Can colored dissolved organic material protect coral reefs by reducing exposure to ultraviolet radiation?

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Can Colored Dissolved Organic Material Protect Coral Reefs by Reducing Exposure to Ultraviolet Radiation?

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
College of Marine Science
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Dedication

This dissertation is dedicated to my father, Theodore Anthony Ayoub, DDS, and my grandmother, Sadie Ayoub.
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Can Colored Dissolved Organic Material Protect Coral Reefs by Reducing Exposure to Ultraviolet Radiation

Lore Michele Ayoub

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 of watersheds and destruction of coastal wetlands have reduced natural sources of CDOM to reefal waters.

I tested the null hypothesis that CDOM does not differ between reefs that differ in coral health, and that water transparency to UVR is not a factor in reef health. I measured absorption of UVR and UV irradiance at various reefs in the Florida Keys that differ in distance from shore and degree of anthropogenic development of the adjacent shoreline. My results show that intact shoreline - associated reefs and inshore reefs tend to be exposed to lower intensities of UVR, and lower degrees of photic stress, than developed shoreline - associated reefs and offshore reefs. Absorption due to CDOM ($a_{g20}$) was higher, and photic stress, as revealed by increased production of UV-absorbing compounds, Mycosporine – like Amino Acids (MAAs), was lower at the surface compared to the bottom.
The following results support my conclusion: $a_{g,320}$ and UV attenuation coefficients ($K_d$ ‘s) were higher at intact compared to developed shoreline – associated reefs, and at inshore compared to offshore reefs. Spectral slope, $S$, was higher at offshore compared to inshore reefs, indicating a higher degree of photobleaching of CDOM. Relative expression of MAAs was higher at developed compared to intact shoreline – associated reefs, at offshore reefs compared to inshore reefs, and at the surface compared to the bottom. Solar energy reaching the benthos at two inshore reefs of the same depth (6m) was approximately an order of magnitude higher at the reef near developed shoreline compared to the reef near intact shoreline, and may be due to greater degree of diffuseness of the underwater light field combined with lower $a_g$ at the developed shoreline - associated reef.
1. Introduction

In the last three decades of the 20th century, scientists, reef managers and the public witnessed the decline of coral reefs, first locally, then over entire reef tracts and regions. By the late 1990s, most scientists recognized that reef decline was worldwide (e.g., Dight and Scherl 1997, Eakin et al. 1997, Risk 1999). Bryant and others (1998) estimated that more than half of the world's coral reefs were threatened by human activities such as sewage and industrial pollution, deforestation, and overfishing. Their report was released as the 1997-98 ENSO event triggered coral mass bleaching events unprecedented in global scale and intensity (e.g., Hoegh-Guldberg 1999, Wilkinson 2002). Subsequent prognoses on the condition of reefs have not been encouraging (e.g., Buddemeier 2001, Birkeland 2004, Hoegh-Guldberg et al. 2007, Baker et al. 2008). For example, a decline in species richness for all habitat types from 1996 to 2001 and a general decline in stony coral cover from 1996 to 2003 have been observed in the Florida Keys National Marine Sanctuary (Somerfield et al. 2008). As a consequence, scientists and reef managers are increasingly seeking to determine what factors can enhance resiliency of reef communities (e.g., Nystrom et al. 2000, Knowlton 2001, McClanahan et al. 2002).

The relationship between coral mass-bleaching events and elevated sea-surface temperature (SST) is well established (Goreau and Hayes 1994, Brown 1997, Hoegh-Guldberg 1999). In addition, corals do not bleach in the absence of light (e.g., Lesser and
Mass bleaching events typically occur when sea conditions are unusually calm (e.g., Glynn 1996, Fabricius et al. 2004) and thermal bleaching appears to be caused by photoinhibition and photodamage to photosystem II of the zooxanthellae (e.g., Fitt et al. 2001, Lesser 2004, Smith et al. 2005). Several reported exceptions to the correlation between mass bleaching and SST indicate that clouds or direct shading can reduce bleaching in corals (e.g., Mumby et al. 2001, Fabricius et al. 2004). In addition to supraoptimal insolation and temperature, ocean acidification due to increasing CO₂ is a current and future threat to reef health, by compromising carbonate accretion and thus formation of coral skeletons (Hoegh-Guldberg et al. 2007).

According to the Coral Reef Evaluation and Monitoring Project (CREMP), since 1996 inshore patch reefs have consistently exhibited lower rates of decline than offshore, clear water reefs at similar depths (NOAA 2002, Somerfield et al. 2008). Depending on degree of shoreline development, inshore patch reefs tend to be closer to seagrass beds, mangroves and terrestrial sources of colored dissolved organic material (CDOM), which strongly absorbs short wavelength visible and ultraviolet (UV) radiation. While a commonly accepted hypothesis is that inshore patch reefs are better adapted to high temperature variability than offshore reefs, my dissertation will explore another hypothesis: differences in water transparency, and the resulting differences in solar radiation reaching the benthos, may play a role in the differences in rates of decline of coral cover between inshore patch reefs and offshore shallow reefs. The null hypothesis is thus, that differences in water transparency, and the resulting differences in solar radiation reaching the benthos, do not play a role in differences in rates of decline of coral cover between inshore patch reefs and offshore shallow reefs.
The UV-absorbing capacity of CDOM can potentially protect inshore patch reefs from photooxidative stress. As an illustration, absorption due to CDOM decreases going from mangroves to inshore and offshore reefs and is lowest in offshore, open ocean blue water (Figure 1.1). The decrease in absorption results in increased transparency to short wavelength, high energy blue and UV solar radiation at offshore sites relative to inshore sites.

To examine my hypothesis, samples of whole water were collected from the surface (approximately 0.5 to 1 m) and from the depth of coral growth, and downwelling cosine irradiance profiles of *in situ* ultraviolet radiation (UVR) and photosynthetically
active radiation (PAR), were measured at various locations along the Florida reef tract. To address my hypothesis (see above), I measured irradiance and absorption due to CDOM at reefs varying in proximity to shoreline (inshore and offshore reefs) and compared these results to inshore - offshore site differences in percent coral cover and rates of decline in coral cover. I compared in situ light (irradiance) measurements and CDOM absorption and at reefs that differ in type of shoreline (intact and developed). I also measured absorption due to particulates, and chlorophyll concentration ([chl]). The attenuation coefficient ($K_d$), was calculated from in situ irradiance or total absorption (the sum of absorption due to CDOM, particulates, and pure water). Because $K_d$ is not affected by the time of day, i.e., the sun angle, this coefficient is a convenient quantitative expression for comparing water transparency and thus penetrability of UVR and PAR among sites.

Mycosporine-like amino acids (MAAs) are UV-absorbing compounds found in photosynthetic organisms. Because they are induced by supraoptimal exposure to UV and visible radiation, MAAs can be used as an indicator of photooxidative stress. I used relative MAA expression to compare MAA production by phytoplankton in the water column among sites.

Considering the angular structure or diffuseness of the underwater light field, greater diffuseness results in increased scattering, and thus increased likelihood of an object being irradiated (Kirk 1994). I used a radiative transfer model, Hydrolight®, to compare the diffuseness of the underwater light field between intact and developed shoreline - associated reefs.
Chapter 2. Background: aspects of in-water optics

2.1. Electromagnetic radiation and the solar spectrum

In this chapter, I shall introduce essential concepts and definitions relating to my study of water transparency and solar radiation in reef environments. For a more complete discussion, see Kirk (1994).

Solar radiation is a type of electromagnetic energy which consists of a spectrum of energy characterized by different wavelengths and frequencies (Fig. 2.1). Wavelength, \( \lambda \), and frequency, \( \nu \), are related by the speed of light, \( c \), a constant in a given medium:

\[
\lambda = \frac{c}{\nu}
\]  

According to (2.1), as wavelength increases, frequency decreases. Each wavelength of radiation has an associated energy, \( E \), which varies with frequency:

\[
E = h\nu = \frac{hc}{\lambda}
\]  

where \( h \) is Planck’s constant and has the value of \( 6.63 \times 10^{-34} \) J \cdot s. Thus, as wavelength decreases, its associated energy increases (Kirk 1994).
Figure 2.1. Spectra of nonionizing solar radiation (A) and ultraviolet radiation (B) showing main radiation bands, their nomenclature, and approximate wavelength limits. Other synonyms: UV-A, black light; UV-B, sunburn or erythemal radiation; UV-C, germicidal radiation (from Acra et al. 1990, compiled from WHO 1979, Parmeggiani 1983, and Harvey et al. 1984).

Nonionizing solar radiation can be categorized into visible and invisible radiation (Fig. 2.1). While some organisms, including coral, have the ability to capture UVR and fluoresce it to wavelengths useable in photosynthesis (Kawaguti 1969, Schlichter et al. 1986), solar radiation in the visible range (400 – 700 nm), commonly referred to as Photosynthetically Available Radiation (PAR), is the major source of energy for photosynthesis. Ultraviolet radiation (UVR, 100 – 400 nm) occurs at wavelengths shorter than visible light, therefore the energy in a photon of UVR is higher than in a photon of visible radiation. Ultraviolet radiation is energetically differentiated into four categories: Vacuum UV (100 – 200 nm), UV-C (200 – 280 nm), UV-B (280 – 320 nm, or 315 nm, depending on source), and UV-A (315 or 320 – 400 nm) (Acra et al. 1990, Kirk 1994).
At the other end of the spectrum, infrared radiation (700 – 1400 nm), which is experienced as heat, occurs at wavelengths longer than visible light.

### 2.2. Atmosphere – UV interactions

The components of the atmosphere that most strongly absorb UVR are sulfur dioxide (SO$_2$) and ozone (O$_3$) (Roscoe 2001). UV-C does not reach the earth in appreciable intensities due to effective absorption by stratospheric ozone (Figs. 2.2, 2.3). UV-B is less effectively absorbed by ozone, and thus does reach the Earth’s surface in amounts inversely proportional to stratospheric ozone concentration (Acra et al. 1990). Methyl halide aerosols, such as anthropogenic methyl bromide and chlorofluorocarbons, in the presence of sunlight, can break down stratospheric ozone. At the same time as it absorbs UV, sulfur dioxide promotes the formation of more reactive chlorofluorocarbons which are more effective at breaking down ozone, and thus indirectly result in increased UVR reaching the Earth’s surface. The rate of ozone depletion is affected by temperature, circulation and cloud albedo (Figs. 2.2, 2.3). Explosive volcanism contributes to atmospheric [SO$_2$] and therefore can cause increases in UVR reaching the Earth’s surface (Roscoe 2001).
Figure 2.2. Interactions between ozone depletion and climate change. The arrows indicate direction of influence. The effects of climate change on ozone and UVR are discussed in the text (adapted from Clark 2001 in UNEP 2003).
A general term for a continuous measure of the effects of solar radiation as a function of wavelength is the spectral weighting function (SWF). An SWF quantifies the effectiveness (or ‘weight’) of solar radiation, for example, UVR or PAR, at causing some response in relation to wavelength. Two specific types of SWFs are action spectra and biological weighting functions. Action spectra are based on responses to narrowband (monochromatic) irradiance and are defined for both biological and chemical effects. Biological weighting functions are determined under broadband (polychromatic) irradiance and reflect the simultaneous (and sometimes competing) effects of multiple wavelength-dependent processes as they occur in nature (Neale and Kieber 2000).

An action spectrum illustrates the differential importance of different wavelengths of light in inducing the effects of solar exposure (Neale and Kieber 200). For example,
effectiveness at producing erythemal (skin) and DNA damage (Fig. 2.4) and photoinhibition of photosynthesis in Arctic phytoplankton increase exponentially with decreasing wavelength in the UV range (Cullen and Neale 1997). The same effect has been found for corals. Lesser (2000) examined action spectra for the effect of UV on photosynthesis at different depths in the coral *Montastrea faveolata*, finding a steep and rapid decrease with increasing wavelength. Action spectra and biological weighting functions are used to determine biological amplification factors and have been used to assess the environmental impacts of increased surface UV irradiances resulting from stratospheric ozone depletion (Micheletti *et al.* 2003).

Figure 2.4. Example of an action spectrum for erythemal and DNA damage (http://www.temis.nl/uvradiation/info/uvaction.html).

Changes in UVB reaching the Earth’s surface due to changes in stratospheric ozone can be expressed in terms of a radiation amplification factor (*RAF*) (Rundel and
Nachtey 1978, Rundel 1983, Smith and Cullen 1995). Since the relationship between UVB dose and ozone concentration is nonlinear, the RAF can be most generally expressed using an equation relating the change in biological effective irradiance, or dose rate, \( E_{Be(\lambda)} \), to the change in total atmospheric column ozone concentration or ozone thickness, \( \omega \) (Madronich and Granier 1992, Madronich 1993, Booth and Madronich 1994):

\[
RAF = \left[ \frac{(\Delta E_{Be(\lambda)})_2}{(E_{Be(\lambda)})_1} \right] \left[ \frac{\Delta \omega_2}{\omega_1} \right] 
\]

(2.3)

Congruently, the effect of changes in ozone on UV exposures can be expressed as:

\[
RAF = \left[ \frac{(UV_{\lambda})_2}{(UV_{\lambda})_1} \right] \left[ \frac{\Delta \omega_2}{\omega_1} \right] 
\]

(2.4)

Radiation amplification factors can in turn be used to calculate the increase of biologically effective irradiance in response to ozone depletion. Published values of RAFs for different processes have been reviewed by Madronich et al. (1998).

As another example, the percent change in absorption due to CDOM, \( a_g \), can be related to the proportional change in \( E_{Be(\lambda)} \) by a biological amplification factor, \( B \) (Smith and Cullen 1995):

\[
B = \left[ \frac{\Delta a_g}{a_g} \right] \left[ \frac{\Delta E_{Be(\lambda)}}{E_{Be(\lambda)}} \right] 
\]

(2.5)

Combining these two factors, the percent change in ozone can be related to the biological effect by the total amplification factor, \( A \):

\[
A = RAF \times B 
\]

(2.6)
The total amplification factor can be used to describe the effect of ozone depletion on a biological or chemical process such as photosynthesis. For example, Lesser (2000) determined that RAFs for the effect of UV (290 – 400 nm) exposure on photosynthesis in the coral *Montastrea faveolata* varied from 0.15 to 0.23, while earlier estimates of RAFs for DNA damage and for the inhibition of photosynthesis in free-living phytoplankton are much higher (-2.0 and -0.5 to 0.95, respectively) (Madronich 1993).

Compared to those mentioned above, modeled RAFs for the effects of changing CDOM concentrations based on *in situ* CDOM and UV data specifically from the Florida Keys are much higher: at 6.0 m, RAFs were 1.65 for photosynthesis inhibition and 3.26 for DNA damage (Zepp et al. 2008). Accordingly, a 30% increase in UV transparency (as expressed by a 30% decrease in the diffuse attenuation coefficient for UV, $K_{dUV}$, (see section 3.2.3.) can result in an 85% increase in photoinhibition and over 200% increase in DNA damage (Zepp et al. 2008). The RAFs were lower at shallower depths: at 3 m, 30% decrease in $K_{dUV}$ can result in a 30% increase in UV-induced photosynthesis inhibition and a nearly 100% increase in DNA damage (Zepp et al. 2008). Zepp et al. (2008) estimated that DNA damage decreases much more rapidly with depth than does photosynthesis inhibition due to the spectral dependence of UV dose rates on these effects. Based on CDOM photobleaching experiments for a water sample from the Florida Keys, Looe Key, absorption can decrease 7% per day (Zepp 2003).

Osburn *et al.* (2001) determined spectral weighting functions for the photobleaching of CDOM in lakes. Based on their model, a 25% increase in UVB radiation results in an 8% increase in photobleaching of CDOM. Generally, photobleaching increases with decreasing wavelength: the largest absolute loss of absorbance occurs at the shortest wavelengths (Kieber *et al.* 2007). Additionally, history of exposure affects photobleaching efficiency: with increasing exposure, the wavelength of
maximum photobleaching may shift to lower wavelengths (Osburn *et al.* 2001, Akella and Uher 2006). Del Vecchio and Blough (2002) found that while the largest losses of absorption are observed at the irradiation wavelength, monochromatic irradiation (irradiation with one wavelength) results in absorption loss across the entire spectrum.

2.3. Annual cycle of UVR

The annual cycle of UVR in the Lower Keys is characterized by maxima from May to August and minima from December to January (Fig. 2.5). Comparing equatorial regions to other geographic locations, as latitude decreases, UVA exposure increases and more nearly approximates that seen at the equator (Acra *et al.* 1990). In the northern hemisphere, for all UVR wavelengths from 285 to 340 nm, the solar UVR flux decreases as latitude increases for all times of year except the June solstice, when the relative irradiance is lowest at the equator (Acra *et al.* 1990).
Figure 2.5. Mean daily UV-B and UVR at the Mote Marine Laboratory in the Lower Keys (latitude 24.5°N, longitude 81.6°W) during 2002 - 2003. The data were measured by Yankee Environmental Systems UVB and UVA pyranometers at one-minute intervals (from Zepp 2003).

This latitude - UV relationship is relevant for the Florida Keys, which lie at approximately 25° latitude: the highest measured UV irradiance in the subtropical latitudes of the Keys occurs between May and August (Fig. 2.5). Maximum insolation, without the influence of the atmosphere, occurs from May to August at the latitude of the Florida Keys (Figure 2.8 in Kirk 1994; Figure 2.5). Because of the relatively high UV irradiance at this time of year, we would expect the highest deleterious response to irradiance, such as bleaching, from May though August. Consequently, this is the optimal time of year to record the most acute stress associated with solar irradiance.
2.4. UVR – environment interactions

In nature, solar radiation is scattered and reflected as well as absorbed by particulate and dissolved material. The wavelength dependence of scattering in air, Rayleigh scattering, is $1/\lambda^4$. Due to the higher refractive index of water, the wavelength dependence of Rayleigh scattering in water deviates from the in air value, to $1/\lambda^{4.32}$. Thus, shorter wavelengths, such as UVR, are more highly scattered compared to longer wavelengths such as visible light, resulting in increased UV irradiance relative to PAR (Kirk 1994).

Incident spectral irradiance typically reaches its highest intensity at 480 nm (Figs. 2.3 and 2.6). Although intensity decreases at lower wavelengths, the higher energy associated with UVR results in higher efficiency in altering the biological, chemical and physical environment (see Fig. 2.4).

Figure 2.6a. Incident spectral irradiance (on land) measured with a LiCOR-1800 spectroradiometer at 10-minute intervals on May 25, 2005 at NURC, Key Largo, FL.
Figure 2.6b. Median incident spectral irradiance (above water) on May 25, 2004 (15:50 to 16:10) and on July 6, 2004 (16:00), on land (Keys Marine Lab or NURC, Key Largo, FL).

Irradiance intensity at any wavelength is determined by the absorbing and scattering properties of the water column. In highly transparent, relatively shallow waters, the reflective properties of the bottom can influence irradiance intensity in the overlying water column. The light-absorbing and -scattering constituents of the water column can be categorized as dissolved material, particulate material, and water molecules. The most significant optically active components include phytoplankton, mineral particles and detritus, and CDOM (Kirk 1994). While pigment-containing particles, and to a lesser extent, detrital particles, can contribute to UVR absorption (Ayoub et al. 1997, Vincent et al. 2001, Belzile and Vincent 2002, Frenette et al. 2003, Zepp 2003), CDOM is the predominant and most consistent attenuator of UVR in most oceanic waters (Kirk 1994,

Figure 2.7 illustrates absorption and incident downwelling irradiance spectra for a coral reef site in the Florida Keys in May 2004. As mentioned above, these data illustrate that particulate matter can play a significant role in UVR attenuation, with absorption increasing at decreasing wavelengths. These data also show that, even in relatively clear reefal waters, CDOM is typically the major attenuator of UVR. Pure water absorbs minimally in the visible wavelengths to 580 nm, but absorbs increasingly strongly in the red to infrared range (Fig. 2.7 and Kirk 1994). In studies at an offshore reef, Conch Reef (30 m), in the Florida Keys, Lesser (2000) found that UVR down to 310 nm penetrates significantly to the depth of coral growth. Thus CDOM can play a vital role in protecting reefs from UVR.
2.5. CDOM composition

Here, I present some essential topics relating the importance of CDOM and ocean color to water transparency. More detailed reviews of ocean color and CDOM can be found in Del Castillo (2005) and Coble (2007), from which much of the following is summarized.

Though the chemical composition, origin and dynamics of CDOM in aquatic systems are still poorly understood due to their complexity (Coble 2007), CDOM is
defined operationally by the method used to separate suspended and dissolved material. Typically the most common methods are filtration through glass fiber filters (fine, pore size 0.7 µm) and polycarbonate or polysulfone membranes (0.2 µm pore size). Dissolved organic matter in seawater is composed of countless organic compounds, the majority of which are classified as humic substances, due to their original discovery and study in soil chemistry. Humic substances are typically divided into humic and fulvic acids, which have been separated based on their different solubilities (McKnight and Aiken 1998) or molecular weights (Osburn and Morris 2003), though the chemical differences separating humic and fulvic acids are not clear cut.

There are four pathways associated with the formation of fulvic and humic acids: 1) decomposition products of modified lignins, 2) microbially decomposed lignin products, 3) phenols and other plant biochemicals, and 4) polymerization products of sugars, amino acids, and other small particles (Fig. 2.8). In any given terrestrial ecosystem, all four pathways may occur, but not to the same extent or in the same order of importance. Lignin pathways predominate in poorly drained soils and wet sediments (swamps, etc.) (Waksman 1932). Production from lignins can occur via microbial decomposition of lignin by aerobic pathways to directly produce humic acids (Stevenson 1982). Synthesis from lignins via polyphenols may be of considerable importance in certain forest soils. Fluctuations in temperature, moisture and irradiation in terrestrial surface soils under a harsh continental climate may favor humus synthesis by sugar-amine condensation (J. Weber in http://www.ar.wroc.pl/~weber/powstaw2.htm#1).
Figure 2.8. Pathways for the formation of humic substances (from J. Weber in http://www.ar.wroc.pl/~weber/powstaw2.htm#1).

Nonhumic pigment-like components of marine CDOM, such as amino acid or protein-like substances, may be an indicator of elevated biological activity (Coble et al. 1998). These proteins and pigments may be truly dissolved or result from disruption of phytoplankton cells during sample preparation (filtration) (Coble 2007).

2.6. CDOM optical properties

The photochemical properties of CDOM can be ascribed to compositional makeup. Marine and terrestrial humics differ in the amounts of aliphatic and aromatic groups, and these differences explain the differences in their optical properties. Marine humics are less aromatic, have lower C/N ratios, and contain more carboxylic groups and sugars than
do terrestrial humics (Coble 2007). Both terrestrial and marine CDOM have absorbance spectra that increase exponentially toward shorter wavelengths, with no discernible peaks. This lack of features fits the explanation that CDOM is a complex mixture of compounds that have overlapping absorption spectra, with no single compound dominating (Coble 2007). The smoothness of the absorption spectrum at wavelengths greater than 350 nm may also result from intramolecular electronic interactions (Del Vecchio and Blough 2004b).

Terrestrial CDOM is more highly aromatic and molecularly complex than marine CDOM, resulting in higher absorption and “red-shifted” fluorescence upon analysis of excitation - emission spectra (“EEMS”, Del Castillo 2005). In addition, most studies have found that the spectral slope is lower for higher molecular weight (“fresher”) terrestrial CDOM than for marine CDOM (Del Vecchio and Blough 2004a).

2.7. CDOM sources, sinks and pathways

Sources of CDOM to coral reefs include decomposed terrestrial and wetland plants, including mangroves, as well as exudates from bacteria, phytoplankton, seagrasses and coral (Fig. 2.9) (Anderson et al. 2001, Stabenau et al. 2004). Intact shorelines with coastal mangrove hammocks are a vital source of CDOM to fringing and other nearshore coral reefs. Comparing coral reefs with differing predominance of seagrass, Boss and Zaneveld (2003) reported that CDOM absorption of UV and PAR is higher in pore waters of coral reefs characterized by higher densities of seagrass: grass-covered sediment are found to be sources of what these authors refer to as CDM (Colored Dissolved Material = CDOM + nonalgal particles) to the water column. Seagrass roots promote the production of CDOM via oxidation of sediment POC, by injecting photosynthetically – derived O$_2$ into the sediments (Burdige et al. 2004).
As UVR is absorbed by CDOM, the CDOM is broken down, or photobleached, producing less absorptive forms of CDOM (Morris and Hargreaves 1997, Vodacek et al. 1997, Nelson et al. 1998). In times of drought, photobleaching can be pronounced because runoff decreases, reducing CDOM supplies. In addition, calm weather increases stratification of the water column, resulting in increased UV exposure: exponential degradation of CDOM will occur and UV transparency will increase (Morris and Hargreaves 1997). The resultant smaller, more labile photoproducts of CDOM are available for bacterial degradation, allowing more UVR to pass through the water column.
(Miller and Moran 1997). At some point, CDOM can no longer be broken down and becomes recalcitrant (Aluwihare et al. 2005). While the cycle of CDOM photobleaching and increased UV transparency may continue, consistent sources of CDOM can disrupt this positive feedback loop: mangrove hammocks and seagrasses can provide regular pulses of CDOM to reef waters (Moran et al. 1991) with each tidal cycle. Also relevant to coral reefs is the interaction of tidal cycles and CDOM sources offshore from reefs: CDOM rich plumes from the Bahama Banks may sink to depth after cooling and subsequently be brought onshore via tidal cycles, and thus potentially protect benthic organisms from UVR (Otis et al. 2004).

CDOM is an important component of the trophic pathways of plankton communities, including the microbial loop (Fig. 2.10). CDOM is consumed by bacteria, at the same time zooplankton and phytoplankton excrete CDOM as waste or exudate (Steinberg et al. 2004). Bacteria play a dual role in the cycling of CDOM. Bacteria act as a sink by remineralizing CDOM, and as a source by exuding CDOM metabolically and breaking down plant material (Nelson et al. 2004). While bacteria consume as well as produce CDOM, they are in turn consumed by zooplankton (Wotton and Wotton 1994). In open ocean areas not influenced by highly colored, coastal sources of CDOM such as rivers and mangroves, exudates of phytoplankton and zooplankton are an important source of CDOM (Nelson et al. 2004, Steinberg et al. 2004).
Especially for coastal ecosystems, rivers are major sources of terrestrial CDOM. In Chapter 3, I will discuss riverine inputs of CDOM specifically for the Florida Keys.

Land use can have a consequential influence on CDOM delivery to coastal waters. Water quality studies of storm waters in South Florida have shown that wetlands and pastures exhibited highest color (235 and 227 Pt-Co units) subsequent to residual runoff (173 Pt-Co units), while runoff from citrus, row crops, urban, and golf course areas were appreciably lower (Graves et al. 2004). This difference was attributed to more rapid runoff at the sites characterized by lower CDOM because grasses at these sites are more heavily managed and limit both production and leaching of CDOM sources such as humic and tannic acids. Thus, reduction of sources of CDOM can occur not only by
replacing mangroves and coastal hammocks with buildings, but also by replacing wetlands or forests with sod and other managed vegetation. Extensive development in the Florida Keys has displaced natural vegetation and thus decreased CDOM runoff to coastal waters.

2.8. Remote sensing of UVR and coral reefs: application of the spectral slope of $a_g$

Up to now, the application of satellite algorithms for estimating UV irradiance has relied upon measurements made for PAR. *In situ* sea-truthing of coral reefs is needed to formulate algorithms for estimating UVR in oceans. Coastal areas such as coral reefs possess an additional challenge of being located in shallow waters where bottom reflectance and terrigenous inputs can complicate satellite-derived estimates of irradiance. As previously mentioned, absorption due to CDOM, $a_g$, increases exponentially as wavelength decreases, beginning at approximately 490 nm. The spectral slope of $a_g$ in the UV range, and the relationship between UVR and PAR, can be elucidated by sea-truthing of $a_g$, which would enable improved estimation of UV irradiance at greater spatial scales.

Absorption at any wavelength can be derived from spectral shape or slope scaled from absorption derived from remotely sensed $a_g$. Twardowski et al. (2004) have evaluated the application and interpretation of a single exponential model describing $a_g$ as a function of wavelength, using 412 nm as the reference wavelength, a wavelength retrieved by satellites:

$$a_g(\lambda) = a_g(412) \left( \frac{\lambda}{412} \right)^{-6.92}$$

(2.7)
In general, the spectral slope, $S$, is used to estimate $a_g$ at one wavelength, $\lambda$, from another, satellite-derived wavelength ($\lambda_0$) using a nonlinear fit of the form:

$$a_g(\lambda) = a_g(\lambda_0) e^{S(\lambda_0-\lambda)}$$

(2.8)

(Blough and Del Vecchio 2002).

The traditional usage of $S$ is in the visible light range. Algorithms for differentiating between terrestrially- and marine-derived organic matter have been determined (Stedmon and Markager 2001). The spectral slope of $a_g$ has been shown to vary depending on location (Carder et al. 1989, Vodacek et al. 1997, Nelson et al. 1998, Twardowski et al. 2004). The estimates by Carder et al. (1989) of $S$ for the Gulf of Mexico are 0.0141 nm$^{-1}$. Lee et al. (1999) reported a spectral slope of 0.01433 nm$^{-1}$ for the range 400–500 nm in Florida Keys waters based on a model estimating $a_g$ from remote sensing reflectance. The spectral slope for UVR is expected to be much higher than for the 400–500 nm range (see Fig. 2.7, $a_g$). Kopelevich et al. (1989) estimated the spectral slope for the region 280–490 nm in the open ocean to be 0.017 ± 0.001 nm$^{-1}$.

Because spectral slope increases in surface waters in summer due to increasing photobleaching (Nelson et al. 1998; Del Vecchio and Blough 2002), it can be used to compare the degree of photobleaching between water bodies. While CDOM production by phytoplankton and zooplankton can be especially important in offshore, clear surface waters and the open ocean, advection and bleaching can balance net production (Nelson et al. 2004, Steinberg et al. 2004). For example, waters with no significant bacterial production of CDOM and high transparency typically have higher spectral slopes than more highly colored waters with fresh or consistent sources of CDOM (Blough and Del Vecchio 2002).
2.9. Photobiology of UVR and effects on aquatic ecosystems

Ultraviolet radiation, including UVA, has been shown to cause stress responses such as genetic damage to bacteria, phytoplankton and other organisms (Karentz et al. 1994, Huot et al. 2000), decreased growth rate, lethal effects on larvae and adult organisms (Gleason and Wellington 1995), and photoinhibition in phytoplankton (Smith and Cullen 1995), as well as bleaching (Lesser 2004, Lesser and Farrel 2004, Vincent and Neale 2004) (Fig. 2.11). Other effects of UVR include suppressed calcification and skeletal growth (Roth et al. 1982) and coral bleaching (Glynn 1996, Lesser and Farrell 2004). The increase in DNA damage to bacterioplankton that has resulted from decreases in stratospheric ozone concentration has been modeled by Huot et al. (2000). Zepp et al. (2008) estimated that DNA damage decreases much more rapidly with depth than does inhibition of photosynthesis.

Figure 2.11. Pathways between UV radiation exposure and cellular stress. Damage can occur directly by photochemical degradation of biomolecules (pathway 1 or indirectly via the production of reactive oxygen species such as hydrogen peroxide and superoxide radicals (pathway 2a), which then cause more widespread oxidative damage within the cell (2b). The net stress is manifested in terms of: the increased energy demands of
protection and repair; compositional changes (e.g., lipid content), which may affect the nutritional quality of the cells for higher trophic levels; an impairment of growth rate resulting from the photochemical damage and from the increased energy requirements; and, under severe exposures, an increased rate of mortality (from Vincent and Neale in de Mora 2000).

Photooxidation is the conversion of a reduced molecule to an oxidized form in the presence of molecular oxygen via a set of chemical reactions that are initiated by photolysis (Glossary of Meteorology 2000). One type of photooxidative damage to the photoautotrophic symbionts of corals, the zooxanthellae, is known as "bleaching" (Gleason and Wellington 1993). Coral bleaching is a response to environmental or biotic stress in which zooxanthellae are expelled or their photosynthetic pigments are lost (Glynn 1996). One mechanistic explanation is that bleaching is induced by excessive solar radiation, resulting in photooxidation-induced photoinhibition, that is, decreased efficiency in the light-harvesting capacity of the photosynthetic apparatus of the symbionts (Lesser et al. 1990, Jones et al. 1998). Oxidative stress occurs via reactive oxygen species (ROS), resulting in damage to photosystem II, which in turn leads to bleaching of zooxanthellae, or zooxanthellae exocytosis (bleaching of coral) (Lesser 2006). ROS formation associated with exposure to elevated temperature and solar radiation is believed to be an important factor leading to coral bleaching (Lesser 2006).

Thorough reviews of biological effects of UVR on coral reefs have been published by Shick et al. (1996) and, more recently, by Lesser (2004). These effects include solar and thermal stress-induced coral bleaching, as well as decreased photosynthesis and growth in zooxanthellae due to damage to DNA, proteins, and lipids (Shick et al. 1995). Photoinhibiton of photosynthesis in zooxanthellae can be due to exposure to elevated temperature alone (Iglesias – Prieto et al. 1992), UVR alone
Supraoptimal intensities and durations of exposure to visible light, particularly blue light, also have been shown to induce photoinhibition and loss of photosynthetic symbionts in corals (Jokiel and York 1982, Fitt and Warner 1995) and benthic Foraminifera (Williams and Hallock 2004). Stabenau et al. (2006) have shown that increases in UVR intensity on the coral surface in conjunction with the onset of high sea surface temperatures, due to stratification and resulting increased photobleaching of CDOM, correlates with decreased coral photosynthetic efficiency. Exposure to high solar irradiance leads to a lower bleaching threshold temperature and an overall shorter time to actually ‘‘bleach’’ compared to corals exposed to lower solar irradiances (Lesser and Farrell 2004).

Production of heat shock proteins (HSPs) in coral host tissue has been observed to be upregulated in response to thermal stress (Black et al. 1995). Bioindicators of photooxidative and thermal stress such as MAAs, HSPs, and decrease in photosynthesis, present parameters for comparing reef health and environmental stressors between reefs (Fisher 2007). The effects of UVR on gene expression include pyrimidine dimer formation in DNA, which interferes with DNA replication and transcription, cessation of cell division, and mutations of essential genes that may cause cell death (Anderson et al. 2001, Moran and Zepp 2000). Sublethal effects include decreased growth and reproduction, permeability of membranes and transport of molecules into the cell, disruption of the electron transport chain, inactivation of membrane transport functions, and RNA damage (Moran and Zepp 2000).

Ultraviolet radiation specifically has been shown to cause DNA damage, DNA mutations and cell death in marine organisms such as corals (Banaszak and Trench 1995a,b, Shick et al. 1995, Lesser 1996). Although it is generally thought that UVR
attenuates quickly, some natural water bodies, especially coral reefs, are characterized by high transparency to UVR (Gleason and Wellington 1993, Lesser 2004). For example, the intensities of some higher wavelengths of UVR can approach the intensity of PAR at depths subsurface to 2m in Kane‘ohe Bay, Hawai‘i (Gleason and Wellington 1993, Gulko 1995). Other effects of UVR on aquatic biota on the organismal level have been summarized by Haeder et al. (1998, 2003), Anderson et al. (2001), Vincent and Neale (2004), Hoogenboom et al. (2006), and many others.

Although UVB has higher energy than UVA and blue light per unit wavelength, Osburn et al. (2001) reported that UVA and low wavelength PAR are more effective in photobleaching CDOM because of their greater total energy. On the other hand, Fine et al. (2002) have shown that UVR (280 – 400 nm) can ultimately shield corals from some bacterial infections.

While overexposure to both UVR and PAR induces photoinhibition, PAR intensity must be high enough to support photosynthesis (Yentsch et al. 2002). Thus there is an optimal depth range where intensity of UVR and PAR are below damaging levels and intensity of PAR is sufficient for growth and development (Alonso et al. 2004).

2.10. Defenses against UVR: Mycosporine-like amino acids (MAAs)

Mycosporine-like amino acids (MAAs) are UV-absorbing compounds with maximal absorbance at 310 – 360 nm (Shick et al. 1999). Because MAA production is induced by exposure to UVR (Dunlap et al. 1986, Banaszak et al. 1998, Lesser 2000),
theories on MAA induction are relevant to my study of photobiology, CDOM and coral reefs.

MAAs can be produced by symbiotic zooxanthellae (Schick et al. 1999) as well as by phytoplankton (Morrison and Nelson 2004). While exposing corals to UVR can induce UV-protective mechanisms such as production of MAAs (Shick et al. 1996, Dunlap and Shick 1998, Morrison and Nelson 2004, Shick 2004), and DNA-repair enzymes (Banaszak and Lesser 1995, Kufrner et al. 1995, Anderson et al. 2001), prolonged overexposure to UVR can also reduce photosynthetic rates and simultaneously reduce MAA production (Lesser and Farrell 2004). In addition, production of MAAs may decrease with increasing temperature, leaving zooxanthellae more susceptible to damage caused by exposure to UVR (Lesser et al. 1990). MAAs also may have an antioxidant activity (Dunlap and Yamamoto 1995, Kim et al. 2001, Suh et al. 2003).

Results from studies monitoring PAR and MAA production have been ambiguous. While increases in blue wavelengths of PAR can induce production of UV-absorbing MAAs, since PAR and UVR co-vary, as blue wavelengths of PAR increase, the concurrent increase in UVR may actually be responsible for MAA induction (Jokiel et al. 1997, Moisan and Mitchell 2001). Other hypotheses propose that photosynthetically usable energy (PAR) absorbed in excess of the processing capacity of cellular biochemistry may be passed on to a genetic pathway to induce MAAs (Moisan and Mitchell 2001), or that disruption of a metabolic pathway may cause MAA accumulation (Goes et al. 1995).

Other coral defenses against UVR include behavioral defenses or production of mucus containing MAAs, melanin, fluorescent pigments, antioxidants such as superoxide
dismutase (SOD), photoreactivation, and enzymatic photorepair (Shick et al. 1996). See Chapter 5 for a more detailed discussion of MAAs and their relevance to CDOM and UVR transparency in the Florida Keys.

2.11. Stratospheric ozone depletion and bleaching

Mass bleaching events in corals have traditionally been attributed to above-normal water temperature (Atwood et al. 1992, Goreau and Hayes 1994, Glynn 1996, Lesser 1997). Although estimates of ozone depletion predict stabilization of the ozone layer for the coming decade, Montza et al (2009) found that the growth (i.e., accumulation in the atmosphere) rates for certain CFCs, which destroy ozone, were approximately two times higher in 2007 than in 2004 due to lack of regulation in developing countries (Figure 2.12), and that the concentrations of ozone-depleting gases did not begin to decline until 1998 (Hoffman and Montza 2009).

In addition, the same study (Montza et al. 2009) showed that CFCs emissions increased in 1998, concurrent with peak bleaching events for coral reefs and large benthic foraminifers (Amphistegina sp.) (Berkelmans et al. 2004, Hallock 2006a,b). Amphistegina are particularly sensitive to the shorter (300 - 490 nm) wavelengths of solar radiation (Williams and Hallock 2004). Thus, the severity of the 1998 peak coral bleaching event may have been a result of the combined effects of CFC-induced ozone depletion, allowing more UVR to reach coral reefs, together with supraoptimal temperatures. From a management perspective, elucidating the roles of UVR and stratospheric ozone in reef health can support further regulations on CFCs.
Figure 2.12. Monthly hemispheric means and growth rates of HCFCs from weighted measurements of surface-air collected in flasks at remote locations (Northern Hemisphere (red) > global mean (green) > Southern Hemisphere (blue)). Tropospheric growth rates are plotted relative to the right hand axis and are derived from 12 month differences in global surface means over the previous 12 months (e.g., Jan 99 – Jan 98; grey plus symbols) or from monthly differences smoothed over annual periods (black line) (from Montzka et al. 2009).
2.12. Statement of hypothesis

My study will investigate the distribution of CDOM on coral reefs in the Florida Keys. The basic idea is that reefs most distal from sources of CDOM experience the highest intensities of high energy blue and UV wavelengths, reefs with inconsistent CDOM sources receive variable intensities of the highest energy solar radiation, and reefs with consistent sources of CDOM experience lowest intensities of highest energy solar radiation compared to optimal wavelengths for photosynthesis. I further propose that (a) CDOM-rich reef sites will be characterized by higher coral cover and lower rates of decline in coral cover than low or highly variable CDOM sites; (b) that relative MAA expression will be greater on reefs that experience consistently lower and/or more variable $a_g$; and (c) because absorption decreases diffuseness (see Chapter 6) as well as increases attenuation in the underwater light field (Kirk 1994, Gregg 2002), that reefs with lower $a_g$ will be characterized by greater exposure to high energy blue and UV radiation.

Spectral and qualitative differences in photobleaching of CDOM depend on location (Del Vecchio and Blough 2002). I further suggest that spectral slope from open ocean (blue water) sites will indicate higher degrees of CDOM photobleaching, i.e., higher spectral slopes, due to the higher exposure to low wavelength radiation; coral reefs will exhibit intermediate degrees of CDOM photobleaching, depending on location, offshore (higher degree of CDOM photobleaching) or inshore (lower rates of CDOM photobleaching); and inland waters, which are less transparent than ocean or reef water, will typically exhibit the lowest degree of CDOM photobleaching. Though spectral slope has been measured for open-ocean and inland waters, my study is the first to quantify
spectral slope for coral reefs.

Mangroves are one of the most significant sources of CDOM to coral reefs (Zepp et al. 2002, Zepp 2003, Jaffe et al. 2004); they also serve as a physical barrier, protecting shorelines from the destructive effects of storms, tidal waves and tsunamis (Danielsen et al. 2005). The results of my study will provide information useful to management on the importance of protecting and maintaining mangrove shorelines and elucidate the effects increased UVR and thus, of stratospheric ozone depletion, on coral reefs.
3. Introduction to the Florida Keys, Study Sites, and Methodology

3.1. Objectives

The goal of this chapter is to present background information on the study area and methodology used in subsequent chapters.

3.2. Introduction

3.2.1. Geomorphology and water circulation patterns of the Florida Keys

The general arcuate pattern of the Florida Keys is a consequence of the bathymetry of the shelf edge and the action of the Florida Current, which controls many of the environmental parameters (depth, current, and therefore nutrient and light availability) of this area (Randazzo and Halley 1997). Hawk Channel, an ~10 m deep topographic depression along the Atlantic side of the Keys, is relatively deeper than the inner shelf (0 – 3 m) and reef bank (0 – 5 m), and shallower than the seaward shelf break (30 m) (Lee and Smith 2002) (Fig. 3.1). Hawk Channel transports water from Biscayne Bay from the north, the Loop Current and Florida Bay from the west, and the Florida Current from the south and east.

The southwest Florida Shelf and the Atlantic side of the Florida Keys coastal zone are directly connected by passages between the islands of the Middle and Lower Keys (Fig. 3.1). CDOM-rich outflows from the Everglades and other areas of South Florida supply CDOM to coastal reef waters in the Middle and Lower Keys via Florida Bay.
Movement of water between these regions depends on a combination of local wind-forced currents and gravity-driven transports through the passages, produced by cross-Key sea level differences on time scales of several days to weeks (Lee and Smith 2002; Smith and Lee 2003; Johns et al. 2006), which arise because of differences in physical characteristics (shape, orientation, and depth) of the shelf on either side of the Keys. In some regions, inshore (patch) reefs may be located adjacent to or within Hawk Channel (Lidz et al. 2003, Peters et al. in press), and so may receive CDOM rich waters via Hawk Channel.

Figure 3.1. Study sites in the Lower, Middle and Upper Florida Keys included offshore and inshore (patch) reefs that differ in degree of development of associated shoreline. Algae Reef, near intact, mangrove shoreline, is slightly southwest of Carysfort Reef. Key Largo 6m (KL6m) Reef, offshore the city of Key Largo, is west of Molasses Reef. Onshore to offshore transect through John Pennekamp Park, Algae Reef and Carysfort reef sampled in September 2004 is indicated by double line. Also indicated are the
inshore and offshore CREMP study sites in the Lower, Middle and Upper Florida Keys sampled in 2006 and 2007. Inshore sites are circled in green. Others (uncircled) represent offshore sites. Long-term mean volume transport (m$^3$/s) through the Keys passages is represented as yellow arrows (from Johns et al. 2006). Not represented in the map are the following sites: Coral Gardens (Middle Keys) and Long Key (CREMP site, Middle Keys) as well as East Washerwoman (Lower Keys) and West Washerwoman (CREMP site, Lower Keys) and White Banks (Upper Keys) (adapted from Ramirez et al. 2007, Lee and Smith 2002, Randazzo and Halley 1997).

The higher mean water level of the eastern Gulf of Mexico and variations in the strength and location of the Loop Current have important influences on mean transports through the passages between Keys. The long-term mean volume transports through the primary channels of the Middle Keys are $-55$ m$^3$/s each for Channels 2 and 5, $-260$ m$^3$/s for Long Key Channel, and $-370$ m$^3$/s for the Seven-Mile Bridge Channel, where negative mean values represent outflows from Florida Bay (Lee and Smith 2002; Fig. 3.1a). The Seven-Mile Bridge Channel accounts for about 50% of the flow, Long Key Channel for about 35%, and Channels 2 and 5 account for about 7% each. Florida Bay is rich in CDOM from the wetlands of the Everglades. Thus, the general region of the Middle Keys can potentially receive more CDOM than the Upper or Lower (Williams 2002). Moreover, construction of causeways between islands in the Florida Keys, beginning in the early 1900s, significantly altered patterns of exchange between Florida Bay and the Atlantic shelf (Swart et al. 1999).

The Florida Current, with transport of 30 Sv ($10^6$ m/s), may serve as a longe range transport and/or mixing mechanism CDOM along and away from the Florida Keys (Mitchum, pers. comm.).

The most important local terrestrial sources of CDOM are mangroves and coastal forests. Comparing regions of the Florida Keys, considering the extent of mangrove and coastal forests, the most occur in the Lower Keys (Lidz et al. 2006), followed by the
Upper Keys, while the Middle Keys are most highly developed and have the least mangrove and intact forests. At the same time, the Middle Keys are characterized by higher turbidity than the Upper and Lower Keys, likely due to the passages bringing water from Florida Bay (Porter 2002), which can also carry CDOM.

### 3.2.2. Rivers and Florida Bay as sources of CDOM

The closest riverine input to the Florida Keys occurs indirectly through Florida Bay and Biscayne Bay. Shark River is the major riverine input to the Everglades and Florida Bay. To the north of the Florida Keys, the major riverine input to Biscayne Bay is Miami River (Walker et al. 1994). As a result of extreme weather conditions, other rivers sporadically influence the Florida Keys. Mississippi River plumes can reach the Florida Keys following episodes of extreme precipitation in the Mississippi watershed (Walker et al. 1994).

Riverine input of CDOM is accompanied by nutrients, wastewater, pollutants, agricultural runoff such as pesticides, herbicides, and fertilizer, and suspended material (Coble 2007). Florida Bay nutrient concentrations and turbidity are typically high compared to the oligotrophic conditions found offshore. The intrusions of waters carrying higher nutrient concentrations and suspended material from Florida Bay have been hypothesized as a potential threat to the health of the Florida Reef Tract (Porter et al. 1999). In addition, land use in South Florida is dominated by citrus, pasture, urban, natural wetland, row crop, dairy and golf courses. Such activities rely on large and regular applications of pesticides and fertilizers (Graves et al. 2004). Storm water runoff increases suspended and dissolved pollutant, nutrient, and heavy metal concentrations, which in turn can decrease dissolved oxygen concentration and productivity (Graves et al. 2004), and thus adversely affect the structure and function of biotic communities (Pait et al. 1992 and Kennish 1999 in Graves
et al. 2004). Due to the lack of secondary wastewater treatment in much of the Florida Keys, fecal coliform bacteria and enterococci have been found to accumulate in coral surface microlayers, potentially compromising resiliency of coral reef biota (Lipp et al. 2002).

3.2.3. Annual trends in the Florida Keys

For the period 1997 - 2003, maximum incident UV irradiance at Everglades National Park occurred in July - August (6000 - 6500 DUV), except in 1997 and 1998 where the maximum DUV occurred in May – June (http://www.epa.gov/uvnet/access.html, Everglades NP, FL “everglade_update_may04.pdf”). Maximum mean daily UV-B and UVR at the Mote Marine Laboratory in the Lower Keys for the period of record August 2002 - October 2003 occurred in May through July (Fig. 2.5).

For the period sampled, in the Lower Keys (Key West), maximum water temperature occurred in July and August coincident with wind speed minima (Fig. 3.2a,b, http://www.ncdc.noaa.gov/oa/climate/research/monitoring.html#ustempprcp, http://www.ndbc.noaa.gov/station_history.php?station=kywf1). During this time period, precipitation tended to be highest between June and September (Fig. 3.2a). In the Upper Keys (Molasses Reef) as well as the Middle Keys (Sombrero Key), mean monthly air and wind temperature over the time period 2004 – 2007 occurred in August, coincident with wind speed minima (Fig. 3.3, http://www.ndbc.noaa.gov/station_history.php?station=mlrf1; Fig. 3.4, http://www.ndbc.noaa.gov/station_history.php?station=smkf1).
Figure 3.2a. Temperature and precipitation at Key West (Lower Keys), 2003-2006 (http://www.ncdc.noaa.gov oa/climate/research/monitoring.html#ustempprcp).

Figure 3.2b. Monthly mean wind speed (WSPD), gust (GST), air temperature (ATMP) and water temperature (WTMP) at Key West (Lower Keys) for 2005 – 2007. Wind and temperature data were not available for January and March 2005, and November and December 2007. Wind data not available from March through August 2005, July through December 2006 and January through June 2007; water temperature data were not available for July 2005 (http://www.ndbc.noaa.gov/station_history.php?station=kywf1).
Figure 3.3. Monthly mean wind speed (WSP), gust (D GST), air temperature (ATMP) and water temperature (WTMP) at Molasses Reef (Upper Keys) for 2004 - 2007. Water temperature data not available for January and March 2005 (http://www.ndbc.noaa.gov/station_history.php?station=mlrf1).
3.2.4. Biological Response – Bleaching in the Florida Keys

When the sea surface temperature is warmer than the bleaching threshold temperature, corals experience thermal stress. The commonly accepted cause of mass coral bleaching is thermal stress, thus NOAA’s Coral Reef Watch uses sea surface temperature to monitor the threat of coral bleaching in the FKNMS. Corals are vulnerable to bleaching when the SST exceeds the temperatures they would normally experience in the hottest month. Temperature thresholds for coral bleaching are based on the amount of...
time a reef is subjected to supraoptimal temperatures. NOAA defines the bleaching
threshold temperature ("HotSpot" value) as one degree Celsius (1°C) above the
maximum monthly mean (Goreau et al. 2000). The maximum monthly mean in the
Florida Keys for the sampling period 2005 - 2007 was typically 31°C but reached
approximately 36°C in Key West in 2007 (Figs. 3.2 - 4).

In addition, because normal temperature range differs depending on location, to
determine the risk of coral bleaching for any given location, NOAA has devised the
“degree heating week” (DHW). The DHW product accumulates any coral bleaching
“HotSpots” greater than 1 °C over a 12 - week window, thus showing how stressful
conditions have been for corals in the last three months. It is a cumulative measurement
of the intensity and duration of thermal stress, and is expressed in the unit °C-weeks.
DHWs over 4 °C-weeks have been shown to cause significant coral bleaching, and values
over 8 °C-weeks can cause widespread bleaching and some mortality.

Based on climate predictions, NOAA’s Coral Reef Watch, current conditions, as well
as visual field observations of bleaching, Mote Marine Laboratory of Summerland Key
determines and publishes reports on the threat for mass coral bleaching within the FKNMS
(Table 3.1, http://isurus.mote.org/Keys/current_conditions.phtml). For the time period
of sampling (2005 – 2007), bleaching in the Florida Keys was most severe from July
through the beginning of September, with maximum severity typically in mid to late
August (e.g., Fig. 3.5). Widespread mass bleaching was not reported along the Florida
Table 3.1. Mote Marine Laboratory / Florida Keys National Marine Sanctuary Coral Bleaching Early Warning Network, “Bleachwatch”. Threat of mass coral bleaching within the FKNMS based on current remote sensing and environmental monitoring data, field observations, and climate predictions for sampling years 2005 – 2007 (http://isurus.mote.org/Keys/current_conditions.phtml; reports for 2004 are not available):

<table>
<thead>
<tr>
<th>Year</th>
<th>Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>October 30, 2007</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>October 1, 2007</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>September 10, 2007</td>
<td>HIGH</td>
</tr>
<tr>
<td></td>
<td>August 27, 2007</td>
<td>MODERATE</td>
</tr>
<tr>
<td></td>
<td>August 13, 2007</td>
<td>HIGH</td>
</tr>
<tr>
<td></td>
<td>July 30, 2007</td>
<td>HIGH</td>
</tr>
<tr>
<td></td>
<td>July 16, 2007</td>
<td>MODERATE</td>
</tr>
<tr>
<td></td>
<td>June 29, 2007</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>June 1, 2007</td>
<td>LOW</td>
</tr>
<tr>
<td>2006</td>
<td>October 19, 2006</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>September 19, 2006</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>August 28, 2006</td>
<td>MODERATE</td>
</tr>
<tr>
<td></td>
<td>August 14, 2006</td>
<td>MODERATE</td>
</tr>
<tr>
<td></td>
<td>July 31, 2006</td>
<td>MODERATE</td>
</tr>
<tr>
<td></td>
<td>June 30, 2006</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>June 1, 2006</td>
<td>LOW</td>
</tr>
<tr>
<td>2005</td>
<td>October 18, 2005</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>September 27, 2005</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>September 13, 2005</td>
<td>MEDIUM</td>
</tr>
<tr>
<td></td>
<td>August 30, 2005</td>
<td>MEDIUM</td>
</tr>
<tr>
<td></td>
<td>August 23, 2005</td>
<td>HIGH</td>
</tr>
<tr>
<td></td>
<td>August 16, 2005</td>
<td>MEDIUM</td>
</tr>
<tr>
<td></td>
<td>August 9, 2005</td>
<td>HIGH</td>
</tr>
<tr>
<td></td>
<td>July 26, 2005</td>
<td>MEDIUM</td>
</tr>
<tr>
<td></td>
<td>June 28, 2005</td>
<td>LOW</td>
</tr>
<tr>
<td></td>
<td>June 1, 2005</td>
<td>LOW</td>
</tr>
</tbody>
</table>
Figure 3.5. Overview of BleachWatch Observer reports submitted from August 9 - August 23, 2005 (http://isurus.mote.org/Keys/bleaching/CC_20050823.pdf).

3.3. Methods

3.3.1. Sites and sampling dates

Water samples and in situ optical data were collected at several reefs within the Florida Keys National Marine Sanctuary (FKNMS). Samples were collected in the Upper and Middle Florida Keys in late May, early July and late September 2004, and early May and mid-July 2005 (Table 3.2a, Fig. 3.1). In addition, in September 2004 and July 2005 water samples were collected along a transect from offshore at 75m depth (50m in July 2005), shoreward at 50m and 25m depths, inshore to Carysfort Reef, and finally within a mangrove-lined canal in John Pennekamp State Park, for determination of absorption due to CDOM ($a_g$) (Fig. 3.1). In summer 2006 and 2007, additional reefs were sampled in the
Upper, Middle and Lower Keys that are annually assessed by the Coral Reef Evaluation and Monitoring Program (CREMP) (Table 3.2b,c; Fig. 3.1).

Table 3.2a. Sites and parameters sampled in 2004 and 2005. a = absorption, \( R = R_s \), remote sensing reflectance, C = chlorophyll fluorescence (concentration), S = Spectral underwater flow-through optical instrument package, P = PAR underwater, U = UV and PAR incident, U_u = UV and PAR underwater. BIC underwater spectroradiometer (BSI) was used for all measurements of underwater irradiance. Flow through optical package profile (overnight) at KL6m and Key Largo 3m, July 04. * = surface absorption sample only. Only surface samples were collected at open water sites \( z > 27 \) m. Italics = intact shoreline-associated reef, bold case = mangrove canal, regular case = impacted or developed shoreline-associated reef. In July 2005, only bottom samples were collected at 27 m. The SoDoPF measures chlorophyll fluorescence, backscattering, CDOM fluorescence, transmission of red, green, and blue light, salinity, temperature and depth.
<table>
<thead>
<tr>
<th>Site</th>
<th>2004</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5/25</td>
<td>7/6-8</td>
</tr>
<tr>
<td>Algae Reef (6 m)</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>Carysfort Reef (10m)</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>offshore Carysfort (45 m)</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>offshore Carysfort (30 m)</td>
<td>aRCUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>offshore Carysfort (27 m)</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>offshore Carysfort (25,75m)</td>
<td>aRCPUS</td>
<td>aCP</td>
</tr>
<tr>
<td>offshore Carysfort (50m)</td>
<td>aRCPUS</td>
<td></td>
</tr>
<tr>
<td>Pennekamp - South Creek 2 sites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pennekamp North Creek - 2 sites</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>KL6m (6 m)</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>Molasses 10m, 25 m</td>
<td>aRCPUS</td>
<td>aCP</td>
</tr>
<tr>
<td>White Banks Reef</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>Molasses (KL) 18 m</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>Alina’s Reef</td>
<td>a 5/28</td>
<td>aP</td>
</tr>
<tr>
<td>Dome Reef</td>
<td>a 5/28</td>
<td>aP</td>
</tr>
<tr>
<td>Molasses 12 m, 45 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molasses 27 m</td>
<td>aRCPS</td>
<td>aRCP</td>
</tr>
<tr>
<td>Molasses offshore</td>
<td>aP</td>
<td></td>
</tr>
<tr>
<td>Key Largo 9m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Key Largo 3m</td>
<td>A</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>Long Key viaduct- Post 73</td>
<td>aRCPUS</td>
<td>aRCPUS</td>
</tr>
<tr>
<td>Tennessee 6m</td>
<td>aP</td>
<td>aRCPS</td>
</tr>
<tr>
<td>Tennessee 10m</td>
<td>aRCPUS</td>
<td>aP</td>
</tr>
<tr>
<td>Tennessee 18m</td>
<td>aRCPUS</td>
<td>aP</td>
</tr>
<tr>
<td>Tennessee 25m, 75 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tennessee 27 m</td>
<td>aRCPS</td>
<td></td>
</tr>
<tr>
<td>Tennessee 45 m</td>
<td>aRCPUS</td>
<td>aRCPS</td>
</tr>
<tr>
<td>Conch 10 m, 30m</td>
<td>aRCPU</td>
<td></td>
</tr>
<tr>
<td>Looe Key 6, 10, 25, 50, 75 m</td>
<td>aP</td>
<td></td>
</tr>
<tr>
<td>Marquesas shallow (3 m) &amp; deep (9 m)</td>
<td>aCP</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2b. Sites and samples for Spring/Summer 2006. Measurements at all deep sites: a, C, P, U_u; all shallow sites, unless otherwise noted: see Table 3.1a for description. * = surface absorption sample only. Italics = intact shoreline-associated reef, regular case = impacted or developed shoreline-associated reef.

<table>
<thead>
<tr>
<th>May 28–June 2, 2006 (Middle &amp; Lower Keys)</th>
<th>June 28 -29, 2006 (Upper Keys)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand Key deep (8.6 m) &amp; shallow (4.6 m)</td>
<td>betw. Carysfort deep &amp; shallow (6.7 m)</td>
</tr>
<tr>
<td>Rock Key deep (12.5 m) &amp; shallow (4.3 m)</td>
<td>blue water off Carysfort (30.5 m)</td>
</tr>
<tr>
<td>Key West Offshore (blue water) (76 m)</td>
<td>Turtle (4.6 m) (Patch)</td>
</tr>
<tr>
<td>Western Head (11 m) (Patch)</td>
<td><em>Algae (4 m)</em></td>
</tr>
<tr>
<td>Cliff Green (6 m) (Patch)</td>
<td>Grecian Rocks (7 m)</td>
</tr>
<tr>
<td>Seagrass Patch between Eastern and W. Sambo (4.3 m)</td>
<td>Porter Patch (4 m) (Patch)</td>
</tr>
<tr>
<td>W. Sambo deep (14.3 m) &amp; shallow (6.8 m)</td>
<td>Admiral Patch (5 m) (Patch)</td>
</tr>
<tr>
<td>E. Sambo deep (15.3 m) &amp; shallow (6.4 m)</td>
<td>Conch Deep (15.2)</td>
</tr>
<tr>
<td>offshore (blue water) (65 m)</td>
<td>Molasses Deep (13.7 m)</td>
</tr>
<tr>
<td>West Washerwoman (4.3 m) (Patch)</td>
<td>White Banks (3.7)</td>
</tr>
<tr>
<td>Jaap (a.k.a. Mystery) (2.4 m) (Patch)</td>
<td>KL6m (6.1 m)</td>
</tr>
<tr>
<td>Sombrero deep (13.5 m) &amp; shallow (4.2 m)</td>
<td>Rodriguez Key (3.4 m)</td>
</tr>
<tr>
<td>Alligator deep (12 m) &amp; shallow (6.5 m)</td>
<td></td>
</tr>
<tr>
<td>W. Turtle Shoal (4.1 m) (Patch)</td>
<td></td>
</tr>
<tr>
<td>Dusitan Rocks (3.6 m) (Patch)</td>
<td></td>
</tr>
<tr>
<td>East Washerwoman (5.1 m)</td>
<td></td>
</tr>
<tr>
<td>Looe Key deep (15.2 m) &amp; shallow (6.8 m)</td>
<td></td>
</tr>
<tr>
<td>Blue Water off Looe Key (90 m)</td>
<td></td>
</tr>
<tr>
<td>Coral Gardens (3.7 m)</td>
<td></td>
</tr>
<tr>
<td>Tennessee Shallow (14 m)</td>
<td></td>
</tr>
<tr>
<td>Tennessee Shallow (6.1 m) – (+ a, C )</td>
<td></td>
</tr>
<tr>
<td>Long Key Patch (3.7 m)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2c. Sites and samples for Spring/Summer 2007. Measurements at all deep sites: a, C, P, U_u; all sites, unless otherwise noted: see Table 3.1a for description and Table 3.1c for depths. * = surface absorption sample only. Italics = intact shoreline-associated reef, regular case = impacted or developed shoreline-associated reef.

<table>
<thead>
<tr>
<th>June 5 - 6, 2007 (Upper &amp; Middle Keys)</th>
<th>June 18 - 20, 2007 (Middle &amp; Lower Keys)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tennessee Shallow *</td>
<td>Sand Key Deep *</td>
</tr>
<tr>
<td>Tennessee Deep * - no U_u</td>
<td>Sand Key Shallow bottom – no U_u</td>
</tr>
<tr>
<td>Alligator Deep * - no U_u</td>
<td>Rock Key Deep *</td>
</tr>
<tr>
<td>Conch Deep * - no U_u</td>
<td>Blue Water *</td>
</tr>
<tr>
<td>Molasses Deep * - no U_u</td>
<td>W. Head Patch Reef *</td>
</tr>
<tr>
<td>betw. Carysfort-shallow&amp;deep – no U_u</td>
<td>Cliff Green Patch *</td>
</tr>
<tr>
<td>Blue Water - no U_u</td>
<td>Sea Grass Patch Reef *</td>
</tr>
<tr>
<td>Turtle Reef - no U_u</td>
<td>Sombrero Deep *</td>
</tr>
<tr>
<td>Algae Reef - no U_u</td>
<td>W. Turtle Shoal *</td>
</tr>
<tr>
<td>Grecian Rocks - no U_u</td>
<td>Dusitan Rocks *</td>
</tr>
<tr>
<td>Porter Patch - no U_u</td>
<td>E. Washerwoman Shoal *</td>
</tr>
<tr>
<td>Admiral Patch - no U_u</td>
<td>Blue Water off Looe Key *</td>
</tr>
<tr>
<td>Molasses Shallow - no U_u</td>
<td>Looe Key Deep *</td>
</tr>
<tr>
<td>White Banks - no U_u</td>
<td>W. Sambo Shallow *</td>
</tr>
<tr>
<td>Three Sisters (KL6m) - no U_u</td>
<td>E. Sambo Deep *</td>
</tr>
<tr>
<td></td>
<td>Blue Water off Sambo *</td>
</tr>
<tr>
<td></td>
<td>W. Washerwoman Shoal *</td>
</tr>
<tr>
<td></td>
<td>Jaap a.k.a. Mystery Reef * no U_u</td>
</tr>
</tbody>
</table>
Key Largo 6m (KL6m) Reef and Algae Reef (also 6 m depth) were selected for comparison based on data for coral health reported by Fisher et al. (2007). Algae Reef is located offshore from the intact mangrove-lined, and thus CDOM-rich, coastline of John Pennekamp Park, while KL6m Reef lies offshore from the more developed coastline of the town of Key Largo. I used this contrast in location to elucidate the influence of CDOM from terrestrial sources on coral reef resilience. Fisher (2007) found that the regenerative capacity of corals, coral cover, and abundances of larger foraminifers were all higher at Algae Reef than KL6m Reef. In addition, studies comparing percent coral cover have revealed that corals overall are faring better at inshore reefs compared to offshore reefs (NOAA 2002, Somerfield et al. 2008). In addition, for the period 1996 – 2006, the Upper and Lower Keys show the greatest loss in mean percent stony coral cover (Fig. 3.6, NOAA 2006).

Figure 3.6. Mean percent stony coral cover in the Florida Keys by region, Upper, Middle and Lower Keys. The Upper and Lower Keys stations continue to show the greatest loss in mean percent stony coral cover since the beginning of the project. Mean percent coral cover in the Middle Keys has not changed significantly since 1999. Between 2005 and 2006, a notable decline in mean percent stony coral cover at CREMP stations Sanctuary-
wide occurs in all three regions (from Callahan et al. 2006).
Because CDOM is carried reefward from terrestrial sources during low tide, and
is diluted by ocean water during high tide, the timing of sampling with respect to the tidal
cycle was recorded (Tables 3.3a,b). Tidal tables were obtained from the websites:
http://www.ndbc.noaa.gov/station_page.php?station=mlrf1 for Molasses Reef and
http://co-ops.nos.noaa.gov/tides04/tab2ec3d.html for Carysfort Reef and Largo Sound,
Key Largo.

Table 3.3a. Tidal information for sampling sites (Key Largo 6m (KL6m) Reef, Algae
Reef) on dates sampled in 2004.

<table>
<thead>
<tr>
<th></th>
<th>Molasses Reef</th>
<th>Largo Sound</th>
<th>Carysfort Reef</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>high</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>May 25, 2004</td>
<td>1:14 am</td>
<td>7:24 am</td>
<td>3:36 am</td>
</tr>
<tr>
<td></td>
<td>1:22 pm</td>
<td>7:34 pm</td>
<td>3:44 pm</td>
</tr>
<tr>
<td>July 6, 2004</td>
<td>12:09 am</td>
<td>6:21 am</td>
<td>2:31 am</td>
</tr>
<tr>
<td></td>
<td>12:30 pm</td>
<td>6:33 pm</td>
<td>2:52 pm</td>
</tr>
<tr>
<td>July 7, 2004</td>
<td>10:02 am</td>
<td>17:34 pm</td>
<td>00:37 am</td>
</tr>
<tr>
<td>Sept. 28, 2004</td>
<td>2:46 am</td>
<td>9:02 am</td>
<td>9:30 am</td>
</tr>
<tr>
<td></td>
<td>3:10 pm</td>
<td>9:18 pm</td>
<td>9:46 pm</td>
</tr>
<tr>
<td>Sept. 30, 2004</td>
<td></td>
<td></td>
<td>4:38 am</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10:55 am</td>
</tr>
</tbody>
</table>

Table 3.3b. Sampling (water collection) times for Carysfort, Algae and Key Largo 6m

<table>
<thead>
<tr>
<th>sampling times</th>
<th>May</th>
<th>July</th>
<th>September</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key Largo 6m (KL6m)</td>
<td>13:05 May 25</td>
<td>10:35 July 7</td>
<td>17:20 September 28</td>
</tr>
<tr>
<td>25°01.0 92’N 80°23.844’ W</td>
<td>high tide</td>
<td>high tide</td>
<td>close to high tide</td>
</tr>
<tr>
<td>Algae 25°08.799’N 80°17.579’ W</td>
<td>10:35 May 25</td>
<td>12:04 July 6</td>
<td>11:03 September 28</td>
</tr>
<tr>
<td>between tides</td>
<td>high tide</td>
<td>high tide</td>
<td>between tides</td>
</tr>
<tr>
<td>Carysfort 10m</td>
<td></td>
<td></td>
<td>13:45 September 30</td>
</tr>
</tbody>
</table>
| 25°13.160’N 80°12.428’ W |              |               | between tides (low)
3.3.2. *In situ* and incident irradiance measurements

On most sampling dates in 2004 and before July 2005, the underwater light field was quantified using hand-lowered *in-situ* instruments, including a Licor 192SA underwater quantum sensor for measuring PAR (400-700 nm). Above water incident spectral irradiance, \( E_{d0+}(\lambda) \), was measured using a LICOR 1800 Spectroradiometer from 8:30 am to 6:30 pm on most days of sampling in 2004 (280-850 nm, 1.5 nm intervals, sampling frequency 10-20 minutes).

Beginning in July 2005, a Biospherical Instruments BIC® submersible radiometer was used to measure *in situ* irradiance, \( E_{ds}(\lambda) \). The BIC® was equipped to measure 10 nm wavebands of downwelling cosine irradiance centered at 305, 330, 380 nm (\( \mu \)W/cm\(^2\)/nm), recording the center wavelength, and integrated PAR (400-700nm) (\( \mu \)Einsteins/m\(^2\)/s). A “dark reading”, which measured the signal at each wavelength with the BIC® on deck and the black cap covering the sensor, was made each day of sampling. The dark reading is subtracted from each light measurement at all wavelengths, to correct for the background (voltage) measurement by the BIC®. The dark reading is especially important for the UV measurements at 305 and 330 nm, because this correction could make a substantial difference in irradiance when correcting low signals at these wavelengths. These *in situ* irradiance data were used to calculate the attenuation coefficient \( K_d \) and to calibrate my model for calculating UV irradiance from absorption measurements (see section 3.3.3).
3.3.3. Water samples: collection and in lab optical measurements

During all cruises, water samples were collected from the surface and bottom by SCUBA divers or use of Niskin bottles; additional water samples were collected if stratification was observed. Simultaneous measurements of conductivity and temperature were made on some dates (see Tables 3.2a,b, and c). Sampling typically occurred sometime intermediate between high and low tide, for example in September 2004, sampling occurred between high and low tide, therefore during falling tide (Tables 3.3a,b).

For absorption measurements, discrete water samples (2-3 l) collected just below the surface and at depth of coral growth were filtered through glass fiber/fine (GFF) and 0.2 µm filters to determine the separate contributions of absorption due to dissolved and particulate material. The 0.2 µm filtrate and the GFF filters were analyzed on a UV-Visible spectrophotometer (Perkin Elmer Lambda 18, Hitachi U 3300) respectively for spectral \( a_g(\lambda) \), and spectral absorption due to particles \( a_p(\lambda) \), from 300-800 nm. The quantitative filter pad method was used to determine \( a_p(\lambda) \) (Mitchell 1990, Mitchell et al. 2000). Spectral absorption due to phytoplankton, \( a_{phi}(\lambda) \), was determined by methanol – extraction of the filter pads, and spectral absorption due to detritus, \( a_d(\lambda) \), was determined as the difference between the whole minus methanol extracted filter pad absorption:

\[
a_d(\lambda) = a_p(\lambda) - a_{phi}(\lambda) \tag{3.1}
\]

To estimate the between - site compositional differences in \( a_g \), I compared the slope of \( a_g(\lambda) \) in the UV region (Del Vecchio and Blough 2002) for inshore reefs to offshore, clear water reefs. Spectral slope of \( a_g(\lambda) \) for the the UVB region (280 – 312 nm)
was calculated using least squares linear regression of natural logarithm converted $a_g(\lambda)$ (Carder et al 1989):

$$S(280,312) = \frac{\ln(a_g(312)/a_g(280))}{(312-280)}$$

(3.2)

Differences in spectral slope may indicate different composition and source of CDOM as well as differences in the degree of CDOM photobleaching (Zanardi-Lamardo et al. 2004). The spectral range 280 - 312 nm was used to represent UVB radiation as well as to avoid the error due to inflections in spectral CDOM absorption that occur at wavelengths higher than 312 nm.

Chlorophyll concentrations ([chl]) were measured on solutions of hot methanol extracted pigments from the GFF filters used for absorption measurements using a Turner Fluorometer and methods described by Holm-Hansen and Riemann (1978).

3.3.4. Calculating underwater irradiance from in lab absorption measurements

In the water column, total diffuse attenuation of downwelling irradiance, $K_d$, is due to absorption ($a$) and scattering ($b$) by water molecules, dissolved material, and particulate material, and the angular distribution of light, expressed as $\bar{\mu}$:

$$K_d = (a+b)_{w,p,g} / \bar{\mu}$$

(3.3)

where $\bar{\mu} = \cos \theta$ and $\theta$ is the zenith angle (angle between the sun and plane perpendicular to the surface.

Because coral reef waters are typically characterized by low mineral/particle concentrations, in the absence of in situ scattering measurements, the diffuse attenuation coefficient for downwelling irradiance, $K_d$, can be estimated as the sum of $a_g$, $a_p$, (absorption due to particulate material), and $a_w$ (absorption due to pure water, Morel et al.
When scattering is constant and light measurements are made within two hours of solar noon, the effect of \( \bar{\mu} \) is negligible and the total diffuse attenuation of downwelling irradiance can be estimated solely from absorption:

\[
K_d = a_g + a_p + a_w
\]  

(3.4)

Irradiance reaching the sea floor \((E_{dz})\) can then be estimated as:

\[
E_{dz}(\lambda) = E_{d0+}(\lambda)e^{-K_dz}, \text{ where } z = \text{depth}
\]  

(3.5)

(Kirk 1994). The intensity of irradiance reaching the benthos, \(E_{dz}\), decreases exponentially as a function of depth \((z)\) and \(K_d\), where \(E_{d0+}\) is the irradiance intensity above the water surface.

The relationship in equation (11) can be used to evaluate the discrepancy between measured \(K_d\) and calculated total absorption, \(a_t\) (where \(a_t = a_g + a_p + a_w\)), see Table 3.4, Fig. 3.9) and to compare \(\bar{\mu}\) between sites (see Chapter 6):

\[
K_d = \frac{(a)_{w,g}}{\bar{\mu}} \Rightarrow K_d = a_t / \bar{\mu} \quad \text{or} \quad \bar{\mu} = a_t / K_d
\]  

(3.6)

For collimated light, \(\bar{\mu}\) equals one and thus \(K_d = a_t\) (Kirk 1994). As light becomes more diffuse (or scattered), \(\bar{\mu}\) decreases. The relationship between absorption, \(a_t\), scattering, \(b\), and the average cosine, \(\bar{\mu}\), and its importance to UV exposure on coral reefs, is discussed in Chapter 6.

3.3.5. Sources of Error

3.3.5.1. Irradiance and absorption due to particles

In 2004 and 2005, \(E_{d0+}\) measured using a Li-COR 1800 spectroradiometer, combined with in lab absorption measurements, \(a_t\), were used to estimate \(K_{dz}\) according to Equations (3.4) and (3.6). On all subsequent sampling dates, \textit{in situ} irradiance (UVR and
PAR), measured using a BIC® radiometer (Biospherical Instruments, San Diego, CA) were used to calculate $K_{dz}$ as well as to test the model for calculating $K_d$ from $a_t$ and $E_{d0+}$. Variations of in lab $a_t$ from *in situ* $K_d$ may be due to the angular structure of the light field ($\mu$) or errors in measuring $a_t$ (see below). Overestimation of $a_t$ would result in overestimation of $K_d$. Considering inshore and offshore sites together, the median ratio $a_t/K_d$ ranged from 0.866 to 0.959 for the UV wavelengths (305, 330 and 380 nm) but was markedly lower, namely 0.274, for PAR (Table 3.4, Fig. 3.7). Thus, because the mean $a_t/K_d$ is close to unity for the UV dataset but not for PAR, $a_t$ is a good estimate of $K_d$ for the UV but not for the PAR dataset.

Table 3.4. Median $a_t/K_d$ and 25<sup>th</sup> – 75<sup>th</sup> percentile ranges for inshore and offshore reefs.

<table>
<thead>
<tr>
<th>$a_t/K_d$</th>
<th>305 nm</th>
<th>330 nm</th>
<th>380 nm</th>
<th>PAR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Median $a_t/K_d$ inshore</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>305 nm</td>
<td>0.909</td>
<td>0.890</td>
<td>0.842</td>
<td>0.270</td>
</tr>
<tr>
<td>330 nm</td>
<td>0.784</td>
<td>0.749</td>
<td>0.714</td>
<td>0.208</td>
</tr>
<tr>
<td>380 nm</td>
<td>0.990</td>
<td>0.975</td>
<td>0.924</td>
<td>0.324</td>
</tr>
<tr>
<td><strong>Median $a_t/K_d$ offshore</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>305 nm</td>
<td>1.019</td>
<td>1.038</td>
<td>0.981</td>
<td>0.274</td>
</tr>
<tr>
<td>330 nm</td>
<td>0.246</td>
<td>0.475</td>
<td>0.586</td>
<td>0.229</td>
</tr>
<tr>
<td>380 nm</td>
<td>1.147</td>
<td>1.234</td>
<td>1.203</td>
<td>0.382</td>
</tr>
<tr>
<td><strong>Median $a_t/K_d$ inshore and offshore</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>305 nm</td>
<td>0.959</td>
<td>0.911</td>
<td>0.886</td>
<td>0.274</td>
</tr>
<tr>
<td>330 nm</td>
<td>0.832</td>
<td>0.804</td>
<td>0.737</td>
<td>0.191</td>
</tr>
<tr>
<td>380 nm</td>
<td>1.098</td>
<td>1.130</td>
<td>1.100</td>
<td>0.355</td>
</tr>
</tbody>
</table>
Figure 3.7. Ratio of in lab $a_t$ to in situ $K_d$ ($a_t/K_d$) for inshore (x) and offshore (o) reef sites, 2005 – 2008. Dashes represent medians. Highest outliers occurred at offshore sites.

Considering inshore and offshore reef sites separately, $a_t/K_d$ was higher for offshore reefs than for inshore reefs (see Table 3.4). This could be because particles play a slightly greater role in total absorption at offshore sites (see Table 3.5) and thus cause more scatter in measuring absorption on the filter pad, and consequently, higher $a_t$. In addition, the pathlength corrections using the QFT for $a_p$ may cause the overestimate of $a_p$ and thus proportionately overestimate $a_t$ (Finkel & Irwin 2001). Although the quantitative filter technique is the accepted and widely used method for measuring absorption due to particles ($a_p$), the coefficients used for correcting for the pathlength may vary based on the size and type of particles as well as type of measurement.
equipment (spectrophotometer) and sample preparation techniques (Finkel & Irwin 2001).

Table 3.5. Median $a_g/a_t$ and $a_p/a_t$ and 25th – 75th percentile ranges for inshore and offshore reefs.

<table>
<thead>
<tr>
<th></th>
<th>305 nm</th>
<th>330 nm</th>
<th>380 nm</th>
<th>PAR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Median $a_g/a_t$, inshore</strong></td>
<td>0.892</td>
<td>0.852</td>
<td>0.753</td>
<td>0.509</td>
</tr>
<tr>
<td>25th percentile</td>
<td>0.867</td>
<td>0.799</td>
<td>0.684</td>
<td>0.346</td>
</tr>
<tr>
<td>75th percentile</td>
<td>0.928</td>
<td>0.899</td>
<td>0.841</td>
<td>0.638</td>
</tr>
<tr>
<td><strong>Median $a_g/a_t$, offshore</strong></td>
<td>0.871</td>
<td>0.7809</td>
<td>0.678</td>
<td>0.347</td>
</tr>
<tr>
<td>25th percentile</td>
<td>0.825</td>
<td>0.758</td>
<td>0.605</td>
<td>0.212</td>
</tr>
<tr>
<td>75th percentile</td>
<td>0.903</td>
<td>0.851</td>
<td>0.764</td>
<td>0.465</td>
</tr>
<tr>
<td><strong>Median $a_p/a_t$, inshore</strong></td>
<td>0.090</td>
<td>0.104</td>
<td>0.116</td>
<td>0.192</td>
</tr>
<tr>
<td>25th percentile</td>
<td>0.0583</td>
<td>0.0741</td>
<td>0.0787</td>
<td>0.126</td>
</tr>
<tr>
<td>75th percentile</td>
<td>0.109</td>
<td>0.141</td>
<td>0.158</td>
<td>0.263</td>
</tr>
<tr>
<td><strong>Median $a_p/a_t$, offshore</strong></td>
<td>0.106</td>
<td>0.135</td>
<td>0.155</td>
<td>0.268</td>
</tr>
<tr>
<td>25th percentile</td>
<td>0.082</td>
<td>0.107</td>
<td>0.126</td>
<td>0.216</td>
</tr>
<tr>
<td>75th percentile</td>
<td>0.134</td>
<td>0.174</td>
<td>0.195</td>
<td>0.339</td>
</tr>
</tbody>
</table>

Recent studies have shown that freezing the filter pads may result in exaggeration of the MAA peak due to extracellular release of MAAs, compared to lower absorption in their normal, intact shape (Laurion et al. 2003). Using a ratio such as relative MAA expression (see Chapter V) can cancel out this exaggeration, but large MAA peaks may affect $a_p$, especially $a_{p,330}$. Also, the MAA absorption observed using the frozen filter – QFT method may not represent in vivo absorption by MAAs, where the pigments would be intact in the cells (Laurion et al. 2003). Large colloids (diameter ~ 0.4 – 1 µm) can be captured on the GFF filters (nominal pore size 0.7 µm) and thus can also be a source of measurement error, because they play a significant role in particulate scattering: in the water column, scattering by large colloids can exceed that of pure water by an order of magnitude.
3.3.5.2. Absorption due to colloids

Small colloids range from 0.01 – 0.02 µm, and thus can be present in the 0.2 µm filtrate used to determine absorption due to CDOM ($a_g$). Small colloids can play an important role in the overall colloidal backscattering in the ocean. The combined backscattering of small and large colloids is typically higher than that of pure seawater over most of the visible spectrum: the scattering coefficient of large colloids from 350 – 700 nm can be up to two orders of magnitude higher than that due to pure water (Stramski and Wozniak 2005). Small colloids can contribute 44% to total backscattering at 350 nm (Stramski and Wozniak 2005) and thus can be a significant cause of pathlength amplification (error in $a_g$) in the UVR. Thus, the contribution of colloids to particulate backscattering may result in overestimation of $a_g$.

Optimally, to account for all size components in the water column, the 0.2 µm filtrate used in this study to measure $a_g$ should be subtracted from the 0.7 µm filtrate (from $a_p$ preparation) to determine absorption due to particulate material and colloids ($a_p$) between 0.2 and 0.7 µm. This size fraction has not been accounted for in my dataset. Typical organisms in the 0.2 to 0.7 µm size fraction include prochlorophytes, very small green phytoplankton, as well as some small cyanobacteria (blue – green algae) (Carder et al. 1986), thus their exclusion could also result in underestimates of [chl].

The warm, oligotrophic water-loving cyanobacteria *Trichodesmium sp.* was visually observed in the water column at many sampling sites, and was also often observed as “puffs” and “tufts”, referring to their shape, on the GFF filter upon measuring $a_p$, in turn resulting in higher $a_p$ as well as [chl] (see section 3.3.3.).
4. Colored dissolved organic material protects coral reefs by controlling exposure to UVR

4.1. 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., 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
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. 4.1). We propose that CDOM is protecting inshore patch reefs from exposure to the most extreme solar radiation and damaging effects of photooxidative stress.
4.2. 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. 4.2) 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. 4.2).

Figure 4.2. 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 adapted from A. Ramirez).

Total absorption can be partitioned into absorption due to dissolved material, $a_g$, particulate material, $a_{PM}$, and pure water, $a_w$ (Kirk 1994). Using measured $a_g$ and $a_p$, and published values of $a_w$ (Morel et al. 2007):

$$a_t(\lambda) = a_g + a_p + a_w$$

(4.1)
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 small 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 1994):

$$K_d = a_g + a_{PM} + a_w$$

(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, water 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 Mitchell et al. (2000) 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, $a_d(\lambda)$, was determined by methanol extraction of pigments and subtracted from $a_{PM}(\lambda)$ to determine spectral absorption due to phytoplankton, $a_{phi}(\lambda)$:

$$a_d(\lambda) = a_p(\lambda) - a_{phi}(\lambda)$$

(Kirk 1994). 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. (4.3) and:
\[ E_{d\lambda}(\lambda) = E_{d0}(\lambda) * e^{-K_d(\lambda)z} \]  \hspace{1cm} (4.4)

where \( z \) represents depth in meters (Kirk 1994). After July 2005, \( K_d \) was calculated from \textit{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 the visible wavelengths (integrated from 400 – 700 nm) using a BIC (Biospherical Instruments, Inc.) radiometer.

4.3. Results and Discussion

Absorption due to CDOM decreased going offshore from mangroves to inshore reefs, offshore reefs and finally blue water (Fig. 4.3), exhibiting the progressive dilution of land-sourced CDOM.

Figure 4.3. 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 higher at reefs associated with developed shoreline,
such as KL6m ($E_{d6m \text{ } 320nm} = 0.01 - 0.084 \text{ W/m}^2$) than at reefs offshore from extensive mangrove shoreline, such as Algae Reef ($E_d320nm = 0.008 - 0.057 \text{ W/m}^2$) (Fig. 4.4).

Figure 4.4. $E_{d6m \text{ } 320}$ at intact shoreline-associated reefs compared to developed shoreline-associated reefs as computed from $a_t \text{ } 320$ and $E_{d0 \text{ } 320}$. $E_{d6m \text{ } 320}$ was consistently lower at intact shoreline-associated reefs.

Over the period of sampling, 2004 – 2007, the 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. 4.5). 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, causing greater runoff and thus
increased CDOM over the reef (http://www.ncdc.noaa.gov oa/climate/research /monitoring.html#ustemprrcp).

Figure 4.5. Relative contribution of $a_g$ to $a_t$ in the UV at 305, 320, 330, 380 nm. 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 visible light; mean $a_g/a_t$ typically declined at all wavelengths as the summer progressed.

The difference in $E_{d6m}$ (ex: $E_{d6m 320}$) between intact and developed reefs may be due to $a_g$ (ex: $a_g 320$), which was higher at intact shoreline-associated reefs compared to developed shoreline – associated reefs considering all dates sampled in 2004 – 2007 (Fig. 4.6, Table 4.1).
Figure 4.6. $a_g_{320}$ at intact shoreline–associated reefs ($n = 10$) compared to developed shoreline–associated reefs ($n = 10$). Comparing medians, $a_g_{320}$ was higher at intact shoreline–associated reefs.

Table 4.1. Medians and 25th–75th percentile ranges for $a_g_{320}$ at intact shoreline–associated reefs compared to developed shoreline–associated reefs.

<table>
<thead>
<tr>
<th>$a_g_{320}$</th>
<th>median</th>
<th>25th–75th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>intact</td>
<td>developed</td>
</tr>
<tr>
<td></td>
<td>median</td>
<td>25th–75th percentile</td>
</tr>
<tr>
<td></td>
<td>intact</td>
<td>developed</td>
</tr>
</tbody>
</table>

Comparing $a_g$ between inshore and offshore reefs, $a_g$ was higher at inshore reefs at all wavelengths (e.g., $a_g_{330}$, Fig. 4.7). $a_g_{330}$ was higher at inshore reefs ($n = 26$, median = 0.665, 25th percentile = 0.362, 75th percentile = 1.516) than offshore reefs ($n = 22$, median = 0.361, 25th percentile = 0.240, 75th percentile = 0.488). $K_d_{330}$ was also higher at inshore reefs ($n = 26$, median = 0.670, 25th percentile = 0.458, 75th percentile = 0.878) than
offshore reefs \((n = 22, \text{median} = 0.419, 25^{\text{th}} \text{ percentile} = 0.254, 75^{\text{th}} \text{ percentile} = 0.548)\). Concurrently, \(K_d\) calculated from \textit{in situ} measurements using a BIC radiometer was higher at inshore reefs (ex: \(K_d_{330}\), Fig. 4.7; Table 4.2). The difference in \(K_d\) between inshore and offshore reefs decreased with increasing wavelength, excepting discrepancy from this trend at 305 nm due to immeasurably low irradiance intensities (Table 4.2).

Thus, difference in water transparency between inshore and offshore reefs was greater for UVR than for PAR. Results for 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 inshore reefs compared to offshore reefs in the Florida Keys.

![Figure 4.7](image)

Figure 4.7. Absorption due to CDOM at 330 nm \((a_{g,330})\) and the attenuation coefficient of downwelling irradiance at 330 nm, \(K_{d,330}\). \(a_{g,330}\) was higher at inshore reefs \((n = 26, \text{median} = 0.665, 25^{\text{th}} \text{ percentile} = 0.362, 75^{\text{th}} \text{ percentile} = 1.516)\) than offshore reefs \((n = 22, \text{median} = 0.361, 25^{\text{th}} \text{ percentile} = 0.240, 75^{\text{th}} \text{ percentile} = 0.488)\). \(K_{d,330}\) was higher at inshore reefs \((n = 26, \text{median} = 0.670, 25^{\text{th}} \text{ percentile} = 0.458, 75^{\text{th}} \text{ percentile} = 0.878)\).
than offshore reefs ($n = 22$, median = 0.419, 25th percentile = 0.254, 75th percentile = 0.548). Dashes represent medians.

Table 4.2. Comparison of $K_d$ between inshore and offshore reefs.

<table>
<thead>
<tr>
<th>$K_d(\lambda)$</th>
<th>median inshore</th>
<th>median offshore</th>
<th>25th – 75th percentile inshore</th>
<th>25th – 75th percentile offshore</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_d 305$</td>
<td>1.14</td>
<td>0.77</td>
<td>0.78 – 1.74</td>
<td>0.57 – 1.06</td>
</tr>
<tr>
<td>$K_d 330$</td>
<td>0.76</td>
<td>0.50</td>
<td>0.53 – 1.25</td>
<td>0.38 – 0.65</td>
</tr>
<tr>
<td>$K_d 380$</td>
<td>0.35</td>
<td>0.23</td>
<td>0.22 – 0.58</td>
<td>0.21 – 0.30</td>
</tr>
<tr>
<td>$K_d PAR$</td>
<td>0.22</td>
<td>0.17</td>
<td>0.20 - 0.29</td>
<td>0.13 – 0.22</td>
</tr>
</tbody>
</table>

The ratio of downwelling irradiance at 6m ($E_{d6m}$) to incident irradiance above the water surface ($E_{d0}$), $E_{d6m}/E_{d0}$, for 305, 330, 380 nm and PAR for inshore versus offshore reefs was calculated from in situ measurements of $K_d$ according to equation (4.4) (Figs. 4.8a,b). Median $E_{d6m}/E_{d0}$ at each wavelength was consistently lower at inshore reefs compared to offshore reefs, although the 25th to 75th percentile ranges consistently overlap (Table 4.3). Thus, likely as a result of higher $a_g$ and thus higher $K_d$, inshore reefs were exposed to higher UVR and visible light than offshore reefs. Outliers occurred at 380 nm (2.42) and PAR (6.64) but are not included in this data analysis. The euphotic zone depth, $E_{d6m}/E_{d0}$ of 1% for PAR reflects the depth where PAR is 1% of its surface value (Lee et al 2007). Significantly, $E_{d6m}/E_{d0}$ for all UV wavelengths exceeded 1%.
Figure 4.8a. $E_{d6m}/E_{d0}$ for 305, 330, and 380 nm for inshore versus offshore reefs sampled 2004 – 2007 (in = inshore, off = offshore). Dashes represent medians.

Figure 4.8b. $E_{d6m}/E_{d0}$ for PAR for inshore versus offshore reefs sampled in 2004 – 2007 (in = inshore, off = offshore). Dashes represent medians.
Table 4.3. Medians and 25\textsuperscript{th} to 75\textsuperscript{th} percentile ranges for $E_{d6m}/E_{d0}$ at 305, 330, 380 nm and PAR.

<table>
<thead>
<tr>
<th>$E_{d6m}/E_{d0}$ (Å)</th>
<th>median</th>
<th>25\textsuperscript{th} – 75\textsuperscript{th} percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{d6m}/E_{d0}$ 305</td>
<td>inshore</td>
<td>offshore</td>
</tr>
<tr>
<td></td>
<td>0.00105</td>
<td>0.0192</td>
</tr>
<tr>
<td>$n$</td>
<td>26</td>
<td>32</td>
</tr>
<tr>
<td>$E_{d6m}/E_{d0}$ 330</td>
<td>0.0104</td>
<td>0.0678</td>
</tr>
<tr>
<td>$n$</td>
<td>27</td>
<td>32</td>
</tr>
<tr>
<td>$E_{d6m}/E_{d0}$ 380</td>
<td>0.123</td>
<td>0.245</td>
</tr>
<tr>
<td>$n$</td>
<td>27</td>
<td>31</td>
</tr>
<tr>
<td>$E_{d6m}/E_{d0}$ PAR</td>
<td>0.267</td>
<td>0.390</td>
</tr>
<tr>
<td>$n$</td>
<td>27</td>
<td>31</td>
</tr>
</tbody>
</table>

Spectral slope of $a_g$ in the UV, $S_{(280 – 312 \text{ nm})}$, was higher at offshore sites compared to inshore sites (Fig. 4.9, Table 4.4). Comparing inshore reefs by region, median $S$ was the same in the Lower and Middle Keys, and higher in the Upper Keys. Comparing offshore reefs by region, median $S$ for was lowest in the Lower Keys and increased going from the Middle to Upper Keys. Thus, in addition to higher exposure to UVR (Fig. 4.8, Table 4.3), because $S$ increases with increasing photobleaching of CDOM (Del Vecchio and Blough 2002), CDOM at offshore reefs was more highly photobleached.
Figure 4.9. Spectral slope, S, (280 – 312 nm) for the Upper, Middle, and Lower Keys, inshore versus offshore sites. Dashes represent medians. Medians for inshore reefs in the Lower and Middle Keys were equal, and lower than that for the Upper Keys. Median for offshore reefs was lowest in the Lower Keys and increased going from the Middle to Upper Keys.

Table 4.4. Medians and 25th to 75th percentile ranges for S (280 – 312 nm) for inshore versus offshore reefs by region (Lower, Middle, and Upper Keys).

<table>
<thead>
<tr>
<th></th>
<th>median</th>
<th>25th – 75th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>inshore</td>
<td>offshore</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower Keys</td>
<td>0.0253</td>
<td>0.0282</td>
</tr>
<tr>
<td>n</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Middle Keys</td>
<td>0.0253</td>
<td>0.0294</td>
</tr>
<tr>
<td>n</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Upper Keys</td>
<td>0.0271</td>
<td>0.0314</td>
</tr>
<tr>
<td>n</td>
<td>34</td>
<td>10</td>
</tr>
</tbody>
</table>
As presented in section 4.1, we propose that declining percent stony coral cover in the Florida Keys may be exacerbated by increased exposure to UVR. Comparing percent stony coral cover and $a_g_{320}$, low percent stony coral cover co-occurs most frequently with low $a_g_{320}$ (Fig. 4.10) and the sites where this occurs are mostly offshore sites where $a_g$ is low (Fig. 4.11). Co-occurrence of low percent stony coral cover with low $a_g_{320}$ was high (17 (1 – 1) and 15 (1 -2)), while co-occurrence of higher scaled combinations were relatively low (between 0 and 5). In all but two cases (combination 1 – 3), low % coral cover was consistently accompanied by low $a_g_{320}$ (Table 4.5). Percent stony coral cover was consistently higher at inshore reef sites compared to offshore reefs, and did not always co-occur with high $a_g_{320}$ (Fig. 4.9). An explanation of the negative relationship between $a_g_{320}$ and percent stony coral cover may be that corals need light for photosynthesis, so the inshore reefs may be light limited at high $a_g$. Inshore reefs are more often exposed to high $a_g$ than low $a_g$, suggesting that longer term light history has greater influence on percent coral cover than instantaneous $a_g$ measurements.
Figure 4.10. The number of occurrences of different combinations of scaled % stony coral cover and $a_{g320}$. There were large numbers of low % stony coral cover – low $a_{g320}$, (17 (1 – 1) and 15 (1 -2)), while occurrences of higher scaled combinations were relatively low (between 0 and 5). In all but 2 cases (combination 1 – 3), low % coral cover was consistently accompanied by low $a_{g320}$. 


Figure 4.11. Percent stony coral cover versus $a_{g\,320}$ for the CREMP sites sampled in 2006 and 2007. Low percent stony coral cover (% coral cover) co-occurs most frequently with low $a_{g\,320}$. High percent coral cover occurs only at inshore reefs. Percent coral cover data courtesy of M. Callahan, CREMP, FWRI, St. Petersburg, FL.

Table 4.5. Scaling gradients for % stony coral cover (%cc) and $a_{g\,320}$.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>%CC</td>
<td>%CC &lt; 0.1</td>
<td>0.1 &lt; %CC &lt; 0.2</td>
<td>%CC &gt; 0.2</td>
</tr>
<tr>
<td>$a_{g,320}$</td>
<td>$a_{g,320}$ &lt; 0.4</td>
<td>0.4 &lt; $a_{g,320}$ &lt; 0.8</td>
<td>$a_{g,320}$ &gt; 0.8</td>
</tr>
</tbody>
</table>

Relative expression of MAAs declined with increasing $a_{g\,320}$ (Fig. 4.12). Throughout the sampling period 2004 – 2007, relative MAA expression was significantly higher at reefs associated with developed than at reefs associated with intact shoreline (see Chapter 5, Fig. 5.7).
Figure 4.12. Relative expression of MAAs declined with increasing $a_g(320)$ for intact and developed reefs in 2004 – 2005.

4.4. Conclusions

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 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 foraminiferal elements 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 foraminiferal elements (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 foraminiferal elements at a reef associated with intact shoreline (Algae Reef) compared to a reef associated with developed shoreline (KL6m Reef) (Fisher 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).

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.
5. Mycosporine-like Amino Acids as indicators of photo-oxidative stress

5.1 Introduction

Mycosporine-like amino acids (MAAs) are UV-absorbing compounds with maximal absorbance at 310 – 360 nm (Shick et al. 1999). MAAs also may have an antioxidant activity (Dunlap and Yamamoto 1995, Kim et al. 2001, Suh et al. 2003). Because MAAs are induced by exposure to UVR (Dunlap et al. 1986, Banaszak et al. 1998, Lesser 2000), theories on MAA induction are relevant to my study of photobiology and photochemistry of CDOM and coral reefs.

MAAs can be produced by symbiotic zooxanthellae (Shick et al. 1999) as well as by phytoplankton (Morrison and Nelson 2004). While exposing corals to UVR can induce UV-protective mechanisms such as production of MAAs (Shick et al. 1996, Dunlap and Shick 1998, Morrison and Nelson 2004, Shick 2004) and DNA-repair enzymes (Banaszak and Lesser 1995, Kuffner et al. 1995, Anderson et al. 2001), prolonged overexposure to UVR can also reduce photosynthetic rates and simultaneously reduce MAA production (Lesser and Farrell 2004). In addition, production of MAAs may decrease with increasing temperature, leaving zooxanthellae more susceptible to damage caused by exposure to UVR (Lesser et al. 1990).

Results from studies monitoring visible light (400 - 700 nm) and MAA production have been ambiguous (Jokiel et al. 1997, Moisan and Mitchell 2001). Increases in blue wavelengths of light can induce production of UV-absorbing MAAs, however, visible
and UVR co-vary, thus as blue wavelengths of light increase, the concurrent increase in UVR may actually be responsible for MAA induction. Another hypothesis proposes that photosynthetically usable energy (PUR) absorbed in excess of the processing capacity of cellular biochemistry may be passed on to a genetic pathway to induce MAAs (Moisan and Mitchell 2001). Goes et al. (1995) suggest that disruption of a metabolic pathway may cause MAA accumulation.

According to Hader, MAAs, which are located in the outer cytoplasmic layers of the algal cell, prevent up to 7 out of 10 UV photons from reaching the central targets (e.g., the DNA in the nucleus) (http://www.photobiology.info/Hader.html). MAAs are a diverse group of compounds and as such display a range of absorption maxima (http://www.photobiology.info/Hader.html). The MAAs can be extracted from the cells and separated by HPLC. The absorption spectra of the separated MAAs show different absorption maxima spread out over the UV-A region (http://www.photobiology.info/Hader.html; Figure 5.1). Light absorption by MAAs occurs between 310 to 360 nm and depends on the organisms sampled (Dunlap and Shick 1998). Other compounds, such as DNA and amino acids, absorb at lower UV wavelengths (Fig. 5.2).
Figure 5.1. Absorption spectra for several different MAAs. The absorption spectra of the separated MAAs show different absorption maxima spread out over the UV-A region (http://www.photobiology.info/Hader.html).

Figure 5.2. Relative MAA expression is calculated from the spectral absorption due to phytoplankton, $d_{\text{phi}}$ or $\varphi$. It is the ratio of the peak to the trough in the UV range.
Phytoplankton rely on negative and positive phototaxis to optimize their exposure to light. Over the course of the morning, phytoplankton can move from the surface to deeper depths (http://www.photobiology.info/Hader.html). Nevertheless, phytoplankton may utilize MAAs as a means of adapting to high light environments (Klisch and Haeder 2000). For example, Morrison and Nelson (2004) found that in clear ocean waters, absorption in the UV region by surface-dwelling phytoplankton is typically associated with MAAs and is higher in the summer than winter, indicating that MAAs are produced in response to higher exposure to solar radiation.

Although many studies have investigated MAA production (see Dunlap and Shick 1998), few studies have compared seasonal and geographical differences in MAA production in reefal waters. My study provides the first analysis of water column MAA production on reefs in the Florida Keys. Not only do MAAs protect organisms from UV damage, but, because MAA production is induced by UVR as well as visible light, their presence in the water column may reflect UV exposure and thus photic stress. This project tests the following hypotheses: 1) within sites, MAA production does not depend on depth, and 2) between sites, MAA production does not differ comparing offshore reefs and inshore reefs and comparing intact and developed reefs. The expected results are that, due to higher exposure of solar irradiance at the surface and offshore, respectively, relative MAA expression will be higher at the surface compared to the bottom, offshore compared to inshore, and at developed compared to intact shoreline – associated reefs.
5.2. Methods

Spectral absorption due to phytoplankton \(a_{\text{phi}}\) (see Chapter 3) for intact and developed shoreline-associated reefs was examined for MAA peaks in the UV range. I used relative MAA expression (relative UV pigment peak height, Morrison and Nelson 2004; see Figure 5.2) as an expression of organismal stress due to exposure to solar radiation, especially UVR. Using chlorophyll as an indicator of phytoplankton biomass, I compared the absorption peak at 320 nm to chlorophyll concentration \([chl], \mu g/l\) (see Chapter 3), to determine whether MAA production is proportional to phytoplankton biomass. I also examined the ratio maximum MAA absorption: maximum absorption by chlorophyll \(a_{\text{phi} 683}\) to determine the amount of MAA produced relative to absorption due to chlorophyll.

5.3 Results and Discussion

Chlorophyll concentration \([chl]\), an indicator of phytoplankton biomass, did not correlate with relative MAA expression (Fig. 5.3). Relative MAA expression tended to range from 1 – 2 regardless of \([chl]\). Relative MAA expression values above 2 were due to surface samples (blue box in Fig. 5.3) and in one case, the lowest value above 2, due to a bottom sample at a developed shoreline – associated reef (KL6m). Thus, MAA production does not increase with increasing \([chl]\). Because \([chl]\) is an index of phytoplankton biomass (Huot et al. 2007), it can be deduced that relative MAA production is not solely dependent on phytoplankton biomass, and low relative MAA production is not indicative of low phytoplankton biomass.
Figure 5.3. Relative MAA expression versus [chl] for all dates sampled from 2004 - 2007 where data for both relative MAA expression and [chl] were available.

Figure 5.4 illustrates relative MAA expression versus $a_{g\ 320}$ for all sites sampled in 2004 through 2007. The highest values for relative MAA expression occurred at low ($< 0.5 \text{ m}^{-1}$) $a_{g\ 320}$. I determined from the number of observations of relative MAA expression greater than 2 ($n = 8$) and the number of observations of $a_{g\ 320}$ less than 0.5 ($n = 34$) compared to the total number of observations ($n = 63$), that the probability of all eight relative MAA values greater than 2 occurring by chance is $(34/63)^8 = 0.007$ or 0.7%. Therefore, there is high probability that high relative MAA production is associated with low $a_{g\ 320}$. In addition, while many samples, surface and bottom, had lower values of relative MAA production co-occurring with $a_{g\ 320}$ less than 0.5 m$^{-1}$, all relative MAA
expression values greater than 2 were surface samples with $a_{g\ 320}$ less than 0.5 m$^{-1}$. Thus depth, i.e. exposure to light, as well as $a_g$, plays an important role in MAA production.

Figure 5.4. Relative MAA expression versus $a_{g\ 320}$ for all sites sampled in 2004 through 2007 where data for both $a_{g\ 320}$ and relative MAA expression were available. The chance of all eight relative MAA values greater than 2 occurring by chance is 0.007 (0.7%).

Because the surface is exposed to higher intensities of solar irradiance compared to the bottom (see Chapter 2), it would be expected that, within sites, relative MAA expression would be higher for surface samples compared to bottom samples. Relative MAA expression tended to be higher and more variable for surface samples (median = 1.346, 25$^{\text{th}}$ to 75$^{\text{th}}$ percentile range = 1.195 to 1.615) than for bottom samples (median = 1.208, 25$^{\text{th}}$ to 75$^{\text{th}}$ percentile range =1.125 to 1.356, Figure 5.5).
Figure 5.5. Relative MAA expression for surface samples compared to bottom samples. Dashes represent medians. Relative MAA expression tended to be higher and more variable for surface samples (median = 1.346, 25th to 75th percentile range = 1.195 to 1.615) than for bottom samples (median = 1.208, 25th to 75th percentile range = 1.125 to 1.356).

Because of the discrepancy between surface and bottom samples, I compared surface and bottom samples separately for relative MAA expression at inshore versus offshore reefs (Fig. 5.6, Table 5.1). Comparing surface and bottom samples, relative MAA expression was significantly higher at the surface at offshore reefs. For inshore reefs, though the median was higher at the surface than the bottom, the 25th – 75th percentile ranges overlapped, thus I can only conclude that the inshore surface samples tended to be higher but the difference may not be significant. Comparing medians for surface and bottom samples at inshore versus offshore reefs, relative MAA expression
tended to be higher at offshore surface compared to inshore surface and at offshore bottom compared to inshore bottom.

Figure 5.6. Relative MAA expression comparing surface and bottom samples at inshore versus offshore reefs. Dashes represent medians.

Table 5.1. Medians, 25th – 75th percentile ranges, and number of samples (n) for relative MAA expression at inshore versus offshore reefs, surface versus bottom.

<table>
<thead>
<tr>
<th>Relative MAA expression</th>
<th>inshore surface</th>
<th>inshore bottom</th>
<th>offshore surface</th>
<th>offshore bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>median</td>
<td>1.290</td>
<td>1.000</td>
<td>1.506</td>
<td>1.115</td>
</tr>
<tr>
<td>25th percentile</td>
<td>1.082</td>
<td>1.050</td>
<td>1.354</td>
<td>1.001</td>
</tr>
<tr>
<td>75th percentile</td>
<td>1.371</td>
<td>1.322</td>
<td>1.922</td>
<td>1.233</td>
</tr>
<tr>
<td>N</td>
<td>30</td>
<td>14</td>
<td>21</td>
<td>10</td>
</tr>
</tbody>
</table>

Relative expression of MAAs decreased with increasing $a_{g, 320}$ for intact and developed shoreline associated reefs in 2004 – 2005 (Figure 4.7). Throughout the sampling period 2004 – 2007, relative MAA expression was significantly higher at reefs
associated with developed shoreline (median = 1.190, 25th to 75th percentile range = 1.109 to 1.220, than at reefs associated with intact shoreline (median = 1.353, 25th to 75th percentile range = 1.337 – 1.650, Fig. 5.7). Values of relative MAA expression above 2 were for surface samples, and were higher for developed shoreline – associated reefs. At the same time, $a_{g\,320}$ was significantly higher and had a lower range at intact shoreline – associated reefs (see Fig. 4.6, Table 4.1) where relative MAA expression was lower. Thus $a_{g\,320}$ may be playing a photo-protective role against UVR.

Figure 5.7. Relative MAA expression of intact shoreline – associated reefs compared to developed shoreline - associated reefs. Dashes represent medians.

Comparing medians for relative MAA expression for surface samples only by region, Upper, Middle and Lower Keys, relative MAA expression tended to be highest in the Middle Keys, and the 25th – 75th percentile ranges all overlap (Fig. 5.8, Table 5.2). The Lower Keys has the lowest 25th to 75th percentile range. The outliers for the Upper
Keys are as follows: the highest outlier is an offshore reef near developed shoreline (Molasses), the second highest outlier is an inshore reef near developed shoreline (KL6m Reef); and the third highest outlier is an inshore reef near intact shoreline (Algae Reef). The two outliers in the Middle Keys occurred at an offshore site, Tennessee Reef (deep and shallow site, sampled on the same date).

![Graph](image)

**Figure 5.8.** Relative MAA expression by region, Lower, Middle, and Upper Keys. Dashes represent medians.

**Table 5.2.** Medians, 25th – 75th percentile ranges, and number of samples (n) for relative MAA expression comparing regions, Lower, Middle and Upper Keys.

<table>
<thead>
<tr>
<th>Relative MAA expression</th>
<th>Lower Keys</th>
<th>Middle Keys</th>
<th>Upper Keys</th>
</tr>
</thead>
<tbody>
<tr>
<td>median</td>
<td>1.325</td>
<td>1.625</td>
<td>1.315</td>
</tr>
<tr>
<td>25th percentile</td>
<td>1.220</td>
<td>1.294</td>
<td>1.178</td>
</tr>
<tr>
<td>75th percentile</td>
<td>1.466</td>
<td>1.751</td>
<td>2.487</td>
</tr>
<tr>
<td>n</td>
<td>13</td>
<td>3</td>
<td>11</td>
</tr>
</tbody>
</table>
At the same time, mean $a_g$ at the surface was significantly lower and had a lower range in the Upper Keys compared to the Lower Keys (Fig. 5.9, Table 5.3). $a_g$ for the Middle Keys tended to be lower than the Lower Keys and higher than the Upper Keys. Thus, in the Lower Keys, low relative MAA expression co-occurred with high $a_g$. The Lower Keys have more extensive of mangroves compared to the Upper Keys (Lidz et al. 2003), and while the Middle Keys receive CDOM – rich waters from Florida Bay, the constancy and proximity of terrestrial-sourced, locally produced CDOM with each tidal cycle might play a bigger role in UV photo-protection in the Lower Keys than the pulses of CDOM-rich water from Florida Bay in the Middle Keys. Although median relative MAA expression as well as $a_g$ were low in the Upper Keys, the Upper Keys had more and higher outliers compared to the Lower Keys.
Figure 5.9. \( a_g \) at only the surface for the Florida Keys by region, Lower, Middle and Upper Keys.

Table 5.3. \( a_g \) at the surface only for the Florida Keys by region, Lower, Middle and Upper Keys.

<table>
<thead>
<tr>
<th>( a_g ) surface only</th>
<th>Lower Keys</th>
<th>Middle Keys</th>
<th>Upper Keys</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_g ) median (m(^{-1}))</td>
<td>0.539</td>
<td>0.352</td>
<td>0.272</td>
</tr>
<tr>
<td>25\textsuperscript{th} percentile</td>
<td>0.364</td>
<td>0.272</td>
<td>0.214</td>
</tr>
<tr>
<td>75\textsuperscript{th} percentile</td>
<td>0.614</td>
<td>0.593</td>
<td>0.311</td>
</tr>
<tr>
<td>( n )</td>
<td>19</td>
<td>12</td>
<td>29</td>
</tr>
</tbody>
</table>

Considering surface and bottom samples together, the trends in \( a_g \) between Upper, Middle and Lower Keys are the same as for surface samples only (Fig. 5.10, Table 5.4), while the median \( a_g \) considering surface and bottom samples together were slighting higher. Thus, \( a_g \) for surface samples are generally lower than bottom samples.
Figure 5.10. $a_g_{330}$ at the bottom and surface for the Florida Keys by region, Lower, Middle and Upper Keys.

Table 5.4. $a_g_{330}$ at the surface and bottom for the Florida Keys by region, Lower, Middle and Upper Keys.

<table>
<thead>
<tr>
<th>$a_g_{330}$ surface &amp; bottom</th>
<th>Lower Keys</th>
<th>Middle Keys</th>
<th>Upper Keys</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_g_{330}$ median (m$^{-1}$)</td>
<td>0.543</td>
<td>0.419</td>
<td>0.281</td>
</tr>
<tr>
<td>25$^{\text{th}}$ percentile</td>
<td>0.421</td>
<td>0.427</td>
<td>0.270</td>
</tr>
<tr>
<td>75$^{\text{th}}$ percentile</td>
<td>0.635</td>
<td>0.870</td>
<td>0.386</td>
</tr>
<tr>
<td>$n$</td>
<td>52</td>
<td>23</td>
<td>28</td>
</tr>
</tbody>
</table>

In conclusion, relative MAA expression was higher at the surface than at the bottom, at offshore reefs compared to inshore reefs, and at developed shoreline – associated reefs compared to intact shoreline – associated reefs. In general, high relative MAA expression co-occurred with lower $a_g_{320}$ or $330$. 

The species composition at the surface may produce higher amounts of MAAs as a means of adapting to the high intensities and durations of low wavelength radiation at the surface. Surface-dwelling phytoplankton may accumulate higher amounts of MAAs compared to bottom-dwelling phytoplankton, in response to high irradiance, allowing them to adapt to conditions of high irradiance at the surface (Klisch and Haeder 2000). MAA production may also decrease in nitrogen deficient waters, making organisms in N poor waters more susceptible to UV damage (Klisch and Haeder 2008).

Variability in relative MAA expression increased going from the Lower to Upper Keys. Given the degree of shoreline development in the Key Largo area of the Upper Keys, in contrast with the significant amount of mangrove shoreline at John Pennekamp Park, the high variance in the Upper Keys may be due to greater variability in the degree of shoreline development in this region (Appendix A). While the Middle Keys receive substantial input from CDOM- and particle-rich Florida Bay (Lidz et al. 2006, Porter 2002), the lowest relative MAA expression was seen in the Lower Keys, which has the highest amount of intact shoreline.

Because surface samples, offshore sites, and sites near developed shoreline have higher amounts of MAAs compared to bottom samples, inshore sites, and sites near intact shoreline, where $a_g \, \text{UV}$ is higher, I deduced that offshore sites and sites near developed shoreline sites are exposed to higher levels of photic stress. The phytoplankton apparently have acclimated to high light by producing more MAAs. Photic stress compromises resistance to other biotic and abiotic stressors on reefs, and can contribute to the relative decline in offshore, clearer water reefs, relative to inshore, less transparent reefs (see Chapter 4). Combined with CREMP’s observations of higher rates of decline at offshore
reefs, these results on MAA production allow me to reject the hypothesis that UVR does not play an important role in coral reef decline. CDOM, as a photoprotective barrier to UVR, may protect coral reefs from photooxidative stress.

Chlorophyll concentration ([chl], µg/l) was significantly lower in the Upper Keys (mean=0.252, SD=0.111) compared to the Middle (mean=0.326, SD=0.109) and Lower Keys (mean=0.342, SD=0.079) (p = 0.0313 and 0.00168, respectively). Comparing the Middle and Lower Keys, [chl] was not significantly different (p = 0.597) (Figure 5.11, Table 5.5). At the same time, $a_g_{320}$ was lowest and relative MAA expression was relatively high in the Upper Keys, especially compared to the Lower Keys. Thus, high CDOM co-occurs with lower production of UV-protecting compounds (MAAs) and higher production of chlorophyll, an indicator of phytoplankton biomass. These results support the hypothesis that CDOM may be protecting organisms, as exhibited here by phytoplankton, from photo-oxidative stress.
Figure 5.11. [chl] by region in the Lower, Middle, and Upper Keys. Dashes represent medians.

Table 5.5. Medians, 25th and 75th percentiles, and number of samples (n), for [chl] for the Lower, Middle, and Upper Keys.

<table>
<thead>
<tr>
<th>[chl] µg/l</th>
<th>lower</th>
<th>middle</th>
<th>upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>median</td>
<td>0.345</td>
<td>0.334</td>
<td>0.239</td>
</tr>
<tr>
<td>25th percentile</td>
<td>0.286</td>
<td>0.263</td>
<td>0.177</td>
</tr>
<tr>
<td>75th percentile</td>
<td>0.398</td>
<td>0.403</td>
<td>0.323</td>
</tr>
<tr>
<td>n</td>
<td>22</td>
<td>16</td>
<td>35</td>
</tr>
</tbody>
</table>

5.4 Future Work

The dynamic nature of exposure to solar radiation, behavioral and physiological species acclimations to solar radiation, and the time scales of these processes are an exciting aspect that this project did not address. While some studies have
investigated the time scales of MAA production at one depth in culture, other studies have investigated MAA production over seasonal time scales, *in situ* analysis of phytoplankton number and species, together with time scales of phototaxis and MAA production, should be explored further.
Chapter 6. Spatial Variability of Inherent and Apparent Optical Properties on Coral Reefs

6.1. Background

Coral reefs in the Florida Keys, as well as worldwide, are experiencing decline in coral cover, increase in disease and bleaching, and associated stresses that result in overall decline in coral health (see Chapter 3). Among factors that have been implicated in the cause of coral reef decline are temperature and solar radiation (Lesser and Farrell 2004).

The underwater light field is a result of incident irradiance interacting with the absorption and scattering processes that occur in the water column, as well as the pathlength (depth). Gregg (2002) describes the angular structure of the underwater light field: “The direct downwelling stream contains the irradiance directly transmitted by the sun, traversing the air-sea interface, and proceeding forward at an angle described by the solar zenith angle modified by the refractive index of seawater. Each scattering and absorbing event in the water column removes irradiance from the direct downwelling stream.

“Whereas the downwelling direct irradiance receives no contributions in the water column and steadily decreases as the result of absorption and scattering processes, the downwelling diffuse irradiance gains forward-scattered downwelling direct irradiance and backscattered upwelling diffuse irradiance in the water column. This irradiance stream
travels along a path defined as the average cosine for downwelling diffuse irradiance” (Gregg 2002, p. 6). Thus, diffuse irradiance is amplified by scattering and the downwelling light stream is enhanced by forward scattering. A coral reef where overlying water is characterized by relatively lower absorption may incur higher irradiances due to the angular distribution of light through the water column until it ultimately reaches the bottom. The reflective properties of the bottom may also increase the amount of upward scattering of light, and thus light, reaching the benthos (Lee et al. 1998, 1999; Boss and Zanefeld 2003).

6.2. Objectives

The goal of this chapter is to use field data from two Upper Keys patch (inshore) reefs to compare differences in the amount of light reaching the benthos based on modeled radiance distribution determined using HydroLight™.

6.3. Methods

See Chapter 3 for sample collection and field measurements. Scattering, $b$, was measured using an ac-9 (WET labs ©) according to Voss et al. (2003). Methods for in lab measurements of absorption ($a_g$, $a_p$) and chlorophyll concentration [chl] are also detailed in Chapter 3, as are field site locations and characteristics. KL6m is located near developed shoreline, while Algae Reef is located near intact mangrove shoreline (Fig 3.1).

HydroLight™ (© Sequoia Scientific), a radiance distribution modeling program, was used to derive radiance distribution parameters $K_d$ and $\mu_d$ from in lab measurements of
total absorption, \(a_t\), and in situ measurements of scattering, \(b\), for two inshore reefs KL6m Reef and Algae Reef differing in UV transparency as a result of differences in \(a_g\). Because in situ scattering, \(b\), was measured only on September 28, 2004, this analysis is limited to one dataset collected at each site on this date. Hydrolight© - derived (modeled) attenuation coefficients for downwelling irradiance, \(K_d\), and the average cosine of downwelling irradiance, \(\mu_d\), at four different UV wavelengths, 305, 320, 330 and 380 nm, were compared between sites. Also, modeled \(K_d\) was compared to estimates of \(K_d\) based on in lab measurements of \(a_t\).

6.3.1. Calculating underwater irradiance

The natural light field is not collimated but diffuse. In the water column, total diffuse attenuation of downwelling irradiance, \(K_d\), is due to absorption \((a)\) and scattering \((b)\) by water molecules, dissolved material, and particulate material, and the angular distribution of light, the average cosine of downwelling irradiance, \(\mu_d\):

\[
K_d = (a + b)_{w, p, g} / \mu_d
\]

where \(\mu_d = (E_d - E_u)/E_{d0} = \cos \theta\) and \(\theta\) is the zenith angle (angle between the sun and plane perpendicular to the surface; see following section for derivation). When scattering is constant and light measurements are made within two hours of solar noon, the effect of \(\mu_d\) is negligible and the total diffuse attenuation of downwelling irradiance can be estimated solely from absorption.

\[
K_d = a_g + a_p + a_w
\]

where \(a_p\) is absorption due to particulate material and \(a_w\) is absorption due to pure water. Irradiance reaching the sea floor \((E_{dz})\) can then be estimated as:
\( E_{d\ell}(\lambda) = E_{d0}(\lambda) e^{-K_d z} \), where \( z \) = depth \hspace{1cm} (6.3)

(Kirk 1994).

When \( \bar{\mu} \) is not constant and \( b \ll a \), the following is true:

\[ K_d = \frac{(a)_{w, p, g}}{\bar{\mu}} \quad \text{or} \quad K_d = \frac{a_t}{\bar{\mu}} \] \hspace{1cm} (6.4)

where \( a_t \) is total absorption due to water molecules, particulate material and gelbstoff.

### 6.3.2. The angular distribution of light

According to Kirk (1994, p. 9 – 10), “Irradiance (at a point of a surface), \( E \), is the radiant flux incident on an infinitesimal element of a surface, containing the point under consideration, divided by the area of that element; it is the radiant flux per unit area of a surface:

\[ E = \frac{d\Phi}{dS} \] \hspace{1cm} (6.5)

Irradiance has the units W m\(^{-2}\), or quanta (or photons) s\(^{-1}\) m\(^{-2}\) where one mol photons is 6.02 x 10\(^{23}\) (Avogadro’s number) photons. One mole of photons is frequently referred to as an *einstein*.

The relationship between \( E \), radiant flux per unit surface area, and radiance, \( L \), is shown in my Figure 6.1. “The projected area of the element of surface is \( dS \cos \theta \) and the corresponding element of solid angle is \( d\omega \). Thus, the radiant flux on the element of surface within the solid angle \( d\omega \) is:

\[ d\Phi = L(\theta, \phi) dS \cos \theta d\omega \] \hspace{1cm} (6.6)
Figure 6.1. Radiance \( L \) on a point in a surface, from a given direction, is the radiant flux in the specified direction per unit solid angle per unit projected area of the surface (after Kirk 1994).

"Then, Irradiance, \( E \), can be expressed as:

\[
E = \frac{d\Phi}{dS} = L(\theta, \phi) dS \cos \theta d\omega dS = L(\theta, \phi) \cos \theta d\omega.
\]

The total downward irradiance at that point in the surface is obtained by integrating with respect to solid angle over the whole upper hemisphere:

\[
E_d = \int_{2\pi} L(\theta, \phi) \cos \theta d\omega
\]

(6.7)

The scalar irradiance, \( E_\theta \), is the integral of the radiance distribution at a point over all
Scalar irradiance is thus a measure of the radiant intensity at a point, which treats radiation from all directions equally. In the case of irradiance, on the other hand, the contribution of the radiation flux at different angles varies in proportion to the cosine of the zenith angle of incidence of the radiation: a phenomenon based on purely geometrical relations (Figure 6.1, eqn. 6.9) and sometimes referred to as the Cosine Law. The \textit{downward} scalar irradiance, $E_{0d}$, is the integral of the radiance distribution over the upper hemisphere" (Kirk 1994, pp. 9 – 10):

$$E_{0d} = \int_{4\pi} L(\theta,\phi) d\omega$$

(6.9)

Because the object of my study is to estimate the amount of light reaching the bottom, or benthos, the parameter of concern is the average cosine, $\bar{\mu}$, in the downward direction, $\bar{\mu}_d$. Again, quoting Kirk (1994, p. 10), “The average cosine for downwelling light, $\bar{\mu}_d$, at a particular point in the radiation field, may be regarded as the mean value, in an infinitesimally small volume element at that point in the field, of the cosine of the zenith angle of all the downwelling photons in the volume element. It can be calculated by summing (i.e., integrating) for all elements of solid angle ($d\omega$) comprising the upper hemisphere, the product of the radiance in that element of solid angle and the value of $\cos \theta$ (i.e. $L(\theta,\phi) \cos \theta$), and then dividing by the total radiance originating in that hemisphere”:

$$\bar{\mu}_d = \frac{E_d}{E_{0d}} = \frac{\int_{2\pi} L(\theta,\phi) \cos \theta d\omega}{\int_{2\pi} L(\theta,\phi) d\omega}$$

(6.10)
Thus, $\bar{\mu}_d$ is related to the cosine of the zenith angle as the downward irradiance at a point compared to the radiance distribution over the upper hemisphere. Consequently, $\bar{\mu}_d$ is also called the average cosine for downwelling light and is unitless. The average cosine of light describes the angular structure of the light field ranging from collimated light plane perpendicular to the surface, where the zenith angle ($\theta$) is 0 ($\cos 0 = 1$ and thus $\bar{\mu}_d = 1$) to maximally diffuse light, where $\theta = 90^\circ$ ($\cos 90 = 0$ and thus $\bar{\mu}_d = 0$). Multispectral $K_d$ and $\bar{\mu}_d$ can be estimated or modeled from single-wavelength estimates of $a_g$ and $b$ using $Hydrolight^©$ (version 5). The ratio of in lab measurements of total absorption, $a_t$, to independently measured, in situ $K_d$ is an estimate of the average cosine of light, $\bar{\mu}$, 

$$\bar{\mu} = a_t/K_d$$  

(6.11) 

(Kirk 1994).

Except when the single-scattering albedo is very low (less than 0.1), which only occurs in very clear oceanic water at long wavelengths (greater than 650nm), scattering dominates $\bar{\mu}_d$. Otherwise the effect of absorption dominates $\bar{\mu}_d$: light that does not have the shortest pathlength is more rapidly removed (absorbed), so that the light that is traveling vertical to the surface of the water penetrates most deeply; secondarily scattered light results in increase of light in the forward direction, leaving the underwater light field more vertical and making $\bar{\mu}_d$ closer to 1 (Berwald et al. 1995; Kirk 1994).

For optically clear waters, where absorption dominates light attenuation, $\bar{\mu}_d$ will be close to one for the entire depth profile and at infinite depths $\bar{\mu}_d$ would be close to one as well, consistent with the absorption effect. Thus, light becomes more vertical or collimated at deeper depths, and $\bar{\mu}_d$ increases (becomes closer to unity). In more highly
scattering, low absorbing waters, scattering plays a greater role, light becomes more diffuse and $\bar{\mu}_d$ decreases (deviates from unity).

### 6.4. Results and Discussion

Table 6.1 compares calculated estimates of $K_d$ and $\bar{\mu}_d$ at 330 nm ($K_{d330nm}$) using *Hydrolight*© (version 5), laboratory measurements of absorption, *in situ* measurements of scattering ($b$), as well as other meteorological and optical parameters for KL6m and Algae Reefs. $\bar{\mu}_d$ can also be estimated as the ratio of measured total absorption coefficient ($a_t$) to modeled $K_d$ (see Eqn. 6.5). Comparing modeled (*Hydrolight*©- derived) $\bar{\mu}_d$ between sites, modeled $\bar{\mu}_d$ was lower at the reef site with the lower $a_g$, developed shoreline – associated KL6m Reef (Table 6.1, Table 6.2, Figure 6.2), showing that the light field is more diffuse at KL6m Reef compared to intact shoreline – associated Algae Reef. In addition, modeled reflectance, $R$, was also consistently higher at KL6m (Table 6.3).
Table 6.1. Meteorological data, salinity and bottom type, as well as optical parameters used as input, model bottom type, and output (“modeled”) for *Hydrolight* © version 5.0 for Algae Reef and KL6m Reef on September 28, 2004.

<table>
<thead>
<tr>
<th></th>
<th>Algae Reef</th>
<th></th>
<th>KL6m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Julian Day</td>
<td>272</td>
<td>272</td>
<td>272</td>
</tr>
<tr>
<td>Time (GMT)</td>
<td>16.25</td>
<td>16.25</td>
<td>21.50</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>28.0</td>
<td>28.0</td>
<td>28.8</td>
</tr>
<tr>
<td>Salinity (PSU)</td>
<td>36.0</td>
<td>36.0</td>
<td>36.0</td>
</tr>
<tr>
<td><em>Hydrolight</em> © solar zenith angle (°)</td>
<td>30.47</td>
<td>30.5</td>
<td>30.5</td>
</tr>
<tr>
<td><em>Hydrolight</em> © total ozone (DU)</td>
<td>278</td>
<td>278</td>
<td>278</td>
</tr>
<tr>
<td>actual bottom type</td>
<td>50%-to-mostly sand, coral</td>
<td>50%-to-mostly sand, coral</td>
<td>sand, seagrass, coral</td>
</tr>
<tr>
<td>Winds (m/s)</td>
<td>6.7</td>
<td>6.7</td>
<td>2.5</td>
</tr>
<tr>
<td>[chl] (µg/l)</td>
<td>0.324</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>$a_{430nm}$ in lab (m$^{-1}$)</td>
<td>0.576</td>
<td>0.532</td>
<td>0.323</td>
</tr>
<tr>
<td>$a_g_{330nm}$ (m$^{-1}$)</td>
<td>0.505</td>
<td>0.446</td>
<td>0.257</td>
</tr>
<tr>
<td>$b_{330}$ (m$^{-1}$)</td>
<td>0.801</td>
<td>1.987</td>
<td>1.374</td>
</tr>
<tr>
<td>computed $b_{b_{330nm}}$ (m$^{-1}$)</td>
<td>0.0219</td>
<td>0.0433</td>
<td>0.0142</td>
</tr>
<tr>
<td><em>Hydrolight</em> © $K_{d_{330nm}}$ (m$^{-1}$)</td>
<td>0.718</td>
<td>0.809</td>
<td>0.461</td>
</tr>
<tr>
<td>$a_{430nm} / K_{d_{330nm}}$</td>
<td>0.802</td>
<td>0.657</td>
<td>0.700</td>
</tr>
<tr>
<td>$Hydrolight$ © $\bar{\mu}_d$ ([mineral] = 0)</td>
<td>0.838</td>
<td>0.733</td>
<td>0.745</td>
</tr>
<tr>
<td><em>Hydrolight</em> © model bottom type</td>
<td>avg coral</td>
<td>avg coral</td>
<td>avg coral</td>
</tr>
</tbody>
</table>
Figure 6.2. Comparison of $\mu_d$ for Algae and KL6m Reef surface and bottom at 305, 320, 330 and 380 nm. $\mu_d$ at Algae Reef is higher at all wavelengths than at KL6m, at the surface as well as bottom. See Table 6.3 for values and 25th – 75th percentile ranges.

Table 6.2. Comparison of $\mu_d$ for Algae and KL6m Reef surface and bottom at 305, 320, 330 and 380 nm. Medians and 25th – 75th percentile ranges.

<table>
<thead>
<tr>
<th>$\mu_d$</th>
<th>Algae surface</th>
<th>KL6m surface</th>
<th>Algae bottom</th>
<th>KL6m bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>305 nm</td>
<td>0.84650</td>
<td>0.72930</td>
<td>0.73580</td>
<td>0.69470</td>
</tr>
<tr>
<td>320 nm</td>
<td>0.83970</td>
<td>0.72480</td>
<td>0.72930</td>
<td>0.69360</td>
</tr>
<tr>
<td>330 nm</td>
<td>0.83830</td>
<td>0.76625</td>
<td>0.73370</td>
<td>0.69840</td>
</tr>
<tr>
<td>380 nm</td>
<td>0.83020</td>
<td>0.77305</td>
<td>0.73720</td>
<td>0.7054</td>
</tr>
<tr>
<td>median</td>
<td><strong>0.83900</strong></td>
<td><strong>0.74778</strong></td>
<td><strong>0.73475</strong></td>
<td><strong>0.69655</strong></td>
</tr>
<tr>
<td>25th percentile</td>
<td>0.836275</td>
<td>0.728175</td>
<td>0.7326</td>
<td>0.694425</td>
</tr>
<tr>
<td>75th percentile</td>
<td>0.8414</td>
<td>0.76795</td>
<td>0.73615</td>
<td>0.7054</td>
</tr>
</tbody>
</table>

Table 6.3. Inherent and Apparent Optical Properties (IOPs and AOPs) computed by *Hydrolight*® (version 5) for Algae and KL6m Reef, surface and bottom, at 305, 320, 330
and 380 nm, based upon *in situ* absorption, *a*, and scattering, *b*. \( m_{\text{bar} \ d} = \mu_d \cdot E_d \) for Algae and KL6m Reef, surface and bottom, as computed by *Hydrolight* ® (version 5), was higher at the surface but lower at the bottom at Algae Reef.

<table>
<thead>
<tr>
<th>305 nm</th>
<th>Eod</th>
<th>Ed</th>
<th>( m_{\text{bar} \ d} )</th>
<th>( R = E_u/E_d )</th>
<th>K d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae Reef surface</td>
<td>4.36E-02</td>
<td>3.69E-02</td>
<td>0.8465</td>
<td>1.11E-02</td>
<td>1.06783</td>
</tr>
<tr>
<td>Algae Reef bottom</td>
<td>1.75E-04</td>
<td>1.29E-04</td>
<td>0.7358</td>
<td>4.76E-02</td>
<td>1.15257</td>
</tr>
<tr>
<td>KL6m surface</td>
<td>4.00E-03</td>
<td>3.03E-03</td>
<td>0.7566</td>
<td>1.53E-02</td>
<td>0.66847</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>4.39E-03</td>
<td>3.08E-03</td>
<td>0.702</td>
<td>6.39E-02</td>
<td>0.86556</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>2.35E-03</td>
<td>1.63E-03</td>
<td>0.6947</td>
<td>7.33E-02</td>
<td>0.739</td>
</tr>
<tr>
<td>320 nm</td>
<td>Eod</td>
<td>Ed</td>
<td>( m_{\text{bar} \ d} )</td>
<td>( R = E_u/E_d )</td>
<td>K d</td>
</tr>
<tr>
<td>Algae Reef surface</td>
<td>4.98E-02</td>
<td>4.18E-02</td>
<td>0.8397</td>
<td>1.41E-02</td>
<td>0.8206</td>
</tr>
<tr>
<td>Algae Reef bottom</td>
<td>3.04E-03</td>
<td>2.21E-03</td>
<td>0.7293</td>
<td>5.20E-02</td>
<td>0.91027</td>
</tr>
<tr>
<td>KL6m surface</td>
<td>9.29E-02</td>
<td>6.96E-02</td>
<td>0.749</td>
<td>1.95E-02</td>
<td>0.51754</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>9.28E-02</td>
<td>6.50E-02</td>
<td>0.7006</td>
<td>6.54E-02</td>
<td>0.66056</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>2.36E-02</td>
<td>1.64E-02</td>
<td>0.6936</td>
<td>7.30E-02</td>
<td>0.58013</td>
</tr>
<tr>
<td>330 nm</td>
<td>Eod</td>
<td>Ed</td>
<td>( m_{\text{bar} \ d} )</td>
<td>( R = E_u/E_d )</td>
<td>K d</td>
</tr>
<tr>
<td>Algae Reef surface</td>
<td>3.47E-01</td>
<td>2.91E-01</td>
<td>0.8383</td>
<td>1.44E-02</td>
<td>0.71824</td>
</tr>
<tr>
<td>Algae Reef bottom</td>
<td>7.70E-03</td>
<td>5.65E-03</td>
<td>0.7337</td>
<td>5.12E-02</td>
<td>0.80714</td>
</tr>
<tr>
<td>KL6m surface</td>
<td>1.60E-01</td>
<td>1.19E-01</td>
<td>0.7449</td>
<td>2.16E-02</td>
<td>0.46068</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>4.95E-01</td>
<td>3.90E-01</td>
<td>0.7876</td>
<td>5.67E-02</td>
<td>0.49955</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>4.80E-02</td>
<td>3.26E-02</td>
<td>0.6984</td>
<td>7.06E-02</td>
<td>0.51612</td>
</tr>
<tr>
<td>380 nm</td>
<td>Eod</td>
<td>Ed</td>
<td>( m_{\text{bar} \ d} )</td>
<td>( R = E_u/E_d )</td>
<td>K d</td>
</tr>
<tr>
<td>Algae Reef surface</td>
<td>6.07E-01</td>
<td>5.04E-01</td>
<td>0.8302</td>
<td>2.18E-02</td>
<td>0.3761</td>
</tr>
<tr>
<td>Algae Reef bottom</td>
<td>8.41E-02</td>
<td>6.20E-02</td>
<td>0.7372</td>
<td>5.45E-02</td>
<td>0.43379</td>
</tr>
<tr>
<td>KL6m surface</td>
<td>2.57E-01</td>
<td>1.87E-01</td>
<td>0.7251</td>
<td>3.29E-02</td>
<td>0.28294</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>7.82E-01</td>
<td>6.42E-01</td>
<td>0.821</td>
<td>4.49E-02</td>
<td>0.2644</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>2.22E-01</td>
<td>1.62E-01</td>
<td>0.7264</td>
<td>6.23E-02</td>
<td>0.29202</td>
</tr>
</tbody>
</table>

Although \( E_d \) was not appreciably different at the surface comparing KL6m Reef and Algae Reef, downwelling irradiance reaching the bottom, \( E_{d6m} \), was consistently one order of magnitude higher at KL6m Reef than at Algae Reef, and this effect increased with decreasing wavelength, due to the combined effect of lower \( a_g \) and lower \( \mu_d \) at KL6m Reef relative to Algae Reef (Figs. 6.3, 6.4, Table 6.4).
Figure 6.3. Although modeled $E_d$ at the surface was not very different at Algae Reef compared to KL6m, due to lower $a_g$ and lower $\mu_d$ at the bottom, $E_d$ at the bottom was approximately an order of magnitude higher at KL6m compared to Algae Reef (see Table 6.2).

Because $a_g$ was lower at KL6m Reef than Algae Reef for all sampling dates (2004 – 2007) (for example, $a_g_{330}$, Figure 6.4, Table 6.3), these results for $\mu_d$ for one day in September 2004, where $a_g$ was lower at KL6m Reef, can be considered generally representative for these sites. Sources of error include measurement of $a_p$ and $a_g$ (see Chapter 3), sky conditions, and in situ scattering ($b$).
Figure 6.4. $a_g\,330$ at Algae and KL6m Reefs, surface and bottom, for all sampling dates from 2004 – 2007. $a_g\,330$ was lower at KL6m than Algae Reef, considering surface and bottom samples separately. Dashes represent medians.

Table 6.4. Medians and 25th – 75th percentile ranges for $a_g\,330$ at Algae and KL6m reefs, surface and bottom, for all sampling dates from 2004 – 2007.

<table>
<thead>
<tr>
<th></th>
<th>median</th>
<th>25th – 75th percentile range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae surface</td>
<td>0.313</td>
<td>0.291 – 0.374</td>
</tr>
<tr>
<td>KL6m surface</td>
<td>0.211</td>
<td>0.184 – 0.272</td>
</tr>
<tr>
<td>Algae bottom</td>
<td>0.296</td>
<td>0.266 – 0.364</td>
</tr>
<tr>
<td>KL6m bottom</td>
<td>0.203</td>
<td>0.177 – 0.232</td>
</tr>
</tbody>
</table>

6.5. Conclusions

Higher diffuseness of the light field (lower $\mu_d$) increases the amount of UV irradiance reaching the corals, beyond the increase in scattering with decreasing wavelength according to $\lambda^{-4.32}$ (Kirk 1994). Particle scattering by phytoplankton, detritus or minerals also increases with decreasing wavelength (Gregg 2002). This study shows
that UVR reaching the benthos can be higher at reefs with lower \( a_g \) due to both the lower absorptivity and higher diffuseness of light, and these effects increase with decreasing wavelength. Fisher et al. (2007) reported that lesion recovery in corals, which is a bioindicator of coral condition, was significantly faster at Algae Reef, where \( a_g \), as well as \( a_p \) (absorption due to particulate material, \( a_p = a_t - a_g \) (Table 6.1), are greater than at KL6m reef. Thus, the recovery of corals from physical damage may be enhanced under lower UV conditions.

A typical value for \( \bar{\mu}_d \) at 400 nm for natural waters illuminated by sun and sky is 0.71 (Mobley 1994, p. 551). At lower wavelengths \( \bar{\mu}_d \) would be lower. Thus, to check the accuracy of \( a_{t330nm} / K_{d330nm} \) in estimating \( \bar{\mu}_d \), at 330 nm, one can multiply by approximately a value lower than 0.71, because \( \bar{\mu}_d \) decreases as wavelength decreases. However, because \( a_{t330nm} / K_{d330nm} \) is already lower than modeled \( \bar{\mu}_d \), there is either an error (underestimation) in measuring \( a_{t330nm} \), an error (overestimation) in modeled \( K_{d330nm} \), or an error (overestimation) in modeling \( \bar{\mu}_d \). It is not likely that \( a_p \) has been underestimated, because typically, it is overestimated due to scattering in the cuvette or in the filter pad (see Chapter 3). The error in modeling the apparent optical properties \( K_{d330nm} \) and \( \bar{\mu}_d \), which are dependent upon the angular structure of the light field as well as the components of the water column, therefore may be due to sky conditions.

Thus, differences in actual versus modeled cloud cover could also account for some of the difference between modeled and measured \( \bar{\mu}_d \) (see Table 6.1, \( a_{t330nm} / K_{d330nm} \) compared to \( \bar{\mu}_d \)). Modeled \( \bar{\mu}_d \) is consistently higher than measured \( \bar{\mu}_d \). Modeled \( \bar{\mu}_d \) accounts for sky conditions, while measured \( \bar{\mu}_d \) does not. In the case of increased cloud cover, light is scattered through the atmosphere and the incident light on the ocean
surface is more diffuse under cloudy sky conditions than under clear sky conditions (Gregg 2002, see Fig. 6.5). Cloud cover also alters the spectral distribution of light: cloudy, diffuse sky UV spectra (350-400 nm) represent a greater proportion than clear, diffuse sky UV spectra (20.5%), while cloudy sky red spectra (650-700 nm) represent a smaller proportion than clear sky red spectra (-9.4%) (Fig. 6.6). Frederick et al. (2000) found that monthly integrated broadband UV irradiance usually has peaks in June to July, and that the large variability in UV irradiance reaching the earth’s surface is consistent with changing cloudiness.

Figure 6.5. Depiction of the pathways of irradiance under clear and cloudy skies, and in the oceans. The sizes of the arrows indicate the relative proportions of direct (E_d) and diffuse (E_s) irradiance for clear skies and cloudy skies. Some of the surface irradiance is reflected off the sea surface (1-\rho). These pathways continue into the ocean where an additional diffuse upwelling (E_u) path exists (from Gregg, 2002).
Figure 6.6. Spectral surface irradiance just below the sea surface (after spectral surface reflectance) for clear skies and cloudy skies. The cloudy sky simulation represents the effects of 80 g m\(^{-2}\) liquid water path, which produces about half the total surface solar irradiance as the clear sky model for the same solar zenith angle and atmospheric optical properties (from Gregg 2002).

Because cloudy, diffuse sky conditions present a greater amount of irradiance to the surface than clear, diffuse sky conditions (Gregg 2002), corals at the benthos “see” relatively higher intensity low wavelength, more damaging UVR. Thus, the danger of photo-oxidative stress is potentially greater (Lesser and Farrell 2004) under cloudy, diffuse sky conditions compared to clear, diffuse sky conditions (Fig. 6.6).

In conclusion, the spectral quality of light reaching the benthos on coral reefs is affected by atmospheric variables (clouds, aerosols) as well as by water column properties (pathlength, absorption and scattering by minerals, phytoplankton, and CDOM). Understanding the variables affecting the diffuse nature of light is important in
studying the effects of solar radiation on coral reef biota. Observations of the coincidence of maximum bleaching with maximum solar radiation in the Keys, especially UV radiation, found in my study (Chapters 3, 4, and 5) indicate the necessity of understanding radiative transfer processes, including apparent optical properties such as $\mu_d$.

The cumulative effects of high irradiance over the course of the summer increase coral reef susceptibility to photo-oxidative stress when later summer temperatures peak. Atmospheric and water column effects on the diffuseness of the underwater light field may exacerbate incident solar and temperature stress. Algae Reef, the intact shoreline, higher $a_g$ associated reef, was characterized by higher $a_g$ and $\mu_d$ and lower $E_d$ bottom. Thus, these results agree those presented previously (see Chapters 3, 4 and 5). Diffuseness increases with decreasing wavelength (Kirk 1994). The results in this chapter show that increased diffuseness may cause increase in short wavelength solar radiation reaching the benthos. In conclusion intact shoreline can be an important source of CDOM, protecting coral reefs from photooxidative stress.
Chapter 7. Conclusions and Future Research

7.1. Conclusions

Coral reefs have long been characterized by their remarkable productivity and diversity while thriving in the clearest, most nutrient-poor oceanic regions (e.g., Odum and Odum 1955; Wells 1957). Thus, a major paradox of the response of Florida’s coral reefs to ongoing environmental change is that offshore reefs have declined much faster than inshore reefs (Somerfield et al. 2008).

Coral disease and bleaching are considered among the most important causes of decline in coral populations and percent coral cover on reefs. Mass coral bleaching is so strongly correlated with elevated temperature that NOAA has developed a hotspot bleaching warning system (http://coralreefwatch.noaa.gov/satellite/methodology/methodology.html). Yet the physiological mechanism of bleaching is actually phototoxic-oxidative stress (Lesser 2006). This means that sunlight is required for bleaching to occur. Fitt and Warner (1995) and others have shown that shorter wavelengths of light, either visible or UV, trigger bleaching at lower temperatures than does higher wavelength visible light.

Thus, the underlying goal that prompted my study is to provide evidence that can help to resolve the paradox of why coral populations, in what historically were the best environments, have declined the fastest over the past several decades. My working hypothesis is that CDOM in reef waters can protect corals from the photic component of
photo-oxidative stress that causes mass bleaching, and that human activities have resulted in reduced CDOM concentrations in reef-tract waters.

Major ways that human activities have influenced CDOM distributions in coastal waters is by widespread alteration of watersheds and coastlines, including removal of coastal vegetation and changes in coastal hydrology (e.g., construction of causeways between islands in south Florida). An undeveloped watershed slowly releases its colored (i.e., higher CDOM) freshwater; a developed watershed sheds more and muddier runoff during the rainy season, and minimal runoff during the dry season. This is in contrast with undeveloped shorelines with coastal hammocks and mangroves, which trap sediments coming from both land and offshore, while releasing CDOM with every tidal cycle. While increased CDOM can be photoprotective, sediments, which can smother and block visible light needed for photosynthesis from corals, are not beneficial to coral reefs. Therefore when coastal vegetation is replaced by seawalls and urban or agricultural development, depending upon local weather, coastal waters are alternatively more turbid and more transparent, properties that are stressful for corals and other benthic organisms. Thus, undeveloped and intact shorelines with mangrove and coastal hammocks can support coral reefs by supplying photoprotection via CDOM and reducing smothering and blocking of visible light by sediments.

My study investigated distribution of CDOM in waters of the Florida reef tract. In general, UV-absorbing CDOM was more prevalent on inshore reefs and reefs near intact shorelines, compared to offshore reefs and reefs with developed shorelines. Intact shoreline – associated reefs and inshore reefs were characterized by lower photic stress as illustrated by lower production of UV-absorbing substances in the water column, lower
UVR reaching the benthos, lower rates of CDOM photobleaching and higher percent coral cover compared to developed shoreline – associated reefs and offshore reefs.

Individual findings can be summarized as follows:

1. In reef areas near intact shoreline, where mangroves are a major source of CDOM, absorption due to CDOM \( (a_g) \) decreases going offshore from mangrove coastline to ocean waters beyond the reef. Absorption due to CDOM in the UV \( (a_{g\text{ UV}}) \) is higher at inshore reefs compared to offshore reefs, for example, absorption due to CDOM at 320 nm \( (a_{g\text{ 320}}) \) at offshore reefs is only 64% of that at inshore reefs.

2. CDOM is the major attenuator of UVR: for all reefs sampled, \( a_{g\text{ UV}}/a_{t\text{ UV}} \) ranged from 62% at 380 nm to 91% at 305 nm; over the course of each summer \( a_{g\text{ UV}}/a_{t\text{ UV}} \) decreased, likely due to photobleaching of CDOM.

3. In very shallow waters, less UVR is reaching the bottom at intact shoreline-associated reefs compared to developed shoreline – associated reefs.

4. Considering inshore and offshore reefs together, \( a_{g\text{ UV}} \) is higher in the Lower Keys, which are characterized by larger amounts of mangrove coastline, and Middle Keys, which receive CDOM – rich water inputs from Florida Bay, compared to the Upper Keys.

5. The attenuation coefficient for downwelling irradiance in the UV \( (K_{d\text{ UV}}) \) is higher at inshore reefs compared to offshore reefs, while the difference in \( K_{d\text{ PAR}} \) between inshore and offshore reefs is not as great.
6. Considering each site individually, for the CREMP sites sampled in 2006 and 2007, on a 3-tiered scale of low to high coral cover and low to high $a_g_{320}$, the predominant combination is low % stony coral cover accompanied by low $a_g_{320}$. Percent stony coral cover as well as $a_g_{320}$ were generally higher at inshore reefs compared to offshore reefs.

7. Relative expression of the UV-absorbing MAAs was lower at intact shoreline-associated reefs compared to developed shoreline-associated reefs and tended to be lower at inshore reefs compared to offshore reefs.

8. Considering the Florida Keys by region, relative MAA expression was higher in the Upper Keys compared to the Lower Keys, at the same time $a_g_{320}$ was lower in the Upper Keys compared to the Lower Keys and Middle Keys.

9. Spectral slope, $S$, was higher in offshore reef waters, indicating extensive photobleaching of CDOM, compared to inshore reefs.

10. Diffuseness of the underwater light field increases the probability of light exposure for benthic organisms. Diffuseness was lower at the higher CDOM, intact-shoreline associate reef compared to the developed shoreline-associated reef.

Thus, all of the measured parameters indicate that the inshore reefs, especially those near undeveloped shoreline, are more photo-protected by CDOM than are more developed shoreline and offshore reefs, consistent with my working hypothesis.
The results of this study show that intact shoreline such as mangroves, and other terrestrial sources of CDOM, such as wetlands influencing Florida Bay, play an important role in limiting photo-oxidative stress on Florida Keys reefs. Increasing restrictions on shoreline development to preserve mangrove sources of CDOM to reef-tract waters, and protecting wetlands that through estuaries, bays, and rivers may provide CDOM-rich waters to the reef tract, are an important strategy for reducing photo-oxidative stress and thus increasing resiliency of coral reefs.

The Florida reef tract is well-monitored, but monitoring in itself has not slowed the decline of coral populations. Increased focus on protection of CDOM sources will enhance efforts to protect Florida’s coral reefs, and coral reefs worldwide, from degrading in the face of ocean warming and acidification projected for the future (Hoegh-Guldberg et al. 2007, Baker et al. 2008).

7.2 Future research

To further quantify the role of mangroves and other terrestrial sources of CDOM in protecting coral reefs, controlled lab experiments should continue to study CDOM breakdown rates and processes in response to increasing temperature and acidification. Moreover, ecosystem – based studies should more closely examine the role of CDOM ($a_g$) in coral reef health as expressed by indicators of coral health, such as coral cover, disease and bleaching. Sources of CDOM can be quantified using fluorescence spectroscopy and fluorescence Excitation – Emission Matrices (EEMS) (Moran et al. 1991, Coble 2007).
In addition to local management and monitoring, global networking and monitoring is essential to protecting reefs for the future. Satellite sensors that can measure UVR and CDOM for large spatial areas are planned for future deployment, and algorithms for shallow, reflective coastal waters are continually being improved. The spectral slopes found in this study can be used with existing satellite measurements of PAR irradiance to estimate UVR in these coastal regions, where satellite images are difficult to correct due to bottom reflectance (Lee et al. 1998). With cooperation between optical, physical, and biological oceanographers, current products can be improved and expanded upon, so that, hopefully, the delicate balance of coral reefs and other ocean ecosystems can be maintained.
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Appendices
Appendix A: Map of Florida Keys with waterways, cities, management areas and reefs
Appendix B: Appendix of Important Terms and Abbreviations

(source: http://www.epa.gov/uvnet/glossary.html#totalcolumn)

I. Irradiance - related terms:

Irradiance
The power transferred to a unit area of a surface by radiation from all directions within a hemisphere, measured in watts per square meter (W/m²).

Ultraviolet (UV) / Ultraviolet Radiation (UVR)
A portion of the electromagnetic spectrum with wavelengths shorter than visible light. The sun produces UV, commonly split into three bands: UV-A, UV-B, and UV-C.

Solar UV Index
The solar UV index (UVI) describes the level of solar UV radiation at the Earth’s surface. The values of the index range from zero upward – the higher the index value, the greater the potential for damage to the skin and eye, and the less time it takes for harm to occur. The UV index is computed using forecasted ozone levels, a computer model that relates ozone levels to UV incidence on the ground, forecasted cloud amounts, and the elevation of the forecast cities. Some countries also use ground observations (UNEP 2002).

Spatial and Temporal Variation in UV Exposure
The combination of total ozone and solar zenith angle, which is determined by the geographical position, season and time of the day, can lead to a variety of UV exposure situations (UNEP 2002).

Diffey Weighting
A weighting function that indicates which UV wavelengths are most efficient at burning human skin. When the weighting is multiplied by spectral irradiance and the product is integrated over all wavelengths, the result is diffey-weighted irradiance, a single number indicating the rate at which fair skin will redden.

DUV
Diffey-weighted UV irradiance (watts/m²)

Direct Sun
Refers to a measurement based only on direct radiation from the sun's disk and excluding indirect radiation from the remainder of the sky.
II. Ozone - related terms:

\( \text{O}_3 \) (Ozone)
A molecule consisting of three oxygen atoms. Ozone strongly absorbs short wavelength ultraviolet light and consequently protects life on earth from the damaging effects of this radiation. It is also a very reactive compound, which makes it a harmful air pollutant at the surface. Repeated exposure to ozone can make people more susceptible to respiratory infection and lung inflammation, and can aggravate preexisting respiratory diseases, such as asthma. Sometimes people refer to "good" (stratospheric) ozone and "bad" (surface) ozone.

Ozone layer
That level of the atmosphere which encompasses a peak in ozone concentrations, roughly 12 to 30 km above the surface.

Total Column Ozone
The total amount of ozone in a column of air stretching from the earth's surface to space. More than 90% of the ozone is in the ozone layer at high altitude.

Dobson Unit (DU)
The unit of measure for total ozone or other gases. If you were to take all the ozone in a column of air stretching from the surface of the earth to space, and bring all that ozone to standard temperature (0 Celsius) and pressure (1013.25 millibars, or one atmosphere (atm)), the column would be about 0.3 centimeters thick. Thus, the total ozone would be 0.3 atm-cm, or 300 Dobson Units (DU).

III. Photospectroscopic and optical terms and abbreviations:

\( a_g \) absorption due to CDOM (gelbstoff)
\( a_p \) absorption due to particulate material
\( a_{phi} \) – absorption due to pigmented material or phytoplankton
\( a_w \) absorption due to pure water
\( \mu_d \) - average cosine of downwelling irradiance
\( E \) - irradiance
\( I \) - radiance
\( b \) - scattering
\( K_d \) – attenuation coefficient for downwelling irradiance
\( \phi \) - azimuth angle
\( \Phi \) - radiant flux
\( \omega \) - solid angle
\( \theta \) - zenith angle
[chl] – chlorophyll concentration
CDOM – colored dissolved organic matter
gelbstoff or gilvin – yellow substance, also referred to as CDOM
IV. Biological Response Terms

MAAs - Mycosporine-like Amino Acids - UVR-absorbing compounds with broadband absorption from 310–360 nm (Lesser 2006)

HSP – Heat Shock Proteins - generalized stress response that is evolutionarily conserved; under stressful conditions, HSPs interact with proteins to maintain their conformation and function or in targeting damaged proteins for degradation (Lesser 2004)
About the Author

Lore M. Ayoub received her Bachelor’s degree in Biology from Bloomsburg University in 1982. She attended Lehigh University where she completed a M.S. Degree in Aquatic Ecosystems/Environmental Science, studying the relative contributions of dissolved and particulate material to UV attenuation in temperate lakes. Thereafter she was employed in Bermuda as a scientist and educator.

Her graduate work at the University of South Florida with Dr. Pamela Hallock Muller and Dr. Paula Coble in the College of Marine Science has focused on factors controlling UV attenuation in the Florida Keys, and its influence on coral reef health. Her other projects at USF included population assemblages of fossil foraminifera, literature research on storm water runoff in South Florida, teaching assistantship in Population Ecology and public outreach. She led one scientific field mission using SCUBA for her doctoral research, and received advanced SCUBA certifications including AAUS Scientific Diver and NAUI Nitrox.