Research Article

DMSP in marine macroalgae and macroinvertebrates: Distribution, function, and ecological impacts

Kathryn L. Van Alstyne* and Melany P. Puglisi

Shannon Point Marine Center, Western Washington University, 1900 Shannon Point Road, Anacortes, WA 98221, USA

Abstract. The production of dimethylsulfoniopropionate (DMSP) and its cleavage products are well studied in phytoplankton. However, less is known about their sources, distributions, functions, and impacts in other marine organisms. We examined the distribution of DMSP in benthic macroalgae and macroinvertebrates geographically and taxonomically. In macroalgae, concentrations significantly increased from the tropics to the poles in the northern, but not the southern, hemisphere. The increase in the northern hemisphere was due to an increase in concentrations with latitude in the Chlorophyta. This pattern was generated by a relatively high proportion of species in the order Ulvales (median [DMSP]: 145 μmol g^{-1} dry mass (DM)) at higher latitudes, and a high proportion of species in the orders Caulerpales and Siphonocladales (median [DMSP]: below detection level for both orders) in the tropics. Low DMSP concentrations (< 10 μmol g^{-1} DM) were reported from all red and brown macroalgae, except *Polysiphonia* and *Halopytis*. In macroalgae, some of the reported functions of DMSP and its cleavage products included acting as a compatible solute, an anti-herbivore defense, a reactive oxygen scavenger, and a cryoprotectant. Among macroinvertebrates, DMSP occurred in higher concentrations in cnidarians than in sponges and molluscs. Concentrations in animals harboring endosymbiotic algae were 6.5 times higher than animals without symbionts. This and direct measurements of DMSP from isolated symbionts suggest that endosymbionts are a major source of DMSP for some macroinvertebrates. Diet may be a source of DMSP in animals that lack endosymbionts. The functions and impacts of DMSP in invertebrates are not well known.

Key words. Biogeography; community interactions; phenotypic plasticity; physiological ecology; taxonomic distribution.

Introduction

Early work on the sulphonium compound dimethylsulfoniopropionate (DMSP) focused on its occurrence in benthic marine macroalgae. DMSP was first described as a precursor of dimethylsulfide (DMS) in the red macroalga, *Polysiphonia fastigiata* (Challenger and Simpson, 1948). The DMSP cleavage pathway that generates DMS and acrylic acid was later described in a green macroalga, *Ulva* (previously *Enteromorpha*) *intestinalis* (Bywood and Challenger, 1953). In 1956, an enzyme that could catalyze this reaction, termed DMSP lyase, was identified from a

red macroalga *Polysiphonia lanosa* (Cantoni and Anderson, 1956).

In the past three decades, only a small percentage of studies have focused on benthic or macroscopic algae and invertebrates. In that period, studies of DMSP and its cleavage products, DMS, acrylate, and acrylic acid, have been dominated by work on planktonic microorganisms, particularly phytoplankton. This is largely due to the discovery of the importance of these compounds and their oceanic sources to global sulfur cycling and climate (reviewed by Liss et al., 1994; Malin, 1996; Malin and Kirst, 1997; Malin et al., 1992; Steinke et al., 2002). However, recently there has been a renewed interest in the role of DMSP in shallow-water benthic organisms because benthic coral reef invertebrates have been found to be a significant albeit localized source of atmospheric DMS (e.g., Broadbent and Jones, 2004) and because the cleavage of DMSP has been found to mediate interactions between organisms in temperate intertidal and shallow subtidal communities (e.g., Van Alstyne and Houser, 2003; Van Alstyne et al., 2001).

The purpose of this paper is to provide an overview of the distribution, functions, and impacts of DMSP production in marine benthic macroalgae and macroinvertebrates with a focus on the following questions. 1) What are the geographic distributions of DMSP in marine benthic macroalgae? Are geographic patterns in DMSP concentrations a result of different distribution patterns among taxonomic groups of algae that tend to contain either high or low concentrations of DMSP?, 2) What is the function of DMSP in benthic macroalgae?, 3) What are the consequences of the presence of DMSP and its breakdown products, both to the organisms that contain them and to co-occurring species?, 4) What is the distribution of DMSP in benthic macroinvertebrates?, and 5) What are the sources of the compound in these animals?

To address these questions, we have compiled and analyzed data from previously published papers as well as data from recent surveys of DMSP concentrations conducted in Australasia, the southeastern United States, northeastern Canada, and Guam.

Geographic and taxonomic distribution patterns of DMSP in marine macroalgae

DMSP occurs in diverse taxa of organisms, including algae, vascular plants, invertebrates, and vertebrates (e.g., Ackman and Hingley, 1968; Ackman et al., 1972; Iida and Tokunaga, 1986; Kiene et al., 1996; Van Alstyne et al., 2006b). However, despite its widespread distribution, DMSP does not occur uniformly, even among closely related taxa.

To examine the distribution and abundance of DMSP across geographic regions and taxa of marine macroalgae, we compiled data from several surveys of DMSP concentrations that were conducted throughout the world in which DMSP concentrations were reported on a dry mass (DM) basis (Bischoff et al., 1994; Erickson et al., 2006; Karsten et al., 1994; Lyons et al., unpublished data; Van Alstyne, unpublished data; Van Alstyne et al., 2001). The data were sorted into 8 large-scale geographic regions based on delineations of Cox and Moore (1993) and Briggs (1974) to look at the abundance of DMSP on a global scale. The regions included four climatologically-based divisions in the northern and southern hemispheres, the northern tropical region, the northern warm temperate region, the northern cold temperate region, the northern polar region, the southern tropical region, the southern warm temperate region, the southern cold temperate region, and the southern polar region. Within each of the eight regions, an average DMSP concentration was determined for each reported species. When there were multiple reports within a region, an average was taken of the average values from each site to obtain a single datum for each species within each region. It should be noted that the majority of the DMSP measurements examined here were obtained indirectly by immersing specimens in NaOH in sealed containers and measuring DMS with gas chromatography. It is possible for compounds other than DMSP to generate DMS under these conditions (Howard and Russell, 1995) and the relative contributions of compounds other then DMSP to DMS production in macroalgae and macroinvertebrates is not well known. However, DMSP has been positively identified as a major metabolite in the green macroalga *Ulvaria obscura* with a combination of mass and nuclear magnetic resonance (NMR) spectroscopy (Van Alstyne et al., 2006a) and it is assumed to be the primary source of DMS in other species.

A total of 106 genera were examined. Except when the diversity of species examined in a region was low (1–2 reported species within a region), the number of species within any one genus never exceeded 30% of total number of species in a region. Because of the large number of zero values in the data set, the data did not meet assumptions of normality and homoscedasticity; therefore, Pearson's correlation coefficients were used to examine correlations between DMSP concentrations and coded region values (tropical=1, warm temperate=2, cold temperate=3, and polar=4) when examining mean DMSP concentrations at the phylum level across regions. Analysis of variance was used to compare DMSP concentrations within the genus *Ulva* across regions in the northern hemisphere

as these data did meet the assumptions of normality and homoscedasticity.

DMSP concentrations increased from the tropics to the poles in the northern hemisphere (Fig. 1; r^2=0.271, P<0.001, N=176), but not in the southern hemisphere (Fig. 1; r^2=-0.025, P=0.876, N=43). The trend in the northern hemisphere was driven by increasing DMSP concentrations with latitude in the green algae (r^2=0.577, P<0.001, N=176). In northern hemisphere brown algae, DMSP concentrations decreased significantly with latitude (r^2=-0.378, P=0.030, N=33) and red algae and latitude were not significantly correlated (r^2=0.173, P=0.153, N=70). In general, concentrations of DMSP were very low or below detection in red and brown algal species with two exceptions. Species in the confamilial red algal genera *Polysiphonia* and *Halopytis* tended to have relatively high DMSP concentrations (median ± interquartile range (IQR): 23±122 µmol g^{-1} DM, N=9), whereas in other red algae, the median concentration was much lower (median ± IQR: 0±0 µmol g^{-1} DM, N=65) and did not exceed 1.4 µmol g^{-1} DM. In the brown algae, DMSP concentrations were uniformly low (median ± IQR: 0±0 µmol g^{-1} DM, N=32) and never exceeded 3 µmol g^{-1} DM. Average concentrations in green macroalgae (± 1SD) were 41±82 µmol g^{-1} DM (median ± IQR: 0±17 µmol g^{-1} DM, N=94).

The tendency for green algal DMSP concentrations to increase with latitude in the northern hemisphere was a function of the distribution of DMSP at the ordinal and generic levels (based on the classification scheme of Graham and Wilcox, 1999) coupled with latitudinal differences in distributions of green algae at the ordinal level. DMSP concentrations were significantly different among green algal orders (Kruskal-Wallis test: H=35.9, P<0.001). Concentrations were higher in members of the order Ulvales (median ± IQR: 145±150.5 µmol g^{-1} DM, N=15) than in members of the orders Caulerpales (median: below detection level, N=30), Dasycladales (median: below detection level, N=4), Siphonocladales (median ± IQR: 0±0.2 µmol g^{-1} DM, N=21) and Ulotrichales (median ± IQR: 16±73 µmol g^{-1} DM, N=5). Thus, the overall latitudinal trends in green algal DMSP concentrations were in large part a result of the distributional patterns of high- and low-DMSP containing groups. For example, the median DMSP concentration was low in the tropics because of the high species diversity of siphonaceous green algae in the Caulerpales (*Avrainvillea*, *Caulerpa*, *Halimeda*, *Penicillus*, *Rhipocephalus*, and *Udotea* spp.), which tend to contain little or no DMSP (Fig. 2). On the other hand, members of the Ulvales, which had relatively high DMSP concentrations, made up a
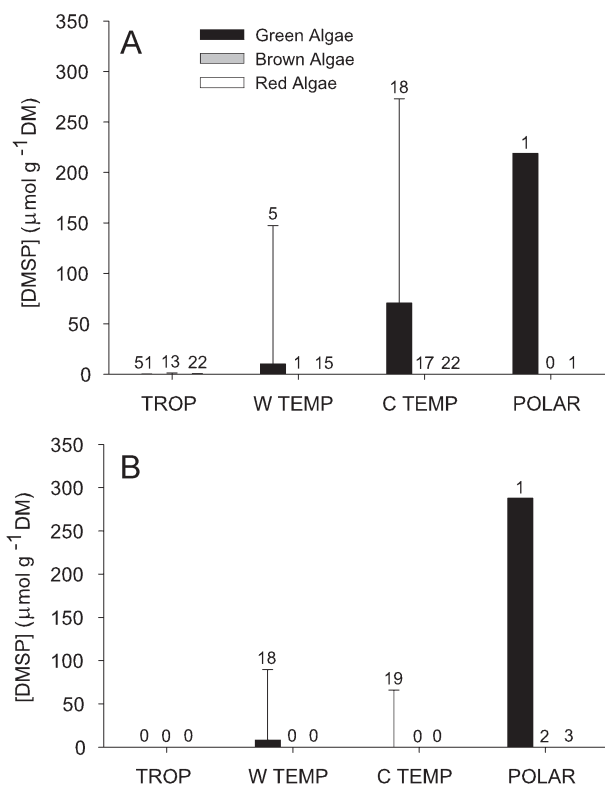

Figure 1. DMSP concentrations in green (black bars), brown (gray bars) and red (open bars) algae from tropical (TROP), warm temperate (W TEMP), cold temperate (C TEMP) and polar regions, as delineated by Cox and Wilcox (1993) and Briggs (1974), for the A) northern and B) southern hemispheres. Vertical bars represent medians (± interquartile range) of species-level DMSP concentrations. Numbers of species are given above the bars. Data were compiled from surveys by Bischoff et al. (1994), Karsten et al. (1994), Van Alstyne et al. (2001), Erickson et al. (2006), Lyons et al. (unpublished data), and from surveys of DMSP concentrations in algae from Florida, Guam, and Australasia (Van Alstyne, unpublished data).

greater proportion of the sampled cold temperate and polar floras, causing the median DMSP concentrations to be higher in those regions.

The high variance within the Caulerpales resulted from significant differences in DMSP concentrations among genera (Kruskal-Wallis test: H=19.9, P=0.030). DMSP concentrations in *Codium* spp. (median: 126 µmol g^{-1} DM, N=2) were higher than concentrations in all other genera in the order (median ± IQR: 0±0 µmol g^{-1} DM, N=25), which never exceeded 1 µmol g^{-1} DM. DMSP concentrations in the Ulvales were more uniformly high with concentrations in 14 of the 15 species being at least 48 µmol g^{-1} DM. The only exception was the tropical chlorophyte *Ulva conglobata* (0.3 µmol g^{-1} DM; Bischoff et al., 1994).

The green algal genus *Ulva* (including *Enteromorpha* which was recently synonymized with *Ulva* (Hayden et al., 2003)) was the only genus with a wide
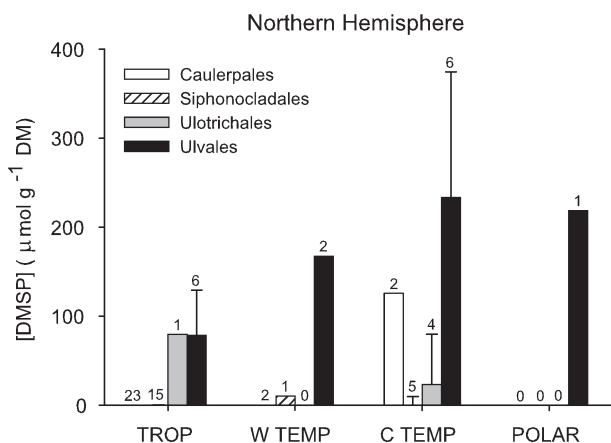
Figure 2. Northern hemisphere green algae. DMSP concentrations of green algal species grouped by algal order and geographic region (tropical (TROP), warm temperate (W TEMP), cold temperate (C TEMP) and polar). Bars are medians ± the interquartile range. Numbers of species are given above the bars.

Figure 3. Mean (± 1 SD) DMSP concentrations in northern hemisphere *Ulva* spp. among regions (tropical (TROP), warm temperate (W TEMP), cold temperate (C TEMP) and polar). Numbers of species are given above the bars. Vertical bars connected by horizontal lines under the abscissa represent means that are not significantly different (Tukey's post hoc test: P<0.05).

enough distribution and for which enough information existed to test the hypothesis that DMSP concentrations within a genus increase with latitude. Concentrations of DMSP in *Ulva* spp. differ significantly among regions (Fig. 3; one-way ANOVA. F=12.16, df=3, P<0.001) with concentrations in the tropics being significantly lower than concentrations in cold temperate and polar regions (Tukey's post hoc test: P<0.05). Similar latitudinal clines also occur within *Ulva lactuca* in Washington State, USA. When DMSP concentrations in *U. lactuca* were compared among populations at six sites over a 70 km distance in the Puget Sound/Northwest Straits region, they increased significantly from the southernmost to the northernmost sites (Van Alstyne et al., 2007).

The trends in DMSP distributions suggest that multiple evolutionary and possible ecological factors are affecting whether or not the compound is produced by macroalgae and the degree to which it is produced. The discontinuous distribution of the compound among taxonomic groups suggests that the ability to produce and store significant amounts of DMSP has evolved multiple times. Multiple evolutionary origins of DMSP production among all organisms are supported by the existence of at least three different synthetic pathways used in the production of DMSP in algae and vascular plants (reviewed by Stefels, 2000). The latitudinal cline in DMSP production, particularly within the genus *Ulva*, suggests that either selective pressures have affected the amounts of DMSP produced at different latitudes or that the amount of compound produced is under environmental control by factors that change with latitude, such as temperature, light availability, or day length. Similar latitudinal trends exist in phlorotannin
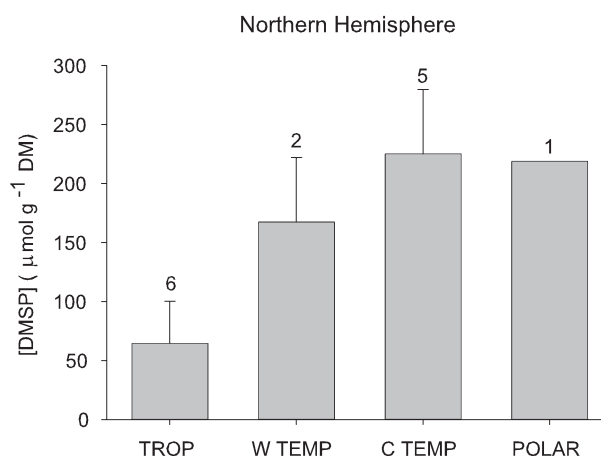
production by brown algae in the Pacific basin (Steinberg, 1986; Steinberg, 1992; Van Alstyne and Paul, 1990), although not in the Atlantic basin (Targett et al., 1992), but the mechanisms generating these patterns are also not known.

Environmental factors affecting DMSP production in marine macroalgae

Variation in concentrations of DMSP can also occur within species on smaller, more localized scales ranging from 10's to 100 of km (Table 1). Variation in DMSP concentrations among populations can span an order of magnitude, but rarely exceed this amount. Within-species differences in DMSP concentrations can be genetically determined, environmentally induced, or affected by some combination of the two. The degree of genetic control of DMSP concentrations is currently unknown. Some environmental factors have been shown to affect DMSP concentrations, and their effects can be species or context specific. For example, in the high intertidal green alga *Ulva intestinalis*, DMSP concentrations increased in response to increases in salinity over a 35 d period, but not over a 48 hr period (Edwards et al., 1987; Edwards et al., 1988). DMSP concentrations have also been shown to be higher in *Polysiphonia lanosa* from Scotland (Reed, 1983b), *Acrosiphonia arcta*, *Ulothrix implexa*, *Ulothrix subflaccida*, *Ulva bulbosa* from Antarctica (Karsten et al., 1992), *Ulva rigida* from Chile (Karsten et al., 1992), and *Blidingia minima* from Germany (Karsten et al., 1992) when algae are maintained in higher salinity media than when they

Table 1. Among-site variation in average DMSP concentrations (in μmol g^{-1} FM) in marine macroalgae. The values given are the minimum and maximum population means for the listed geographic area. FM fresh mass [a] Reed, 1983a, [b] Bischoff et al., 1994, [c] Van Alstyne et al., 2001, [d] Van Alstyne et al., 2007.

Species	Location	Range (μmol g^{-1} FM)	Number of Populations
Phylum Chorophyta			
Codium fragile	Washington/Oregon, USA	0.04 – 0.2[c]	2
Ulothrix flacca	Scotland	19 – 35[a]	2
Ulva californica	Washington/Oregon, USA	60 – 118[c]	3
Ulva compressa	Scotland	25 – 40[a]	3
Ulva intestinalis	Scotland	7 – 34[a]	3
Ulva intestinalis	Washington/Oregon, USA	13 – 25[c]	2
Ulva lactuca	Scotland	23 – 49[a]	4
Ulva lactuca	Washington, USA	74 – 128[d]	6
Ulva taeniata	Washington, USA	37 – 81[c]	3
Phylum Heterokontophyta			
Colpomenia sinuosa	Hainan, China	0.03 – 0.1[b]	3
Sargassum polycystum	Hainan, China	0.17 – 0.18[b]	2
Phylum Rhodophyta			
Hypnea spinella	Hainan, China	0.02 – 0.2[b]	3
Polysiphonia hendryi	Washington/Oregon, USA	8 – 30[c]	3
Polysiphonia lanosa	Scotland	45 – 97[a]	2
Rhodomela confervoides	Scotland	4 – 8[a]	2

are maintained at lower salinities. In contrast, DMSP concentrations in *Ulva lactuca* from Washington, USA changed little over both short (3 to 24 hr) and long (1 to 4 weeks) periods of time when maintained in media that had a range of salinities that was similar to Reed's (1983) study (Van Alstyne et al., 2003).

Light can also affect DMSP concentrations in marine macroalgae. DMSP concentrations in *Acrosiphonia arcta*, *Ulothrix implexa*, *Ulothrix subflaccida*, *Ulva bulbosa*, *Ulva rigida* and *Blidingia minima* increased with increasing light levels when light levels ranged from 0 to 55 μmol photons m^{-2} sec^{-1} (Karsten et al., 1992). However, no changes in DMSP concentrations were observed in *Ulva lactuca* maintained in outdoor tanks at four different noon light levels that ranged from ~400 to 2200 μmol photons m^{-2} sec^{-1} (Van Alstyne et al., 2007). It should be noted that the noon light levels in this experiment were above the amount of light needed to saturate photosynthesis in *U. lactuca*, which is ~30–50 μmol photons m^{-2} sec^{-1}. Screening different wavelengths of light with mylar, a UV-B filter, and Plexiglas, a UV-A and UV-B filter, also had no effect on DMSP production in *U. lactuca* (Van Alstyne et al., 2007).

The geographic patterns discussed earlier and direct experimental manipulations suggest that DMSP concentrations may increase with decreases in temperature. When the Antarctic macroalgae *Acrosiphonia arcta*, *Ulothrix implexa*, *Ulothrix subflaccida*, and *Ulva bulbosa* were grown at 0 °C and 10 °C in the laboratory, the algae consistently had higher DMSP concentrations at the lower temperatures (Karsten et al., 1992).

Reactive oxygen species (ROS) are produced by many algae in response to environmental stresses. Although DMSP itself is not a strong antioxidant, its cleavage products DMS and acrylic acid are effective at consuming ROS (Ross and Van Alstyne, 2007; Sunda et al., 2002). High concentrations of ROS (1–5 mmol H_2O_2) cause decreases in DMSP in *Ulva lactuca* over relatively short time periods (3 hr) as DMSP is cleaved and DMS and acrylic acid are released (Ross and Van Alstyne, 2007).

Functions of DMSP in marine macroalgae and their ecological implications

A variety of functions have been proposed for DMSP and its breakdown products, and different functions have been attributed to these compounds in macroalgae from different locations. For example in *Ulva intestinalis* (previously *Enteromorpha intestinalis*) and *Polysiphonia lanosa* in Scotland, DMSP functions as an osmolyte (Edwards et al., 1987; Edwards et al., 1988; Reed, 1983a). In *Ulva lactuca* from the southeastern United States, DMSP scavenges ROS (Ross and Van Alstyne, 2007). In polar species, it may protect macroalgae from stresses associated with low or freezing temperatures (Karsten et al., 1994). In the northeastern Pacific (Van Alstyne and Houser, 2003; Van Alstyne et al., 2001), it can function as a component of an anti-herbivore defense. The described differences in functions in different regions could be a result of species-specific adaptations to local and regional environmental conditions. However, they

may also be a result of the limited number of locations where research on each function has been conducted.

Many of the species that produce DMSP such as ulvoid green algae and *Polysiphonia* spp., inhabit estuarine and intertidal environments where they can experience hypo- and hyperosmotic conditions as well as extreme fluctuations in salinities on both short-term (minutes to hours) and long-term (seasonal) time scales. DMSP may, in part, be responsible for the ability of these algae to tolerate a large range of osmotic conditions. Experimental manipulations have shown that DMSP accumulates in response to salinity increases in the surrounding seawater (Edwards et al., 1988; Karsten et al., 1992); however, the timing of these responses can differ. In *U. intestinalis,* DMSP accumulated over periods of at least 30 days in response to increases in salinity (Edwards et al., 1988), but increases in DMSP concentrations in response to increased salinity were observed in Antarctic chlorophytes within 72 hr (Karsten et al., 1992). When these algae were cultivated under light and dark conditions at different salinities, DMSP concentrations responded to salinity in the presence of light but did not respond in the dark (Karsten et al., 1992). This is thought to occur because the synthesis of the protein degradation product methionine, the biosynthetic precursor of DMSP, requires light-dependent enzymes (Karsten et al., 1992; Kirst, 1996).

DMSP may also contribute to the persistence of some algae by making them a lower preference food for herbivores relative to other sympatric algae. The DMSP-cleavage reaction is thought to be the basis of an activated defense, a type of chemical defense that allows an alga to avoid autotoxicity by limiting the production of potent defensive compounds to the site of damage. The DMSP-cleavage reaction was first described as an activated defense in microalgae (Wolfe and Steinke, 1996; Wolfe et al., 1997), where it was proposed that DMSP would be enzymatically cleaved into the putative anti-herbivore compounds DMS and acrylate within seconds of damage by grazers. Experimental evidence has demonstrated that DMSP can have a similar function in macroalgae. DMSP lyase-like activity has been reported for the green alga *U. lactuca* (previously *Ulva fenestrata*) and the red alga *Polysiphonia hendryi* (Van Alstyne et al., 2001). In feeding studies in which DMSP, DMS, or acrylic acid were added to artificial foods, the sea urchins *Strongylocentrotus droebachiensis* and *S. purpuratus* avoided foods containing acrylic acid and DMS but preferred foods containing DMSP over control foods (Van Alstyne and Houser, 2003; Van Alstyne et al., 2001). However, the effectiveness of the DMSP activated defense is herbivore-specific. Similar assays with the isopod *Idotea wosnesenskii* have

shown that acrylic acid does not deter feeding but instead stimulates it (Van Alstyne et al., 2001). In a more recent study with the subtropical Atlantic sea urchin *Echinometra lucunter*, the presence of DMS and acrylic acid in artificial foods neither deterred nor stimulated feeding (Erickson et al., 2006).

It is clear that DMSP and its byproducts can have a variety of functions (Kiene et al., 1996) and that there is the potential for DMSP to serve multiple functions within a species. However, it is unlikely that DMSP will be used for all of these functions in any given species or in all species that produce it within a given habitat. Rather, the functions of DMSP and its byproducts are likely to be species-specific and even population-specific.

DMSP in benthic macroinvertebrates

DMSP occurs in measurable amounts in several invertebrate phyla, including members of the Porifera (Van Alstyne et al., 2006b), Cnidaria (Broadbent and Jones, 2002; Broadbent and Jones, 2004; Hill et al., 1995; Jones et al., 1994; Jones and Trevena, 2005; Van Alstyne et al., 2006b), Platyhelminthes (Van Bergeijk and Stal, 2001), Mollusca (Ackman and Hingley, 1968; Brooke et al., 1968; Hill et al., 2000; Iida and Tokunaga, 1986; White et al., 1995) and Arthropoda (Ackman and Hingley, 1968). Concentrations (measured on a fresh mass (FM) basis) are significantly different among phyla (Fig. 4A; Kruskal-Wallis test: H=25.44, DF=2, P<0.001), with cnidarians having the highest concentrations of DMSP and sponges having the lowest. However, this result is confounded by the presence or absence of endosymbiotic algae in these animals. All of the cnidarians, two of the molluscs, and none of the sponge species contain symbionts. When DMSP concentrations are compared according to the presence or absence of symbionts, they are about 6.5 times higher in species with symbionts than in species lacking them (Fig. 4B; Kruskal-Wallis test: H=25.44, DF=2, P<0.001).

For many species, symbionts are clearly the source of some, if not all, of the animals' DMSP. DMSP has been directly measured in cell cultures of zooxanthellae obtained from corals, a clam, a scyphozoan, and a zoanthid (Broadbent and Jones, 2002; Hill et al., 1995) and from cell cultures of the green alga *Tetraselmis* sp., a symbiont of the flatworm *Convoluta roscoffensis* (Van Bergeijk and Stal, 2001). The data from these studies suggest that symbionts play a major role in DMSP production, although they may not be the only source. DMSP concentrations of zooxanthellate cell cultures were approximately 90% and 41% of the concentrations
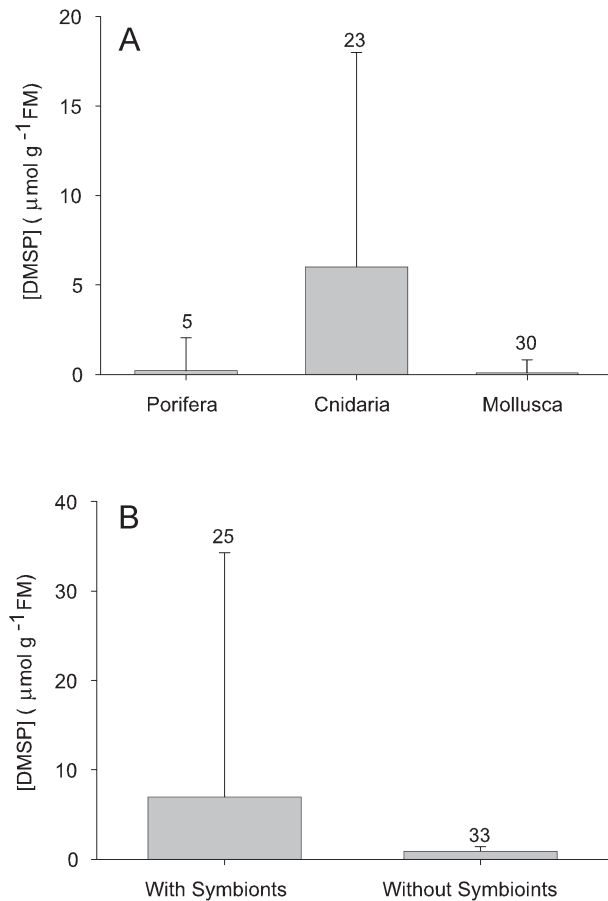
Figure 4. DMSP concentrations (median concentration ± interquartile range) of benthic macroinvertebrates. A) Grouped by phylum (Kruskal-Wallis test: H=25.44, DF=2, P<0.001) and B) grouped by the presence or absence of photosynthetic symbionts (Kruskal-Wallis test: H=30.44, DF=1, P<0.001). Data were compiled from Ackman and Hingley (1968), Brooke et al. (1968), White et al. (1995) Iida and Tokunaga (1986), Hill et al. (2000), and Van Alstyne et al. (2006b). A representative concentration was determined for each invertebrate species in which the data were reported on a per gram (fresh mass) basis. When there were multiple values for a species, an average was taken to obtain a single datum for each species. Numbers of species are given above the bars.

obtained from direct measurements of DMSP from the corals *Montipora verrucosa* and *Pocillopora damicornis*, respectively (Hill et al., 1995). Concentrations were also closely correlated with zooxanthellae densities among 22 cnidarian species from Guam and among individuals within three of these species (Van Alstyne et al., 2006b). In a fourth species, DMSP and symbiont densities were not correlated. The zooxanthellate origin of DMSP in anemones is also supported by DMSP being present in higher quantities in anemones (*Anthopleura elegantissima*) harboring zooxanthellate symbionts (mean ±1 SD: 11±2 µmol g⁻¹ FM, N=5) than in conspecifics that are aposymbiotic (mean ±1 SD: 0.3±0.1 µmol g⁻¹ DM, N=5) or that harbor primarily green algal symbionts (mean ±1 SD: 0.4±0.1 µmol g⁻¹ DM, N=5) (Van Alstyne and Muller-Parker, unpublished).

Species that lack symbiotic algae must either obtain DMSP from their diet or synthesize it *de novo*. Many of the bivalve molluscs that contain DMSP are suspension feeders that consume either phytoplankton, which might contain DMSP, or zooplankton that eat DMSP-producing phytoplankton, providing a plausible dietary source. The distribution of DMSP within the bodies of DMSP-containing bivalves neither confirms nor refutes a possible dietary origin as some species have higher concentrations of DMSP in the digestive gland (White et al., 1995) or viscera (Ackman and Hingley, 1968; Iida and Tokunaga, 1986) than the rest of the body, but many do not (Iida and Tokunaga, 1986). Population level distributions do provide evidence of a dietary source. Concentrations of DMSP are lower in the bivalve *Geukensia demissa* collected at a marsh site where the animals fed primarily on salt marsh detritus that was low in DMSP than from three sites where the animals fed on phytoplankton that should have high DMSP concentrations (White et al., 1995). Snails (*Littorina littorea*) collected from the DMSP-producing green macroalga *Ulva lactuca* also tended to have high concentrations of DMSP (Ackman and Hingley, 1968).

Manipulations of the diets of DMSP-containing animals provide the strongest evidence for dietary uptake of the compound. Oysters (*Crassostrea gigas*) that were held in the lab and not allowed to feed upon foods containing DMSP showed a decline in tissue DMSP levels after 4 months (Ackman and Hingley, 1968). Likewise, DMSP was not detectable in snails (*Littorina sitkana*) fed the red macroalga *Mazzaella splendens* or the brown macroalga *Fucus gardneri* which do not produce DMSP, but it did occur in animals fed the DMSP-producing green alga *Ulva lactuca* (Van Alstyne, unpublished).

The reasons for the production and accumulation of DMSP by invertebrates have not been well studied and, at this point, are mostly speculative. The fact that many of the species producing DMSP inhabit tropical reefs suggests that cryoprotection is not an important function of the compound in these species. Predator deterrence may be a function of DMSP in some coral reef invertebrates as it is in some macroalgae. Another likely function of DMSP in coral reef invertebrates is protecting the host and/or symbionts from oxidative damage in an environment that experiences high levels of radiation, especially in the UV range. Colonies of *Acropora formosa* that are bleached contain more DMSP per symbiont than unbleached colonies (Broadbent et al., 2002) suggesting that

DMSP concentrations increase in response to environmental stresses associated with bleaching or that symbionts containing low concentrations of DMSP either die or leave the colonies more quickly than cells with higher concentrations.

References

Ackman, R. and H. Hingley, 1968. The occurence and retension of dimethyl-β-propiothetin in some filter-feeding animals. J. Fish. Res. Bd. Can. **25:** 267 – 284.

Ackman, R., J. Hingley and K. MacKay, 1972. Dimethyl sulfide as an odor component in Nova Scotia fall mackerel. J. Fish. Res. Bd. Can. **29:** 1085 – 1088.

Bischoff, B., U. Karsten, C. Daniel, K. Kuck, B. Xia and C. Wiencke, 1994. Preliminary assessment of the Beta-Dimethylsulfoniopropionate (DMSP) content of macroalgae from the tropical island Hainan (People's Republic of China). Austral. J. Mar. Freshw. Res. **45:** 1329 – 1336.

Briggs, J., 1974. Marine Zoogeography. McGraw-Hill, New York and London, 475 pp.

Broadbent, A. and G. Jones, 2002. DMSP in corals and benthic algae from the Great Barrier Reef. Estuar. Coast. Shelf S. **55:** 547 – 555.

Broadbent, A. and G. Jones, 2004. DMS and DMSP in mucus ropes, coral mucus, surface films and sediment pore waters from coral reefs in the Great Barrier Reef. Mar. Freshw. Res. **55:** 849 – 855.

Broadbent, A., G. Jones and R. Jones, 2002. DMSP in corals and benthic algae from the Great Barrier Reef. Estuar. Coast. Shelf Sci. **55:** 547 – 555.

Brooke, R., J. Mendelsohn and F. King, 1968. Significance of dimethyl sulfide to the odor of soft-shell clams. J. Fish. Res. Bd. Can. **25:** 2453 – 2460.

Bywood, R. and F. Challenger, 1953. The evolution of dimethyl sulphide by *Enteromorpha intestinalis*. Isolation of dimethyl-ß-carboxyethyl sulphonium chloride from the alga. Biochem. J. **53:** 26.

Cantoni, G. and D. Anderson, 1956. Enzymatic cleavage of dimethylpropiothetin by *Polysiphonia lanosa*. J. Biol. Chem. **222:** 171 – 177.

Challenger, F. and M. Simpson, 1948. Studies on biological methylation. Part 12. A precirsor of the dimethyl sulphide evolved by Polysiphonia fastigiata. Dimethyl-2-carboxy-ethyl-sulphonium hydroxide and its salts. J. Chem. Soc. **3:** 1591 – 1597.

Cox, C. and P. Moore, 1993. Biogeography: An Ecological and Evolutionary Approach. Blackwell, London, 326 pp.

Edwards, D. M., R. H. Reed, J. A. Chudek, R. Foster and W. D. P. Stewart, 1987. Organic solute accumulation in osmotically-stressed *Enteromorpha intestinalis*. Mar. Biol. **95:** 583 – 592.

Edwards, D. M., R. H. Reed and W. D. P. Stewart, 1988. Osmoacclimation in *Enteromorpha intestinalis:* long-term effects of osmotic stress on organic solute accumulation. Mar. Biol. **88:** 457 – 476.

Erickson, A., V. J. Paul, K. L. Van Alstyne and L. Kwiatkowski, 2006. Palatability of macroalgae that use different types of chemical defenses. J. Chem. Ecol. **32:** 1883 – 1895.

Graham, L. E. and L. W. Wilcox, 1999. Algae. Prentice Hall, Upper Saddle River, 640 pp.

Hayden, H., J. Blomster, C. Maggs, P. Silva, M. Stanhope and J. Waaland, 2003. Linnaeus was right all along: *Ulva* and *Enteromorpha* are not distinct genera. Eur. J. Phycol. **38:** 277 – 294.

Hill, R. W., J. W. H. Dacey and A. Edward, 2000. Dimethylsulfoniopropionate in giant clams (Tridacnidae). Biol. Bull. **199:** 108 – 115.

Hill, R. W., J. W. H. Dacey and D. A. Krupp, 1995. Dimethylsulfoniopropionate in reef corals. Bull. Mar. Sci. **57:** 489 – 494.

Howard, A. G. and D. W. Russell, 1995. HPLC-FPD instrumentation for the measurement of the atmospheric dimethyl sulfide precursor β-(dimethylsulfonio)proprionate. Anal. Chem. **67:** 1293 – 1295.

Iida, H. and T. Tokunaga, 1986. Dimethyl sulfide and dimethyl-β-propiothetin in shellfish. Bull. Jap. Soc. Scient. Fish. **52:** 557 – 563.

Jones, G., M. Curran and A. Broadbent, 1994. Dimethylsulphide in the South Pacific, 6th Pacific Congr Mar Sci Technol. James Cook Univ, Townsville, pp. 183 – 190.

Jones, G. and A. Trevena, 2005. The influence of coral reefs on atmospheric dimethylslphide over the Great Barrier Reef, Coral Sea, Gulf of Papua and Solomon and Bismark Seas. Mar Freshw. Res **56:** 85 – 93.

Karsten, U., K. Kuck, C. Daniel, C. Wiencke and G. O. Kirst, 1994. A method for complete determination of dimethylsulfoniopropionate (DMSP) in marine macroalgae for different geographical regions. Phycologia **33:** 171 – 176.

Karsten, U., C. Wiencke and G. O. Kirst, 1992. Dimethylsulphoniopropionate (DMSP) accumulation in green macroalgae from polar to temperate regions: interactive effects of light versus salinity and light versus temperature. Polar Biol. **12:** 603 – 607.

Kiene, R. P., P. Visscher, M. Keller and G. O. Kirst, 1996. Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds. Plenum Press, New York, 430 pp.

Kirst, G. O., 1996. Osmotic adjustments in phytoplankton and macroalgae: the use of dimethylsulfoniopropionate (DMSP). In: R. P. Kiene, P. Visscher, M. Keller and G. O. Kirst (eds.), Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds, Plenum Press, New York, pp. 121 – 129.

Liss, P. S., G. Malin, S. M. Turner and P. M. Holligan, 1994. Dimethyl sulphide and *Phaeocystis:* a review. J. Mar. Syst. **5:** 41 – 53.

Malin, G., 1996. The role of DMSP and DMS in the global sulfur cycle and climate regulation. In: R. P. Kiene, P. Visscher, M. Keller and G. O. Kirst (eds.), Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds, Plenum Press, New York, pp. 177 – 189.

Malin, G. and G. O. Kirst, 1997. Algal production of dimethyl sulfide and its atmospheric role. J. Phycol. **33:** 889 – 896.

Malin, G., S. M. Turner and P. S. Liss, 1992. Sulfur: the plankton/climate connection. J. Phycol. **28:** 590 – 597.

Reed, R. H., 1983a. Measurement and osmotic significance of beta-dimethylsulfoniopropionate in marine macroalgae. Mar. Biol. Lett. **4:** 173 – 181.

Reed, R. H., 1983b. The osmotic responses of *Polysiphonia lanosa* (L.) Tandy from marine and estuarine sites: evidence for incomplete recovery of turgor. J. exp. mar. biol. ecol. **68:** 169 – 193.

Ross, C. and K. L. Van Alstyne, 2007. Intraspecific variation in stress-induced hydrogen peroxide scavenging by the ulvoid macroalga *Ulva lactuca*. J. Phycol. **43:** 466 – 474.

Stefels, J., 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. J. Sea Res. **43:** 183 – 197.

Steinberg, P. D., 1986. Chemical defenses and the susceptibility of tropical brown algae to herbivores. Oecologia **69:** 628 – 630.

Steinberg, P. D., 1992. Geographical variation in the interaction between marine herbivores and brown algal secondary metabolites. In: V. Paul (ed.), Ecological Roles of Marine Natural Products, Cornell University Press, Ithaca, pp. 51 – 92.

Steinke, M., G. Malin and P. Liss, 2002. Trophic interactions in the sea: an ecological role for climate relevant volatiles. J. Phycol. **38:** 630 – 638.

Sunda, W. G., D. Kieber, R. Kiene and S. Huntsman, 2002. An antioxidant function for DMSP and DMS in marine algae. Nature **418:** 317 – 320.

Targett, N. M., L. D. Coen, A. A. Boettcher and C. E. Tanner, 1992. Biogeographic comparisons of marine algal phenolics: evidence against a latitudinal trend. Oecologia **89:** 464 – 470.

Van Alstyne, K. L. and L. T. Houser, 2003. Dimethylsulfide release during macroinvertebrate grazing and its role as an activated chemical defense. Mar. Ecol. Prog. Ser. **250:** 175 – 181.

Van Alstyne, K. L., A. V. Nelson, J. R. Vyvyan, and D. A. Cancilla, 2006. Dopamine functions as an antiherbivore defense in the temperate green alga *Ulvaria obscura*. Oecologia **148:** 304 – 311.

Van Alstyne, K. L., L. Koellermeier and T. Nelson, 2007. Spatial variation in dimethylsulfoniopropionate (DMSP) production in *Ulva lactuca* (Chlorophyta) from the Northeastern Pacific. Mar. Biol. **150:** 1127 – 1135.

Van Alstyne, K. L. and V. J. Paul, 1990. The biogeography of

polyphenolic compounds in marine macroalgae: temperate brown algal defenses deter feeding by tropical herbivorous fishes. Oecologia **84:** 158 – 163.

Van Alstyne, K. L., K. N. Pelletreau and K. Rosario, 2003. The effects of salinity on dimethylsulfoniopropionate production in the green alga *Ulva fenestrata* Postels et Ruprecht (Chlorophyta). Bot. Mar. **46:** 350 – 356.

Van Alstyne, K. L., P. Schupp and M. Slattery, 2006. The distribution of dimethylsulfoniopropionate (DMSP) in tropical Pacific coral reef invertebrates. Coral Reefs **25:** 321 – 327.

Van Alstyne, K. L., G. V. Wolfe, T. L. Freidenburg, A. Neill and C. Hicken, 2001. Activated defense systems in marine macroalgae: evidence for an ecological role for DMSP cleavage. Mar. Ecol. Prog. Ser. **213:** 53 – 65.

Van Bergeijk, S. A. and L. J. Stal, 2001. Dimethylsulfoniopropionate and dimethylsulfide in the marine flatworm *Convoluta roscoffensis* and its algal symbiont. Mar. Biol. **138:** 209 – 216.

White, B., R. W. Hill and J. W. H. Dacey, 1995. Accumulation of DMSP in *Geukensia demissa* depends on trophic interactions. Biol. Bull. **189:** 235 – 236.

Wolfe, G. V. and M. Steinke, 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. Limnol. Oceanogr. **41:** 1151 – 1160.

Wolfe, G. V., M. Steinke and G. O. Kirst, 1997. Grazing-activated chemical defence in a unicellular marine alga. Nature **387:** 894 – 897.

To access this journal online:

http://www.birkhauser.ch/AS