer fjord, (-5 m, -10 m)	15.12.1997, 17.12.1998
Kallymenia antarctica Hariot (Cryptonemiales)	outer fjord (-20 m)	24.12.1997

Table 1: continued

Species	Sample location (depth)	Sampling date
Myriogramme smithii (Hooker fil. et Harvey) Kylin (Ceramiales)	outer fjord (-15 m)	05.01.1998
Neuroglossum ligulatum (Reinsch) Skottsberg (Ceramiales)	outer fjord (-15 m)	10.12.1997
Notophycus fimbriatus Moe (Gigartinales)	inner fjord (-1-0m)	26.11.1997
Pachymenia orbicularis (Zanardini) Setchell & Gardner (Cryptonemiales)	inner fjord (-15 m)	15.01.1998
Palmaria decipiens (Reinsch) Ricker (Palmariales)	eulittoral, inner fjord, outer fjord (-15 m)	05.01.1998
Phycodrys austrogeorgica Skottsberg (Ceramiales)	outer fjord (-20 m)	13.01.1998
Picconiella plumosa (Kylin) de Toni (Ceramiales)	outer fjord (-20 m)	13.01.1998
Plocamium cartilagineum (Linnaeus) Dixon (Ploeamiales)	eulittoral, inner fjord, outer fjord (-6, -15 m)	01.01.1998, 17.12.1997, 05.01.1998
Porphyra endiviifolium Chamberlain (Bangiales)	eulittoral, inner fjord	26.11.1997
Sarcothalia papillosa (Bory) Leister (Gigartinales)	inner fjord (-1-0m), outer fjord (-15 m)	16.12.1997, 09.12.1997
CHLOROPHYCEAE		
Prasiola crispa ssp. ***antarctica*** (Kützing) Knebel (Prasiolales)	supralittoral, in penguin rockeries	10.01.1998
RHODOPHYCEAE	**Kongsfjord, Spitsbergen, Arctica**	
Coccotylus truncatus (Pallas) M.J. Wynne & J.N. Heine (Gigartinales)	inner fjord (-11 m)	27.06.2001
Devaleraea ramentacea (Linnaeus) Giury (Palmariales)	inner fjord (-2 m, -8 m)	10.6.1998, 03.07.2000
Palmaria palmata (Linnaeus) Kuntze (Palmariales)	inner fjord (-2 m, -10 m)	10.6.1998, 03.07.2000
Odonthalia dentata (Linnaeus) Lyngbye (Ceramiales)	inner fjord (-9 m)	22.08.1995
Phycodrys rubens (Linnaeus) Batters	inner fjord (-15 m)	25.05.1996
Polysiphonia arctica J. Agardh (Ceramiales)	inner fjord (-1 m, -12 m)	22.08.1995, 21.06.2000
Porphyra spec. C. Agardh (Bangiales)	inner fjord (-10 m)	04.06.2001
Ptilota gunneri P.C. Silva, C.A. Maggs & L.M. Irvine (Ceramiales)	inner fjord (-13 m)	24.05.1996
Ptilota serrata Kützing (Ceramiales)	inner fjord (-10 m)	18.08.1995
Rhodomela confervoides (Hudson) P.C. Silva (Ceramiales)	inner fjord (-12 m)	08.06.2000
CHLOROPHYCEAE		
Prasiola crispa (Lightfoot) Kützing (Prasiolales)	supralittoral, underneath a coastal bird-cliff (seagull)	13.06.2000

Radiation measurements

Underwater spectra of ambient radiation of wavelengths from 327 to 700 nm were recorded at various depths with a spectroradiometer (Ingenieurbüro M. Kruse, Stubben, Germany). Water transmittance was determined by measuring irradiance at different depths and then by calculating diffuse vertical attenuation coefficients (Kd) of downward irradiance (Kirk 1994).

UVB radiation (UVB, 280-320 nm) in air was measured using a 32-channel single photon counting spectroradiometer equipped with a cosine diffuser, developed at the Physics Department of the Alfred Wegener Institute. The instrument was installed on the roof of the Dallmann Laboratory (Antarctic) as well as on the roof of the NDSC building in Ny-Ålesund (Arctic). The spectroradiometer was computer controlled allowing on-line recordings of the radiation data. Photosynthetically active radiation (PAR, 400-700 nm) in the atmosphere was measured with a Li-Cor datalogger (Li-1000, LI-Cor. Lincoln, USA) equipped with a flat head sensor (LI-190).

Induction experiments

For the induction experiments, low-light (PAR, 15 μmol photons $m^{-2}s^{-1}$) adapted Antarctic cultured (*Gymnogongrus turquetii, Kallymenia antarctica, Neuroglossum ligulatum, Palmaria decipiens*) and Arctic field algae (*Devaleraea ramentacea, Palmaria palmata, Polysiphonia arctica, Rhodomela confervoides*) were transferred to two different radiation conditions; PAR (400 to 700 nm, 25 μmol photons $m^{-2}s^{-1}$) and PAR + UVR (295 to 400 nm, 4.6 W m^{-2}). Daylight fluorescent lamps (Lumilux Deluxe, Osram, Germany), in combination with Q-Panel UVA-340 fluorescent tubes, (Cleveland, USA) emitting a spectrum similar to solar radiation in the UVR range, were used. Spectra emitted by these artificial radiation sources were measured with a Spectro 320 D spectroradiometer (Instrument Systems, Germany).

During the experiment, algae were kept in glass beakers filled with filtered nutrient-enriched sea water with an additional 2.1 mM sodium hydrogen carbonate, as an additional inorganic carbon source. The experiment with the Antarctic algae was performed in a constant temperature room at 0°C under PAR +UVR/dark cycles of 16:8 h. The Arctic algae were investigated at 5 °C under continuous white light with an addition exposure of 11 hours UVR. Glass vessels were covered with specific filters to cut-off UVB + UVA radiation (400 nm cut-off: Folex PR, Folex, Dreieich, Germany),

or with a filter with no transmission under 295 nm (Ultraphan UBT, Digefra, München, Germany).

After 12 days of exposure to the artificial radiation the Antarctic plants were harvested. The Arctic algae were incubated for 6 days, *P. arctica* and *R. confervoides* additionally for 9 and 11 days, respectively. The harvested samples were oven-dried at 50 °C overnight, and then stored in sealed plastic bags under dry and dark conditions prior to MAA analysis.

MAA extraction and analysis

A 25 % aqueous methanol (v/v) extraction was made from 10 – 20 mg dry weight (DW) of the algal samples. After evaporating to dryness under vacuum (Speed Vac Concentrator SVC 100H) dried extracts were re-dissolved in 100% methanol. Samples were analysed with a Waters high-performance liquid chromatography (HPLC) system according to Hoyer *et al.* (2001). All total MAA concentrations are given as means of 3 replicates (±SD) randomly collected from the respective habitat. Means of the replicates from all experiments were taken and expressed as concentration per dry weight (mg g^{-1} DW). Differences in the MAA content under the distinct filter treatments in the induction experiments were statistically verified by using a one – way ANOVA test applying a multiple comparison post test (Tukey – Kramer HDS test) where significant differences occurred (probability at $p < 0.05$).

RESULTS

Radiation data

The ozone values measured over Antarctica (Neumayer Station) during the expedition period (austral summer 1997/98) ranged from 316 to 227 DU (Dobson Unit) with a mean of about 260 DU (Table 1) indicating an ozone depletion of almost 20 % compared to a typical ozone measurement of about 320 DU before 1980. Over the Arctic the ozone concentration is generally higher. Before 1980, an average value of about 450 DU was recorded, but it varied from 421 to 302 DU over Spitsbergen during the expedition time June and July 2000, representing a 23 %-loss of ozone (Table 2).

As a result of the ozone depletion in the stratosphere UVB increases. In December 1997, the average daily dose of UVB in air was higher (40.8 kJ m^{-2}) than in January 1998 (29.9 kJ m^{-2}) as measured on King George Island (Antarctic). Instantaneous UVB and PAR values reached 1.8 W m^{-2} and 1748 μmol photons m^{-2} s^{-1}. On Spitsbergen (Arctic), the average daily doses of UVB were lower in the months June and July 2000 compared to the same season in the Antarctica, 36.6 and 22.3 kJ m^{-2}, respectively, as well as instantaneous UVB and PAR values of 1.23 W m^{-2} and 1440 μmol photons m^{-2} s^{-1} (Table 2). This is also due to its location at a higher latitude than King George Island.

In Potter Cove (Antarctica), the light transmittance through the water was much lower in the inner fjord than in its outer part. A similar situation was found in Kongsfjord (Arctic), in both cases due to the input of turbid melt waters. The K_d values and the corresponding calculated depth for 1 % of remaining radiation for PAR and UVR (327 to 399 nm) are summarized in Table 2.

Table 2: Radiation measurements and ozone data for the expedition periods to Antarctica (1997/98) and Arctic (2000). Ozone data taken from Meterology Observatory of Neumayer Station, Antarctica (70°37´S, 8°22´W) and from TOMS satellite (Total Ozone Mapping Spectrometer), Arctic (78°55N, 11°56E). DU: Dobson Unit

	Antarctica		**Arctica**	
	Date	Units	Date	Units
Ozone				
Max. ozone	8 December 1997	316 DU	5 June 2000	421 DU
Min. ozone	16 November 1997	227 DU	20 July	302 DU
Ozone mean value	November 1997 – January 1998	260 DU	June – July 2000	346 DU
Atmosphere				
UVB (280 – 320 nm)				
Daily dose	average for December 1997	40.8 kJ m^{-2}	average for June 2000	36.6 kJ m^{-2}
Daily dose	average for January 1998	29.9 kJ m^{-2}	average for July 2000	22.3 kJ m^{-2}
example of irradiance at midday (UVB)	23 December 1997	1.80 W m^{-2}	13 June 2000	1.23 W m^{-2}
example of irradiance at midday (PAR)	20 January 1998	1748 μmol photons m^{-2} s^{-1}	21 June 2000	1440 μmol photons m^{-2} s^{-1}

Table 2: continued

	Antarctica		Arctica	
Attenuation coefficient				
$K_{d\ PAR}$	30 December 1998, outer fjord	0.17 m^{-1}; 1% depth: 26.9 m	22 June 2000, outer fjord	0.21 m^{-1}; 1% depth: 21.9 m
$K_{d\ UV\ (327\text{-}399\ nm)}$		0.19 m^{-1}; 1% depth: 24.2 m		0.39 m^{-1}; 1% depth: 11.8 m
$K_{d\ PAR}$	30 December 1998, inner fjord	0.45 m^{-1}; 1% depth: 10.2 m	21 June 2000, inner fjord	0.72 m^{-1}; 1% depth: 6.4 m
$K_{d\ UV\ (327\text{-}399\ nm)}$		1.1 m^{-1}; 1% depth: 4.2 m		0.94 m^{-1}; 1% depth: 4.9 m

MAA inventory

In the species examined, nine different MAAs were detected. Seven were identified as mycosporine-glycine, shinorine, porphyra-334, palythine, asterina-330, palythinol and palythene, and were quantified by using the respective molar extinction coefficient (Karsten *et al.* 1998). Furthermore, two unknown UV-absorbing compounds with absorbance maxima of 324 and 357 nm, respectively, were also detected. The unknown substance-324 has previously been described in the Antarctic isolate of *P. crispa* (Hoyer *et al.* 2001), and has been detected in this study also as the main compound in *P. crispa* from the Arctic. MAA-357 is probably usujirene, the isomeric cis-form of palythene (Tsujino *et al.* 1979). Based on MAA composition the most abundant MAAs were palythine, porphyra-334 and shinorine, followed by asterina-330 in the Antarctic and Arctic field grown algal species presented here. In the case of *Rhodomela confervoides*, there was an almost equimolar concentration of palythinol and porphyra-334 of about 1 mg g^{-1} DW. However, in *Porphyra endiviifolium*, porphyra-334 was quantitatively the most abundant MAA (7.7 mg g^{-1} DW). In Fig. 1 all MAAs are summarized as total MAA concentration.

In Potter Cove (Antarctica), 19 algal species were examined of which one green alga was collected from the supralittoral, 6 red algae from the eulittoral, 7 from the upper, and 14 from the lower sublittoral. Out of them 6 species were found in more than one habitat. In Figure 1A, those algae containing MAAs are summarized, and collecting depths noted. A species not listed, *Georgiella confluens*, was found from the eulittoral

downwards. Only small traces of two different MAAs were detected in individuals of this species collected from the eulittoral, even less were found in those of the upper sublittoral, and nothing in those of the lower sublittoral. No MAAs were detected in four other species (*Hymenocladiopsis crustigena, Myriogramme smithii, Phycodrys austrogeorgica* and *Picconiella plumosa*) collected from the lower sublittoral (15, 20 m).

Ten macroalgal species from the Kongsfjord (Arctic) were analyzed. Red algae were not occurring in the eulittoral, but one green alga (*Prasiola crispa*) was collected from the supralittoral. Four red algal species derived from the upper, 8 from the lower sublittoral, and of those, 3 species were collected from both zones. These 3 species exhibited MAAs with distinct concentrations relating to growth depth (Figure 1B). *Coccotylus truncatus, Odonthalia dentata* and *Ptilota serrata* are deep-water plants, originating from 9 to 15 m depth and growing indeed deeper. These species contained no MAAs, even after exposure to enhanced UVR.

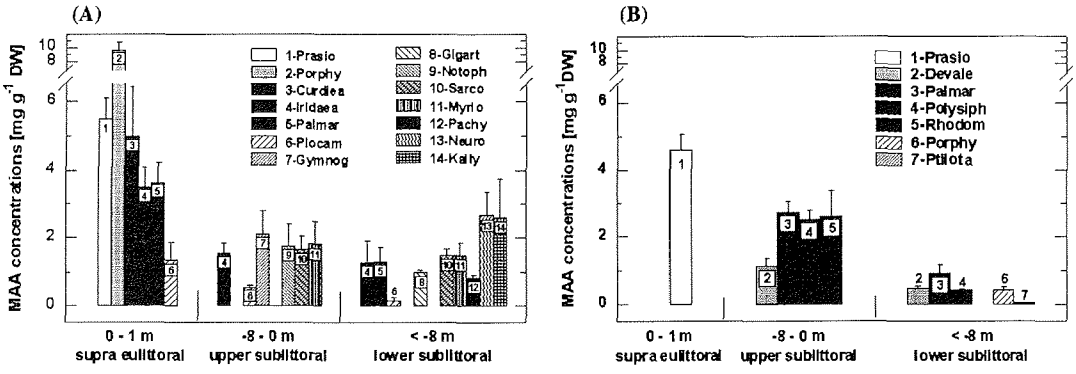

Figure 1: Total concentration of MAAs in macroalgae based on their vertical distribution (**A**) from Antarctica, (**B**) from the Arctic. Means ± SD (n = 3). Abbrevation, (**A**): Prasio – *Prasiola crispa* spp. *antarctica*, Porphy – *Porphyra endiviifolium*, Curdiea – *Curdiea racovitzae*, Iridaea – *Iridaea cordata*, Palmar – *Palmaria decipiens*, Plocam – *Plocamium cartilagineum*, Gymnog – *Gymnogongrus antarcticus*, Gigart – *Gigartina skottsbergii*, Notoph – *Notophycus fimbriatus*, Sarco – *Sarcothallia papillosa*, Myrio – *Myriogramme mangini*, Pachy – *Pachymenia orbicularis*, Neuro – *Neuroglossum ligulatum*, Kally – *Kallymenia antarctica*. (**B**): Prasio – *Prasiola crispa*, Devale – *Devaleraea ramentacea*, Palmar – *Palmaria palmata*, Polysiph – *Polysiphonia arctica*, Rhodom – *Rhodomela confervoides*, Porphy – *Porphyra* spec., Ptilota – *Ptilota gunneri*

In general, the supralittoral and the eulittoral species contained the highest concentrations of MAAs. Eulittoral species were collected from a broad intertidal platform influenced by a semidiurnal tide with an average amplitude of 135 cm in Potter Cove (Antarctica) (Schöne *et al.* 1998). These algae contained total MAA amounts of 9.7 mg g^{-1} DW (*Porphyra endiviifolium*), 4.9 mg g^{-1} DW (*Curdiea racovitzae*), and 3 mg g^{-1} DW (*Iridaea cordata*). As a comparable habitat is absent at Kongsfjord, most species were collected in the sublittoral and exhibited lower MAA concentrations, with increasing growth depth. In the lower sublittoral, all concentrations were found to be under 1 mg g^{-1} DW. In comparison, at Potter Cove, the lower sublittoral species contained higher MAA concentrations up to 2.6 mg g^{-1} DW and on an average about 1.5 mg g^{-1} DW.

Induction experiments

The induction of the MAA synthesis / accumulation after exposure to enhanced UVR was investigated in four red algal species from each polar region. An additional increase of total MAA concentration after incubation under PAR and PAR + UVR was observed in three Antarctic algae (*Kallymenia antarctica*, *Gymnogongrus turquetii*, *Palmaria decipiens*) and in *Devaleraea ramentacea* and *Palmaria palmata* from the Arctic (Fig. 2A, B). The increase in MAA concentration from the initial samples to those under the UVR treatment in *D. ramentacea*, *K. antarctica* and *P. decipiens* was statistically significant ($P < 0.03$, $P < 0.0002$, $P < 0.003$), as was from the initial sample to that under PAR-only in the latter species (Fig. 2A, B). In Antarctic *Neuroglossum ligulatum*, an increase in MAA concentration was observed between the initial sample and the PAR treated sample whilst the plants under the PAR + UVR condition exhibited almost the same values as the control. After 6 days of incubation, in *Polysiphonia arctica* and *Rhodomela confervoides*, no differences were visible between the initial and the treated samples (data not shown). After 9 days, a statistically higher concentration of MAAs was found under PAR-only and UVR conditions in *P. arctica* compared to the initial samples whereas in *R. confervoides* a decrease in MAA concentration was observed under both treatments after 11 days of incubation (Fig. 2B).

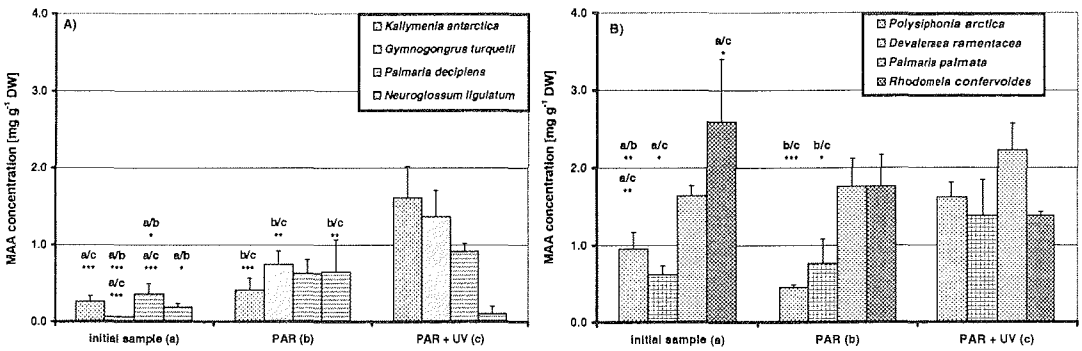

Figure 2: Total concentration of MAAs in (**A**) cultured Antarctic red algae (n = 4-5) after 12 days of exposure and (**B**) field-collected Arctic red algae after 6 (*D. ramentacea*, n = 4-5; *P. palmata*, n = 3-4), 9 (*P. arctica*, n = 4-5), and 11 (*R. confervoides*, n = 4, using the Kruskal-Wallis test) days of exposure under two different radiation conditions using specific cut-off filters. An asterisk indicates a significant difference in the concentrations of MAAs between treatments (*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$). Means ± SD

In *K. antarctica*, shinorine and palythine were the quantitatively dominant MAAs, in *G. turquetii*, shinorine and porphyra-334 were also present in almost equimolar concentrations under the experimental radiation treatments, except in the initial sample, where porphyra-334 was absent. In *P. decipiens* porphyra-334 ocurred in highest concentrations, whereas in *N. ligulatum*, shinorine was the most abundant sunscreen compound in combination with traces of porphyra-334.

In *R. confervoides*, the initial samples contained porphyra-334 and palythinol in almost equimolar concentrations. After 11 days the concentrations increased proportionally. The same concentrations of porphyra-334 and palythine were found in the initial sample of *P. arctica* (ca. 0.3 mg g^{-1} DW). After 9 days of incubation, the concentration of porphyra-334 (0.575 mg g^{-1} DW) increased and was significantly ($P<0.02$) higher than of palythine (0.253 mg g^{-1} DW) under the treatment with UVR. In *P. palmata*, porpyhra-334 was the quantitatively most abundant MAA, whereas shinorine and palythine were detected in low concentrations (both were found to be about 10 % of the porphyra-334 concentration). Initially in *D. ramentacea*, the MAAs porphyra-334 and palythine did not show significant differences in their concentrations, however after the treatment with UVR, the content of porphyra-334 were significantly ($P<0.01$) higher with 1.1 mg g^{-1} DW than that of palythine (0.2 mg g^{-1} DW).

DISCUSSION

The effects of radiation on organisms depend on the intensity, spectral composition and the
duration of the incident radiation. The irradiance regime in the polar regions is one of the parameters that change markedly over the course of the year, as a result of fluctuating daylengths and atmospheric factors such as solar declination, cloud cover, aerosols and ozone concentrations (Lubin *et al.* 1998). Ozone depletion affects the irradiance by a very specific increase in the UVB radiation between the wavelengths 290 and 315 nm (Wängberg *et al.* 1996).

The trend of lower ozone values over the Antarctic compared with the Arctic (WMO 1998) has also been found in this study, correlating well with measurements of higher daily averages of atmospheric UVB in Potter Cove (Antarctica) than in the Kongsfjord (Arctic). However, it has to be considered that the former study site is located at lower latitudes with generally higher UVB values. Nevertheless, an increase in surface UVB also results in an augmentation of irradiance penetrating the water column.

The vertical attenuation coefficents (K_d values) measured in different parts of the Kongsfjord (Arctic) are in the same range as those of previous studies. $K_{d(UVB)}$ values between 0.3 and 1.34 m^{-1} depend on a stratified water column of different layers of turbidity, tidal level, and sun angle (Bischof *et al.* 1998, Hanelt *et al.* 2001). In Wängberg *et al.* (1996), the cited $K_{d(310)}$ values of 0.2 – 0.25 m^{-1} for Spitsbergen were lower than we have found, but can be explained by different measuring locations, i.e. inner versus outer fjord. The K_d values measured in Potter Cove (Antarctic) were slightly lower than those of the Kongsfjord indicating a deeper irradiance transmittance through the water column. In Antarctica, the 1 % depth of 26.9 m for remaining visible light, or even 40 m (Gómez *et al.* 1997), together with the 1 % depth of remaining radiation for UVR of 24 m indicate locally very high transparency and signify characteristic clear ocean waters (Smith and Baker 1981). Consequently, macroalgae might be affected by harmful UVB, particularly in the eulittoral and upper sublittoral, and at some Antarctic locations even much deeper (30 m depth, Karentz *et al.* 1989). The usually higher UVR conditions in Antarctica well explain the high MAA-concentrations of exposed supra- and eulittoral species as photoprotective defense against UV-induced damage. The relatively high production of MAAs in *Kallymenia antarctica* and *Neuroglossum ligulatum*, two Antarctic species collected in the outer

part of Potter Cove, growing at 20 and 15 m depth, respectively, can also be explained by high water transparency for UVR.

Algal species of the upper sublittoral of both polar regions exhibited similar MAA concentrations probably due to similiar radiation conditions at those depths. However, in the Antarctic, the macroalgae of the lower sublittoral usually exhibited only slightly lower MAA contents compared with the algae of the upper sublittoral. This was unexpected as in previous studies an obvious depth gradient in MAA concentrations was documented (Karsten *et al.* 1998, Franklin *et al.* 1999) and as confirmed in this study for the Arctic macroalgae. The relatively high MAA values even in Antarctic lower sublittoral species seems to be related with the higher PAR and UVR penetration depths, as biosynthesis of MAAs is a variable physiological process, controlled by radiation transmittance. In addition, other ecological parameters such as growth in shaded environments, e.g. in the understory, may influence the MAA content. Furthermore, MAA production is a very species-specific process, resulting in great differences in concentrations between species of the same habitat. Additionally, MAA synthesis may be determined on a genetic level, as suggested by those algae that do not have the capability to produce MAAs even after exposure to enhanced UVR as found for 4 Antarctic and 3 Arctic species.

In the Antarctic and Arctic, there are few bipolar species. Some species have a cosmopolitan distribution and some have disjunct bipolar distributions like *Acrosiphonia arcta* (Chlorophyta) (Bischoff & Wiencke 1995). The green alga *P. crispa* is a cosmopolitan species, but for the Antarctic it is described as a subspecies (*P. crispa* spp. *antarctica*). Nevertheless, the Arctic and Antarctic species have many similiarities. The *Prasiola* -samples investigated in this study were growing as nitrophilic species in comparable habitats: in penguin rockeries (*Phygoscelis adeliae*) near Potter Cove (Antarctica) and underneath a coastal bird-cliff (Kongsfjord, Arctic) colonized by breeding seagull *Rissa tridactyla*. Gross morphology of both isolates appears similiar, producing the same UV-absorbing compound (substance-324), which is unknown for red algae. The higher concentrations of MAAs in the Antarctic species was probably due to the higher atmospheric UVB experienced by the alga.

MAA concentrations are generally higher in macroalgae from Potter Cove (Antarctica) than in those from the Kongsfjord (Arctic). Further studies will be necessary to prove this as a general prediction as it might be simply an adaptation to the higher UVB found

in Antarctica. The collecting locations which are all in the inner fjord for the Arctic samples, exhibiting lower Kd values than the outer fjord may also play a role. Furthermore, there is no nutrient limitation at coastal Antarctic waters over the course of the year (Drew and Hastings 1992) which may effect the essentially important nitrogen uptake for the MAA molecules. In contrast, in Kongsfjord (Arctic) a strong depletion of phosphate and nitrate concentrations was found in the open-water period (Aguilera et al. 2002) which might be responsible for reducing the MAA synthesis / accumulation.

For the induction experiment, species of the upper and lower sublittoral were chosen, due to the flexible way they are able to react to environmental radiation changes in respect to MAA synthesis. The Antarctic species were taken from culture and were therefore low-light adapted, resulting in a significant lower initial MAA value compared to the Arctic algae collected from the field. Therefore, any comparison between these two set ups must be considered carefully. However, the experiments generally showed that MAA accumulation can be species – specifically induced by exposure to different light conditions with increasing MAA concentrations observed under high PAR-only treatment or under PAR + UVR as well as an additional increase under both conditions. Differences in MAA concentrations arising from exposure time are variable in the Arctic species. *P. arctica* and *R. confervoides* do not show any changes in MAA concentrations between the initial and harvested samples after 6 days, whereas distinct differences were seen in *P. palmata* and *D. ramentacea*. Furthermore, a MAA increase was found in *P. arctica* after 9 days, indicating species-specific differences in the enzymatic kinetics for the MAA biosynthesis / accumulation. In contrast, 11 days of exposure to UVR might be too high for *R. confervoides*, resulting in a MAA degradation or leakage into the medium, which is also observed in the Antarctic species *N. ligulatum* (Fig. 2A, B). No further induction of MAA formation or accumulation seems possible if species are "loaded-up" with MAAs (data not shown), indicating that each plant may have an maximum threshold of MAAs.

Generally, an induction of MAA synthesis by exposure to light and UVR was observed in species of both polar regions and indicates that more than one mechanism or photoreceptor might be involved in the MAA induction process. This is supported by the results of Franklin *et al.* (1999) who also postulated a signal transduction pathway or even interactions among various photoreceptors involved in the overall process leading to high MAA concentrations. At least, two different photoreceptors should be taken into

consideration referring to two types of induction one by MAA increment of PAR intensity and another by UVR.

The detection of high MAA concentrations in polar macroalgae is ecologically important for a better understanding of how benthic plants are able to cope with the increasing UVB in extreme environments. Furthermore, the investigations were based on algal vertical distribution in the shallow-water ecosystem. The physiological ability to adjust their MAA biosynthesis, depending on the environmental radiation was demonstrated.

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