Colored Dissolved Organic Material Increases Resiliency of Coral Reefs by Controlling Exposure to UVR

L. Ayoub, P. Hallock, P. Coble

College of Marine Science, Univ. South Florida, 140 7th Ave. S., St. Petersburg, FL 33701, USA

Abstract. Although mass coral bleaching events are generally triggered by high seawater temperatures, experiments have demonstrated that corals and reef-dwelling foraminifers bleach more readily when exposed to high energy, short wavelength solar radiation (blue, violet and ultraviolet [UVR]: $\lambda \sim 280 - 490$ nm). In seawater, colored dissolved organic matter (CDOM), also called gelbstoff, preferentially absorbs these shorter wavelengths, which consequently bleach and degrade the CDOM. Alteration and destruction of watershed and coastal wetlands have reduced natural sources of CDOM that are tidally flushed into reefal waters. We have measured absorption of UVR and UV irradiance at various reefs in the Florida Keys that differ in distance from shore and the degree of anthropogenic development of the adjacent shoreline. Our results show that reefs associated with intact shorelines tend to be exposed to lower intensities of UVR than reefs associated with developed shorelines. Absorption due to CDOM at 320 nm (a_{g320}) was less variable at reefs associated with intact shorelines, and higher at inshore reefs compared to offshore reefs. UVR is attenuated more quickly at inshore than offshore, clear-water reefs at similar depths. Spectral slope of a_g, S, was generally greater at offshore sites, indicating a higher degree of photobleaching of CDOM.

Keywords: ultraviolet radiation, coral reefs, absorption coefficient, attenuation coefficient, CDOM

Introduction

Corals worldwide have been declining since the 1970's and the prognosis for the future is not improving (Birkeland 2004; Hoegh-Guldberg et al. 2007). Coral bleaching has become a worldwide phenomenon, and the frequency and intensity of bleaching is increasing (Hoegh-Guldberg 1999; Wilkinson 2002). While the relationship between coral mass-bleaching events and elevated sea-surface temperature (SST) is well established (Hoegh-Guldberg 1999), increasing numbers of studies are revealing that light plays a vital role in coral bleaching. For example, Lesser and Farrell (2004) found that corals do not bleach in the absence of light. Low wavelength ultraviolet radiation (UVR) and blue light can stimulate production of reactive oxygen species causing gene mutation and other damaging consequences to marine invertebrates (Lesser 2006; Levy et al. 2006).

Mass bleaching events typically occur when sea conditions are unusually calm (e.g., Fabricius et al. 2004) and thermal bleaching appears to be caused by photoinhibition and photodamage to photosystem II of the zooxanthellae (e.g., Lesser and Farrell 2004; Smith et al. 2005). The fact that clouds or direct shading can reduce bleaching in corals provides more evidence for the necessary role of light (e.g., Mumby et al. 2001; Fabricius et al. 2004). More recent studies are linking coral disease and photooxidative stress (Lesser 2006).

UVR specifically has been shown to cause DNA damage, DNA mutations or cell death in marine organisms such as corals (Shick et al. 1996). Although it is generally thought that UVR attenuates quickly, some natural water bodies are characterized by high transparency to UVR (Gleason and Wellington 1993).

Pure water absorbs minimally at wavelengths below 490 nm, thus attenuation of the shorter wavelengths of light is primarily due to dissolved and particulate matter (Kirk 1996). Light absorption by colored dissolved organic matter (CDOM) is highest at the shortest wavelengths and exponentially decreases with increasing wavelength. Moreover, the absorption of high-energy radiation causes bleaching and degradation of CDOM (Zepp et al. 2008). Spectrally, photobleaching of CDOM increases with decreasing wavelength from 500 to 280 nm, with the most effective photobleaching occurring in the UV-A region (320 – 400 nm) (Osburn et al. 2001). While an increase in rates of CDOM breakdown may not be biologically significant in turbid, CDOM-rich waters, it may be a major reason why corals in clear waters are reportedly more susceptible to bleaching (e.g.,

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West and Salm 2003) and possibly also to diseases that are not directly related to pollution. For example, as a consequence of the 4% global reduction in stratospheric ozone following the Mt. Pinatubo eruption (Randel et al. 1995), the resultant approximately 8% increase in UV-B reaching the sea surface (Schick et al. 1996) could have increased the rate of CDOM degradation by as much as 24% (Zepp et al. 2003). Other studies estimate a lower percentage change, for example, a 25% increase in UV-B results in a 10% increase in photobleaching according to studies on temperate lakes (Osburn et al. 2001).

As a defense against UVR, corals and other aquatic organisms produce UV-absorbing pigments called mycosporine-like amino acids (MAAs) (Shick et al. 1996). Maximum absorption for MAAs occurs between 305 and 360 nm. Thus, the presence of MAAs can indicate photic stress (Morrison and Nelson 2004).

Exposure to UVR has been increasing in recent decades due to stratospheric ozone depletion, resulting in increased photobleaching of CDOM and, in turn, deleterious effects on marine biota (Fig. 1). We postulate that CDOM is protecting inshore patch reefs from exposure to the most extreme solar radiation and damaging effects of photooxidative stress.
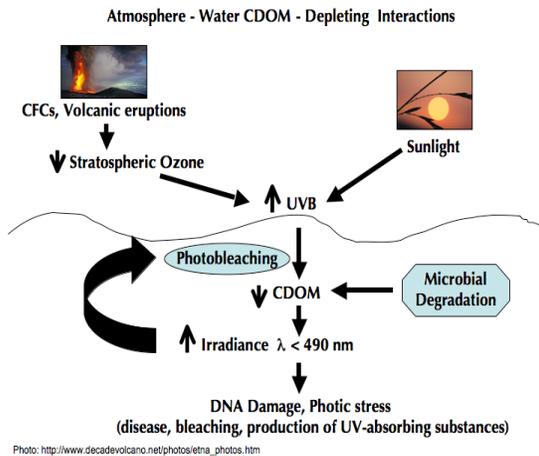

Figure 1. Atmospheric, optical, and biological factors affecting CDOM absorptivity and related biological effects (after Morris and Hargreaves 1997; Zepp et al. 2008).

Material and Methods

In late May, early July and late September 2004, and early May and mid-July 2005, water samples and *in situ* optical data were collected at several reefs in the upper and middle Florida Keys. In addition, in September 2004, absorption due to CDOM (a_g) was measured along a transect (red arrow in Fig. 2) from offshore at 75 m depth, shoreward to 50 m and 25 m depths, inshore to Carysfort and Algae Reefs, and finally within a mangrove-lined canal in John Pennekamp State Park. In summer 2006 and 2007, sampling sites included inshore and offshore coral reefs in the Upper, Middle and Lower Keys that lie within the Florida Keys National Marine Sanctuary (FKNMS) and are part of the Coral Reef Evaluation and Monitoring Program (CREMP) (Fig. 2).
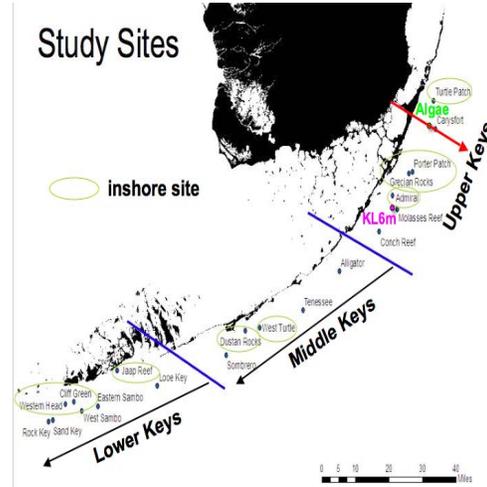

Figure 2. Study sites in the Lower, Middle and Upper Florida Keys included offshore reefs and inshore (patch) reefs that differ in degree of development of associated shoreline. In 2006 and 2007, study sites also included inshore and offshore CREMP study sites in the Lower, Middle and Upper Florida Keys (image collaboration with A. Ramirez).

Total absorption can be partitioned into absorption due to dissolved material, a_{CDOM}, particulate material, a_{PM}, and pure water, a_w (Kirk 1996). Using measured a_{CDOM} and a_{PM}, and published values of a_w (Morel et al. 2007):

$$a_t(\lambda) = a_{CDOM} + a_{PM} + a_w \qquad (1)$$

In natural systems, light is not collimated but diffuse. Measuring irradiance consistently within 2 hours of solar noon minimizes the effect of sun angle and thus pathlength on light attenuation. Total attenuation is due to scattering as well as absorption. Scattering is negligible compared to absorption for this study (Ivey, unpubl. data). Thus, the diffuse attenuation coefficient of downwelling irradiance (K_d) can be estimated from total absorption (Kirk 1996):

$$K_d = a_{CDOM} + a_{PM} + a_w \qquad (2)$$

Water samples were collected from the subsurface (~ 0.5 m) and at the depth of coral growth by SCUBA divers or using Niskin bottles. After filtration of water samples, samples were frozen and transported back to the lab, where spectral absorption (300-800 nm) for CDOM ($a_g(\lambda)$) was measured according to the method described in Mueller and Fargion (2002) and $a_{PM}(\lambda)$ was measured according to Mitchell (1990) using a UV-Visible spectrophotometer (Perkin Elmer Lambda 18 or Hitachi U 3300). Spectral absorption due to detritus,

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$a_d (\lambda)$, was determined by methanol extraction of pigments and subtracted from $a_{PM}(\lambda)$ to determine spectral absorption due to phytoplankton, $a_{phi} (\lambda)$:

$$a_{phi} (\lambda) = a_{PM} (\lambda) - a_d (\lambda) \qquad (3)$$

(Kirk 1996). Relative MAA expression was determined using the method of Morrison and Nelson (2004).

In July 2004, incident solar irradiance reaching the sea surface was measured using a LiCor - 1800 Spectroradiometer (280-850 nm) at a nearby land site at 10-20 minute intervals from 8:30 am – 6:30 pm daily. Intensity of irradiance reaching the benthos was calculated from measurements of in-lab absorption $a_t (\lambda)$ and the *in situ* incident downwelling irradiance $E_{d0} (\lambda)$ according to eqn. (3) and:

$$E_{dz}(\lambda) = E_{d0} (\lambda) * e^{-Kd(\lambda)*z} \qquad (4)$$

where z represents depth in meters (Kirk 1996). After July 2005, K_d was calculated from *in situ* underwater downwelling cosine irradiance ($E_d(\lambda)$) measured at 305, 330, 380 nm (10 nm wavebands, recorded at maximum wavelength minus 5 nm) and PAR (integrated from 400 – 700 nm) using a BIC (Biospherical Instruments, Inc.) radiometer.

Differences in a_g, K_d, spectral slope S, and relative MAA expression were determined using one-way ANOVA statistical tests.

Results

Absorption due to CDOM decreased going offshore from mangroves to inshore reefs, offshore reefs and finally blue water (Fig. 3), exhibiting the progressive dilution of land-sourced CDOM.
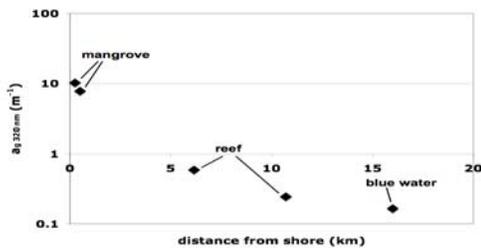

Figure 3. Transect of absorption due to CDOM at 320 an ($a_{g\ 320}$). $a_{g\ 320}$ decreased going from mangrove canals in John Pennekamp Park to inshore and offshore reefs to offshore blue water.

Downwelling UV irradiance at 320 nm at depth = 6m ($E_{d6m\ 320nm}$), modeled from a_{t320} and incident irradiance (E_{d0}), was significantly higher at reefs associated with developed shoreline, such as KL6m ($E_{d6m\ 320nm}$ = 0.01 - 0.084 W/m^2) than at reefs offshore from extensive mangrove shoreline, such as Algae Reef ($E_{d\ 320nm}$ = 0.008 – 0.057 W/m^2) ($p < 0.05$, Fig. 4).

Over the period of sampling, 2004 – 2007, the average contribution of absorption due to CDOM, a_g, to total absorption, a_t, increased with decreasing wavelength, ranging from 60% at 380 nm to over 90% at 305 nm. Thus, CDOM is the major attenuator of UVR. Over the course of each summer a_g/ a_t typically decreased, likely due to photobleaching of CDOM (Fig. 5). The observed increase in a_g/ a_t from May to July 2005 may be due to the higher rainfall which occurred in June and July, ca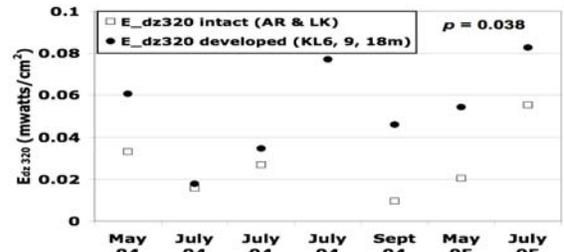using greater runoff and thus increased CDOM over the reef (http://www.ncdc.noaa.gov/oa/climate/research/monit oring.html#ustempprcp).

Figure 4. $E_{d6m\ 320}$ was significantly lower at intact shoreline-associated reefs compared to developed shoreline-associated reefs ($p < 0.05$).
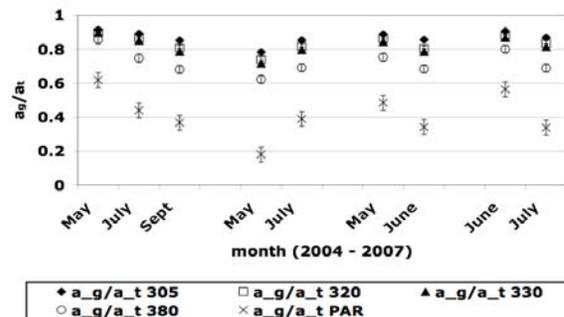

Figure 5. Average relative contribution of a_g to a_t in the UV at 305, 320, 330, 380 nm ranged from 62% at 380 nm to 91% at 305 nm and from 18 – 62 % for PAR. Average a_g/a_t typically declined at all wavelengths as the summer progressed.

Comparing a_g between inshore and offshore reefs, a_g was significantly higher at inshore reefs at all wavelengths (e.g., a_{g320}, Fig. 6, $p = 0.0086$). Concurrently, K_d measured *in situ* using a BIC radiometer was significantly higher at inshore reefs (ex: $K_{d\ 330}$, Fig. 6, Table 1, $p = 0.00297$). Differences in spectral quality were also observed: excepting discrepancy from this trend at 305 nm due to immeasurably low irradiance intensities, the difference in K_d between inshore and offshore reefs decreased with increasing wavelength, with the p value for $K_{d\ PAR}$ an order of magnitude higher than for $K_{d\ UV}$ (Table 1). Thus, difference in water transparency between inshore and offshore reefs was greater for UVR than for PAR.

Both a_g and K_d, two independent measures of UV transparency, illustrate that coral reef biota are exposed to lower intensities of UV irradiance at

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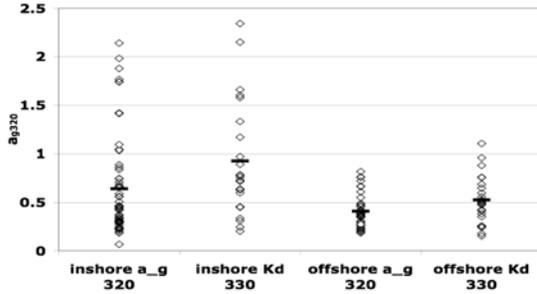inshore reefs compared to offshore reefs in the Florida Keys.

Figure 6. Absorption due to CDOM at 320 nm ($a_{g\,320}$) was significantly higher at inshore reefs ($n = 58$, average = 0.64) than offshore reefs ($n = 38$, average = 0.41) ($p < 0.01$). The attenuation coefficient of downwelling irradiance at 330 nm, $K_{d\,330}$, was significantly higher at inshore reefs ($n = 23$, average = 0.928) than offshore reefs ($n = 25$, average = 0.524) ($p < 0.005$). Dashes represent averages.

K_d (λ)	average		range		std dev		
	in	off	in	off	in	off	p
K_d 305	1.40	0.83	0.32 – 1.30	0.27 – 1.83	0.93	0.38	0.008
K_d 330	0.93	0.52	0.20 – 2.15	0.24 – 1.10	0.59	0.24	0.003
K_d 380	0.42	0.25	0.13 – 0.90	0.066 – 0.56	0.25	0.12	0.003
K_d PAR	0.23	0.18	0.07 - 0.32	0.025 – 0.49	0.06	0.09	0.039

Table 1. Statistical data comparing K_d between inshore and offshore reefs. The difference in K_d between inshore and offshore reefs was greatest for 330 and 380 nm, and least for PAR (in = inshore, off = offshore).

Relative expression of MAAs varied inversely with $a_{g\,320}$ (Fig. 7) and was higher and more variable at reefs associated with developed shoreline (a_{phi_325}/a_{phi_350} = 1.3 – 2.7, CV = 30%) than at reefs associated with intact shoreline (a_{phi_325}/a_{phi_350} range = 1.03 to 1.2, CV = 6%), ($p < 0.05$).
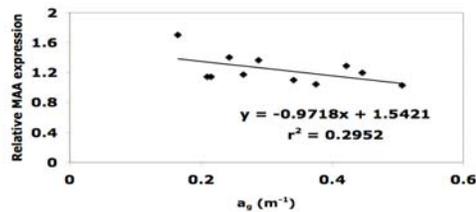

Figure 7. Relative expression of MAAs varied inversely with $a_{g\,320}$ (slope = -0.97) for intact and developed reefs in 2004 – 2005.

Spectral slope of a_g in the UV, $S_{(280 – 312\ nm)}$, was significantly higher at offshore sites (avg. = 0.030, std. dev. = 0.003) compared to inshore sites (avg. =

0.027, std dev. = 0.004) ($p = 0.001$). S is an indicator of photobleaching of CDOM (Del Vecchio and Blough 2002). Thus, in addition to higher exposure to UVR (Fig. 6), CDOM at offshore reefs was more highly photobleached.

Discussion

Though traditionally it has been thought that corals require clear water for photosynthesis, recent trends show that the clearer water reefs are experiencing higher rates of coral decline. In the Florida Keys, distance from shoreline as well as shoreline quality may influence reef health as recent declines in percent coral cover and coral biodiversity have been greater at offshore reefs than inshore reefs (Somerfield et al. 2008) and coral-lesion recovery rates are higher at inshore (patch) reefs near intact mangrove shoreline than developed shoreline (Fisher et al. 2007). Inshore reefs may be closer to seagrass beds, mangroves, wetlands, and other terrestrial sources of CDOM. Our work shows that differences in water transparency, and the resulting spectral differences in solar radiation reaching the benthos, may contribute to different rates of decline in coral cover between inshore patch reefs and offshore shallow reefs.

This study helps to support/explain previous observations in the Florida Keys: 1) lower rates of decline at inshore reefs than offshore reefs (e.g., Somerfield et al. 2008); 2) consistently higher bleaching in larger foraminifers at a reef associated with clearer water (Conch Reef) than at a reef influenced by Florida Bay water (Tennessee Reef) (Williams 2002); 3) occurrence of bleaching in benthic foraminifers (*Amphistegina gibbosa*) in the Florida Keys follows solar cycle, not SST cycle, and increases with increasing UV:PAR (Williams 2002); and 4) higher coral cover, coral-lesion recovery rates and abundances of larger foraminifers at a reef associated with intact shoreline (Algae Reef) compared to a reef associated with developed shoreline (KL6m Reef) (Fisher et al. 2007).

Prior studies also show deleterious effects of UVR on reef organisms. Lab experiments have shown that bleaching in *A. gibbosa* is exacerbated by exposure to blue or UV wavelengths (Williams and Hallock 2004). Studies of bleaching in corals indicate that decline in zooxanthellate photosynthetic capacity follows increase in daylight and precedes temperature peak (Warner et al. 2002*)*, and that UVR and PAR exacerbate supraoptimal temperature effects (Lesser and Farrell 2004). Although MAAs are photoprotective, the energetic cost of MAA production may inhibit growth and recovery from stress (Hoogenboom et al. 2006**)**, and high solar radiation may depress MAA production (Lesser and Farrell 2004**)**.

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Based on modeled entire water column photobleaching in lakes, photobleaching can cause 0.6 to 1.4% decrease in CDOM light absorption over the timescale of tidal flushing (12 hours) (Reche et al. 2000). Offshore reefs and developed shoreline-associated reefs that do not receive consistent, tidally flushed pulses of CDOM are particularly susceptible to increased UV transparency due to photobleaching of CDOM.

In conclusion, UV irradiance may contribute to photooxidative stress and reef decline in the Florida Keys. Management of shorelines to protect sources of photo-protective CDOM such as mangroves, seagrasses, and wetlands may reduce susceptibility to bleaching in corals.

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