Factors Affecting Ultraviolet Exposure in Coastal Waters of the Florida Keys: Effects on Nearshore and Offshore Coral Reef Tracts

By

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Date: ______________

Approved:

Dr. David Hinton, Advisor

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Abstract

We have investigated how the loss of chromophoric dissolved organic matter (CDOM) in the water column due to photobleaching allows for increased penetration of UV radiation near coral reefs in the Florida Keys. Extended exposure to UV may contribute to coral bleaching episodes. CDOM serves as the primary control on UV exposure of corals in this region because it strongly absorbs UV radiation, especially damaging UVB wavelengths. An important fraction of the CDOM pool in Florida Keys coastal waters is transported from Florida Bay, but local CDOM sources including seagrasses, mangroves, and Sargassum colonies may also be substantial. CDOM samples collected along transects near the reefs and from mangrove leaf and Sargassum incubation experiments were exposed to simulated solar radiation for up to 120 hours. Calculated photobleaching rates ($k_{305}$) of CDOM produced by mangrove leaf litter and Sargassum colonies (approx. 0.02 hr$^{-1}$) were an order of magnitude greater than rates measured for the water column samples (0.002 hr$^{-1}$). However, our experiments indicate that photobleaching of CDOM in natural waters near the reefs can still be substantial during summer months and may allow UVB levels at 4 m depth (typical depth of fringing reefs) to increase by as much as 20%. Corals located in shallower waters (2 m) along the reef line may experience up to a 40% increase in UVB exposure due to loss of CDOM.
Introduction

The Role of Chromophoric Dissolved Organic Matter

One of the largest pools of organic carbon in the biosphere is dissolved organic matter (DOM), the magnitude of which is equivalent to terrestrially fixed carbon. Chromophoric dissolved organic matter (CDOM) is a major factor that determines the optical properties of natural waters and directly affects both the availability and the spectral quality of light. Additionally, due to CDOM’s ability to absorb UV wavelengths, it may serve as a protective mechanism for deep water organisms against harmful light impacts (Kowalczuk et al., 2003). CDOM, in combination with phytoplankton pigments made up of mostly chlorophyll, and non-living particles are the main contributors other than the water itself to ocean color. CDOM itself, is a mixture of compounds derived from both plant and animal decomposition, and has both terrestrial and marine origins. In coastal areas, most of the CDOM originates from the organic material in rivers, leached from soils (Coble et al., 2003). CDOM is produced in situ, in the oceans, by the release of organic molecules from organisms as well as phytoplankton decomposition and extraction from bottom sediments (Kowalczuk et al., 2003). Specifically in the Florida Keys a significant source of CDOM are the local mangroves and seagrasses. CDOM is made up of naturally occurring organic compounds, and often has a high reactivity to certain ions in water. CDOM in drinking water sources can react with chlorine added by water treatment plants to form harmful disinfection byproducts. CDOM can also play a role in decreasing the dissolved oxygen concentration in natural waters, leading to a release of nutrients and certain metals from sediments. CDOM can also play a more
beneficial role in natural waters, scavenging trace metals and polyaromatic hydrocarbons (PAHs), binding them, and therefore reducing their bioavailability as well as toxicity to organisms. CDOM also plays a major role in the biogeochemistry of coastal waters through its interactions with UV light. When exposed to sunlight, CDOM is broken down by the UV which then allows for the release of organic compounds that are required for the growth of certain phytoplankton and bacteria. Nitrogen and other essential trace metals may also be released in this process. Dissolved inorganic carbon (carbon monoxide and carbon dioxide) is photoproduced in the breakdown of CDOM by UV, which provides another pathway in carbon cycling in addition to primary production. Lastly, CDOM can act as a protective sunscreen for benthic habitats, by absorbing the damaging UV rays before they reach the benthic habitat depths (Coble et al., 2003).

DOM absorption of sunlight causes various photoreactions affecting its chemical, physical, and biological properties and eventually leads to its degradation (Moran and Zepp, 1997). Sunlight induced degradation of DOM is considered to be a major sink of riverine DOM in the oceans, which plays a significant role within the global biogeochemical carbon cycle. Moran and Zepp (1997) have also shown using size-exclusion chromatography that the absorption of sunlight leads to a decrease in the average nominal molecular weight of DOM.

**The Need for Coral Reef Protection**

CDOM has been identified as the dominant factor in controlling the spectra and intensity of UV-Vis. light penetration to depth (Zepp, 1988). As CDOM is irradiated by UV light, it undergoes photobleaching thereby reducing its ability to absorb UV light. Thus, bleaching of CDOM allows UV to penetrate deeper into the water column. One
effect of increased ultraviolet sunlight penetrating deeper into the water column, is the bleaching of coral reefs. Coral reefs provide ecosystem goods and services to millions of people around the world (Costanza et al., 1997). It is likely that global warming caused by anthropogenic sources has contributed to the extensive coral bleaching that has occurred simultaneously throughout the reef regions of the world (Reaser et al., 2000). Corals provide biodiversity, fisheries, and shoreline protection services that are being depleted with increasing degradation of the reefs. This may also cause the impacts of more localized anthropogenic factors that harm corals to have even greater effects. With global warming, there may be increased UV light and increased warming of the oceans, both of which may cause an increase in the frequency of coral bleaching events. It is necessary to investigate the domestic and international policies regarding coral reefs in order to determine how to maintain these ocean resources and deal with human impacts in the future.

**Current US Coral Reef Legislation**

No coral reef protection bills have ever been passed into law. Some environmental laws pertain to coral reef protection, though none have been created solely to manage, protect, or study corals. Some well known environmental acts, such as the Clean Water Act, and the Coastal Zone Management Act, have specific applications for the management and protection of domestic coral reefs. Executive Order 13089 and the Coral Reef Conservation Act of 2000 are the only domestic coral reef specific legislations created as of today.

The Executive Order 13089 (EO 13089) was signed by Bill Clinton in 1998 and in addition to its mandates, created the Coral Reef Institute, and the Coral Reef Task
Force. EO13089 mandates that “all federal agencies whose actions may affect US coral reef ecosystems shall: (a) identify their actions that may affect U.S. coral reef ecosystems; (b) utilize their programs and authorities to protect and enhance the conditions of such ecosystems; and (c) to the extent permitted by law, ensure that any actions they authorize, fund, or carry out will not degrade the conditions of such ecosystems (Executive Order 13089, 1998).” There are exceptions to this mandate, such as in times of war or national emergency, however for the most part EO 13089 is valid for all agencies at all times.

The order also calls for the federal agencies whose actions do affect coral reef ecosystems to provide for implementations of measures needed to monitor, research, manage, and restore the affected ecosystems, though this mandate is subject to the availability of federal funds for these projects. The Coral Reef Task Force is co-chaired by the Secretaries of the Interior and Commerce (through the administrator of the National Oceanic and Atmospheric Administration (NOAA)). The main goal of the task force is to create a comprehensive program that would research and map coral reefs. Through the task force, the US takes inventory and monitors the corals, and identifies major causes and consequences of coral degradation. The task force also oversees the implementation of coral reef policy and the responsibilities of the agencies as defined in EO 13089 (http://www.coralreef.gov/taskforce/nap/index.html). There are currently 18 voting members of the task force; EPA administrator, Attorney General, Secretaries of Interior, Agriculture, Commerce, Defense, State, Transportation, Director of National Science Foundation, Administrator of USAID, Administrator of NASA, and the Governors of American Samoa, Florida, Guam, Hawaii, Northern Mariana Islands,
Puerto Rico, and the US Virgin Islands. Since its creation in 1998, the task force adopted a National Action Plan to Coral Reef Conservation in 2000 and a National Action Strategy in 2002. The main goal of the National Action Plan is to act as a guide for understanding, protecting, and preserving coral reef ecosystems. The National Coral Reef Institute, established by the same mandate in 1998, has a primary objective of protecting and preserving coral reefs through applied and basic research on coral reef diversity. The National Action Strategy, created in 2002 in accordance with the Coral Reef Conservation Act of 2000, provides a nation-wide status report on implementation of the National Action Plan. It should be noted that EO 13089 has no binding authority, and requires only that federal agencies consider the effects of their actions on coral reef ecosystems.

While there are no other specific policies regarding coral reef protection, there are elements of other marine acts that pertain to the maintenance of coral reefs (http://www.epa.gov/owow/wetlands/guidance/coral.html ). The Rivers and Harbors act of 1899 is still used today in matters concerning navigable waters. This act sets up a permit system for structures and works on domestic navigable waters, which requires consideration of the public interest before permits are awarded. Negative coral reef impacts are generally considered to be against the public interest. The Marine Protection, Research, and Sanctuaries Act of 1972 sets up a permit system for regulation of ocean discharge sites both within and beyond the territorial sea. Permits are awarded for sites that avoid potential damage to coral reef ecosystems, and also take into account transport from the discharge site by currents or storm events. Coral reefs are also considered in both the Coastal Zone Management Act (CZMA) of 1972 and the Clean Water Act of
1977. The permits in each of the previously discussed acts and the Clean Water Act must all be consistent with state management plans as required by the CZMA. These plans are federally approved state plans for managing coastal zones belonging to that specific state. In general, those states that have coral reefs within their coastal zones have included provisions for their protection within their state management plans. According to the CZMA, federal actions affecting the coastal zones must be consistent with the state plans. Lastly, in the Clean Water Act, Coral Reefs are listed as a “special aquatic site” requiring higher level of protection in section 404(b)(1) Guidelines of the CWA. Special Aquatic Sites are recognized by the guidelines as significantly influencing or positively contributing to the general overall environmental health or vitality of the entire ecosystem of a region.

**Current Status of International Coral Reef Policy**

International policy making is extremely difficult today because of barriers to implementation and enforcement. Coral reefs are a global entity and resource, however, and some groups are attempting to acknowledge that. The International Coral Reef Initiative (ICRI) was created in 1994 by the governments of Australia, France, Japan, Jamaica, the Philippines, Sweden, UK, and the U.S. (http://icriforum.org). ICRI emerged out of the recognition that coral reefs and their related ecosystems are facing serious degradation primarily because of anthropogenic stresses. ICRI is based on an informal and voluntary partnership and decisions are made by consensus. This is one main way that developing nations with corals can act as equals with industrialized nations as well as with international environmental and development agencies, scientific associations, the private sector, and non-governmental organizations to decide the best strategies to
conserve the world’s coral reef resources. ICRI has four main objectives. First, for both
governments and international organizations to strengthen commitment and
implementation of programs for coral reef protection at the local, regional, national, and
international levels. The second goal is to integrate coral reef protection into local and
national development and management plans. Thirdly, ICRI seeks to increase policy
implementation as well as research, monitoring, and management of coral reef
ecosystems. The last goal is to coordinate research and monitoring of coral resources on
an international level.

The Convention on Biological Diversity (http://www.biodiv.org) originated at the
1992 Rio Earth Summit where it was signed by 150 nations. It promotes sustainable
development, and has 3 main goals: conservation of biological diversity, sustainable use
of its components, and fair and equitable sharing of the benefits. The ultimate authority
for the convention is the Conference of the Parties; however, it is also reliant on its
scientific body. In 2002 the Convention produced a strategic plan, whose purpose is to
guide its implementation on local, national, and international levels. As a result of the
strategic plan, signing nations to the convention promise to significantly reduce the
current rate of loss of biodiversity at global, national, and local levels. Through the
Jakarta Mandate, the Convention on Biological Diversity focuses on marine and coastal
biodiversity. This mandate concentrates on integrated marine and coastal area
management, sustainable use of living resources, marine and coastal protected areas, and
mariculture and exotic species (Jakarta Mandate). The Convention works with its parties
in order to implement these elements at a local, regional, national, and international level.
The United Nations Environmental Programme (UNEP) Coral Reef Unit is also working for international coral reef policy (http://corals.unep.org/). The Coral Reef Unit works with international partners in order to try to reverse coral reef degradation and increase local, national, and international coral reef conservation and sustainable use. The Coral Reef Unit represents UNEP in the International Coral Reef Action Network (ICRAN), a joint venture by several of the ICRI members aimed at reversing coral reef degradation. The unit works towards building consensus and public awareness on causes for coral reef stress, as well as measures to control them. UNEP, as an intergovernmental organization, aims to work with governments to increase their ability to conserve coral reefs.

**Human Ecology of Coral Reef Policies**

Policy is developed by taking into consideration legislative, administrative, judicial, interest group, and public opinions. Policy making is part science, part policy, and has local, state, regional, national, international implications as well as cross-county, interstate, and international implications. There are three “ecologies” of the ocean, the biophysical ecology which refers to the non-human entities. Corals, fish, marine mammals, marine plant life, all fall within the biophysical ecology of the ocean. The human ecology includes ocean constituents who have interests in and are affected by marine policies. These include ocean users and residents, ocean and coastal industries such as fishing, oil and gas, development, tourism, shipping, etc. Human ecology constituents also include the general public and ocean and coastal interest groups. Lastly, there is the institutional ecology that includes public sector interests in the issues. These
are the legislative, administrative, and judicial branches, of local, state, regional, national, and international governing bodies.

Each type of ecology is involved in coral reef policy making as well (figure 1).

Figure 1: Diagram of Interplay between Human Ecology, Scientific Community, Policy and Management Organizations, and Biophysical Environment for coral reef ecosystems.

The biophysical environment consists of the coral reefs and the surrounding ecosystems, which depend on the coral ecosystems for their existence. The human stakeholders are those groups, individuals, and industries, who have some interest in the status of policies regarding coral reefs. Humans depend on coral reef ecosystems, because the ecosystems provide people with goods and services such as seafood, recreational activities, coastal protection, and cultural and aesthetic benefits (see figure 2) (Moberg and Folke, 1999).
Coral reef existence is integral for the fishing, tourism, and oil and gas industries.

Developers are also extremely interested in coral reef policy because it may impact where development can occur in relation to location of corals, and also may impact what parts of the coastline are safe to develop if they have been protected from erosion by corals.

Non-profit interest groups such as the Coral Reef Alliance, the Global Coral Reef Alliance, and Reef Check are all aiming to raise awareness about the status of corals and how to conserve them. In addition to these stakeholders, ocean residents and users, as well as the general public have interests in coral reef policy. The status of coral reef ecosystems affects many people’s lives because of all of the services they provide, and as a result coral reef policy impacts many people’s lives. The institutional ecology of coral reef ecosystems involves many government agencies, and intergovernmental coalitions.

The Coral Reef Task Force involves many US federal agencies and is headed by NOAA and the Secretary of the Interior. The EPA and USFWS are also individually involved with coral reef policy, in addition to their roles within the task force. International coral policy is headed by the International Coral Reef Initiative, UNEP, the International Coral

<table>
<thead>
<tr>
<th>Goods</th>
<th>Ecological services</th>
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<tr>
<td>Renewable resources</td>
<td>Mining of reefs</td>
</tr>
<tr>
<td>Sea food products</td>
<td>Coral blocks, rubble and sand for building</td>
</tr>
<tr>
<td>Raw materials for medicines</td>
<td>Raw materials for production of lime and cement</td>
</tr>
<tr>
<td>Other raw materials (seaweed and algae for agar, mucin, etc.)</td>
<td>Mineral oil and gas</td>
</tr>
<tr>
<td>Curio and jewellery</td>
<td>–</td>
</tr>
<tr>
<td>Live fish and coral collected for the aquarium trade</td>
<td>–</td>
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</table>

**Figure 2: Goods and services provided by coral reefs (Moberg and Folke, 1999)**

<table>
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</tr>
<tr>
<td>Live fish and coral</td>
<td>–</td>
</tr>
</tbody>
</table>
Reef Action Network, and the Convention on Biological Diversity, all of which aim to bring together as many constituencies as possible, including governments, non-governmental organizations, and scientific bodies to make conclusions on how to manage the global coral reef resources. The US scientific bodies responsible for coral reef research are NOAA, the National Science Foundation, EPA, the National Coral Reef Institute created as a result of EO 13089, the Army Corps of Engineers, and academia.
**Objective & Hypotheses**

This project was designed to investigate the role of photobleaching of CDOM in water samples obtained in the Florida Keys. It has been noted that coral reefs near shore in the Florida Keys region are generally in better health than the fringing reefs (Shank et al., 2006). One possible hypothesis is that the higher inshore CDOM levels protect the corals from damaging extended UV exposure. I hypothesized that bleaching would occur in the water samples, causing a decrease in UV/VIS absorption (and absorption coefficients) with an increase in the amount of irradiation of the samples. Additionally, the fluorescence spectra of the samples were expected to change with increased irradiation. Dissolved organic carbon (DOC) was not expected to have significant changes with irradiation.

**Methods**

Florida Keys water samples from were obtained varying from nearshore patch reefs to an offshore reef tract (figure 3). Samples were named LPALM (nearshore patch reef), FIU 26x (near Hawk Channel), FIU 262 (Mid-Hawk Channel), FIU 263 (offshore reef tract).
The samples were filtered using a 0.2µm filter in order to remove any particles and bacteria. The resulting samples were then split into five 30ml sub-samples. The sub-samples were subjected to simulated solar irradiation using a Suntest Solar Simulator (750W/m²) in quartz test tubes for varying amounts of time, ranging from 0 hours to 120 hours. The samples originating from closer to shore were irradiated for less time because they were darker, 0 hours to 48 hours; the samples originating further out in “blue water” were irradiated for longer periods of time. It was permissible to irradiate samples for different amounts of time because the results will be used to calculate half-lives for each sample. A second set of sub-samples from one sample was also subjected to 24 hours of
irradiation over a course of 3 days time, in order to simulate the diurnal variation of sunlight exposure.

UV-visible spectra were measured in duplicate for the initial water sample and irradiated samples for each cut-off wavelength. Samples were analyzed over the wavelength range of 200 - 900 nm on a Perkin Elmer λ35 UV-visible Spectroscopy System in 10.00 cm quartz cells. Variations in the absorbance spectra have been used to determine presence and abundance of different source contributions to CDOM in aquatic systems (McKnight, 2000). Absorption coefficients $a_\lambda$ were calculated as:

$$a_\lambda = 2.303 \frac{A_\lambda}{l}$$

where $A_\lambda$ is the measured absorbance at wavelength $\lambda$, and $l$ is the pathlength of the quartz cell in meters (Stramska, 2000, Kirk, 1994). Spectral slope coefficients were calculated by fitting absorption coefficients to the equation

$$a_\lambda = a_{\lambda_0} \exp(- S(\lambda - \lambda_0))$$

where $a_{\lambda_0}$ is the absorption coefficient at $\lambda_0$ (i.e., 290 nm) and $S$ is the spectral slope coefficient (Zepp and Schlotzhauer 1981; Blough and Green 1995), using a non-linear least squares method (Sigma Stat, SPSS Inc.). Slopes were calculated for the 280 - 400 nm spectral region.

Specifications for the ISA-SPEX Fluorolog 3 Spectrofluorometer used for the fluorescence spectra measurements were: resolution 0.2 nm; accuracy 0.5 nm; speed 150nm/s; range 0-1300 nm. For DOC analyses accuracy was ensured by comparison of sample analyses to calibration curves generated using American Chemical Society certified potassium hydrogen phthalate (Fisher Scientific Inc., C$_8$H$_5$O$_4$K). Standard
curves were run on the same day as instrumental analyses analysis. Triplicate injections were made for each standard dilution and results were compared with records of previous machine response to ensure accurate results. Few experimental precedents or criteria exist for judging the representativeness or comparability of the diffuse attenuation coefficients measured at the various field sites. Representativeness and comparability were judged by comparisons with the few data in the UV spectral region that were previously obtained in Florida Keys waters. Also, these factors will be evaluated by the investigators and by subsequent research conducted by the investigators or by peers in this research area.

All sample containers used were washed and triple rinsed with 18.2 MΩ or better Milli-Q water. Each sample set contained a system blank consisting of organic free permanganate distilled Milli-Q water produced in our laboratory by standard methods described in Quantitative Analysis, 4th edition, Pierce, Sawyer and Haenisch, 1958. This organic free distilled water (ODW) was analyzed for total organic carbon using a Shimadzu TOC-5050A.

**Results and Discussion**

CDOM concentrations are impossible to measure directly since its exact composition remains unknown, and therefore concentrations cannot be measured in terms of number of molecules per volume of solution. Instead, CDOM concentration is measured based on its intensity of light absorption using a UV/VIS spectrometer. Absorption varies as a function of wavelength and CDOM source. Figures 4, 5, 6, and 7 show the absorption profiles for unbleached samples as it varied with wavelength.
Figure 4: UV and Visible absorption profile for unbleached sample from nearshore patch reef.

Figure 5: UV and Visible absorption profile for unbleached near-land Hawk Channel sample.
Figure 6: UV and Visible absorption profile for unbleached Hawk Channel sample.

Figure 7: UV and Visible absorption profile for unbleached offshore reef tract sample.
The capacity for UV absorbance decreases with increasing distance from shore, as can be seen by the decreasing initial UV absorbance values for each of the sub-samples (table 1).

**Table 1: Unbleached absorbance values for various wavelengths in UV spectrum for each of the samples**

<table>
<thead>
<tr>
<th>Unbleached Absorbance (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>λ</strong> (nm)</td>
</tr>
<tr>
<td>305</td>
</tr>
<tr>
<td>325</td>
</tr>
<tr>
<td>340</td>
</tr>
<tr>
<td>380</td>
</tr>
<tr>
<td>440</td>
</tr>
</tbody>
</table>

Using the absorption profiles for each sample at each time (T₀, T₁, T₂, and Dark Control corresponding to amount of exposure hours) equation (1) was used to calculate the absorption coefficients for each of the sub-samples. The absorbance coefficients were then plotted using a non-linear least squares method (Sigma Stat, SPSS Inc.) as a function of the number of hours exposed to simulated UV light, in order to obtain a k value for each sub-sample, where k is a measure of the bleaching rate for each sub-sample. This was calculated using the equation derived from equation (2),

\[ a(t) = a_{\lambda 0} \exp(-kt) \]  

(3)

Where \( a(t) \) was the absorbance at any time, t, and \( a_{\lambda 0} \) was the absorbance coefficient at a given wavelength, \( \lambda \). Using the fitted non-linear regressions shown in figures 8, 9, 10, and 11 the parameters for these equations were calculated for four key UV wavelengths. Half-life was also calculated using the equation,

\[ t_{1/2} = \frac{-\ln(0.5)}{k} \]  

(4)

This equation was used because CDOM bleaching follows first order degradation kinetics. Table 1 shows the results from these calculations.
Figure 8: CDOM Photobleaching at nearshore patch reef.

Figure 9: CDOM Photobleaching in near-land Hawk Channel
Figure 10: CDOM Photobleaching in Mid-Hawk Channel

Figure 11: CDOM Photobleaching in offshore reef tract
Table 2: Summary of results for determination of rate constant, $k$, and half-life, $t_{1/2}$, for each sub-sample at key UV wavelengths.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>LPALM</th>
<th>FIU 26x</th>
<th>FIU 262</th>
<th>FIU 263</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$</td>
<td>$t_{1/2}$ (hours)</td>
<td>$k$</td>
<td>$t_{1/2}$ (hours)</td>
</tr>
<tr>
<td>305</td>
<td>0.0089</td>
<td>77.88</td>
<td>0.0071</td>
<td>97.63</td>
</tr>
<tr>
<td>325</td>
<td>0.0117</td>
<td>59.24</td>
<td>0.0083</td>
<td>83.51</td>
</tr>
<tr>
<td>340</td>
<td>0.0123</td>
<td>56.35</td>
<td>0.0085</td>
<td>81.55</td>
</tr>
<tr>
<td>380</td>
<td>0.0131</td>
<td>52.91</td>
<td>0.0075</td>
<td>92.42</td>
</tr>
</tbody>
</table>

The data in table 2 show that the half-life of CDOM increases as the distance from shore increases. This is important because the half-life is an indicator of the absorbance capacity of the CDOM. Longer half-lives imply that the CDOM is able to absorb a greater percentage of its original absorbance capacity for a longer period of time. The longer half-lives, however, are associated with the CDOM farther from shore which had significantly decreased initial absorbance from the CDOM closer to shore. Because the FIU 263 had so little initial absorbance, the increased half-life is less of an advantage than if that half-life were associated with nearer-to-shore CDOM. The half-lives for the CDOM collected can also be compared to the half-lives of three seagrasses measured in coastal Florida waters (table 3).

Table 3: Half-Life results for Florida Keys natural water samples compared to half-lives for CDOM resulting from seagrasses and mangrove leaves

<table>
<thead>
<tr>
<th></th>
<th>Photobleaching Half-Life (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPALM (Nearshore Patch Reef)</td>
<td>78 ($\lambda=305$nm)</td>
</tr>
<tr>
<td>FIU 26x (Near-Hawk Channel)</td>
<td>98 ($\lambda=305$nm)</td>
</tr>
<tr>
<td>FIU 262 (Mid-Hawk Channel)</td>
<td>105 ($\lambda=305$nm)</td>
</tr>
<tr>
<td>FIU 263 (Offshore reef tract)</td>
<td>385 ($\lambda=305$nm)</td>
</tr>
<tr>
<td>Thalassia testudinum</td>
<td>20-40 (Stabinau et al., 2004)</td>
</tr>
<tr>
<td>Sargassum</td>
<td>25-30 (Shank et al., 2006)</td>
</tr>
<tr>
<td>Red Mangrove Leaves</td>
<td>30-60 (Shank et al., 2006)</td>
</tr>
</tbody>
</table>
CDOM production and photobleaching of *Thalassia* testudinum (Stabenau et al., 2004), sargassum (Shank et al., 2006), and red mangrove leaves (Shank et al., 2006) was measured in coastal Florida water, similar to the water used in this study.

The diffuse attenuation coefficient, $k_d$, with units of inverse meters, was then calculated as 90% of the initial absorbance coefficient value at 305nm and 70% of the initial value at 380nm. Diffuse attenuation, $k_d$, was then used to calculate an average rate of photobleaching ($k_{avg}$) at a specified depth, $z$ (Hu et al., 2002):

$$k_{avg} = k * (1 - \exp(-k_d z)) * k_d^{-1} z^{-1}$$

(5)

From the $k_{avg}$ values calculated in this equation, overall bleaching for one and two months was estimated for both the nearshore patch reef and offshore reef tract using equation (3). Table 4 shows the results of these calculations.

**Table 4: Summary of results for overall increase in UV penetration at 4 meters after 1 and 2 months of photobleaching.**

<table>
<thead>
<tr>
<th></th>
<th>UVB Increase (305nm)</th>
<th>UVA Increase (380nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Patch Reef</td>
<td>Reef Tract</td>
</tr>
<tr>
<td>1 month</td>
<td>10%</td>
<td>7%</td>
</tr>
<tr>
<td>2 months</td>
<td>18%</td>
<td>13%</td>
</tr>
</tbody>
</table>

While the photobleaching rates for the natural water samples used in this study were much lower than the freshly leached CDOM from mangroves/seagrasses, the photobleaching of natural water CDOM can still account for ~20% increase in UVB (305nm) exposure at 4m depth in the summer months. Additionally, photobleaching can cause up to 40% increase in UVA (380nm) exposure at 4m depth in the summer months for some areas.

The effect of diurnal variation on photobleaching was tested by exposing one LPALM sample to simulated UV light for 24 hours straight and one LPALM sample for
24 hours following an 8 hours “on” 16 hours “off” schedule. Figure 12 and table 5 show the results of this investigation.

![Graph: Nighttime Impacts on CDOM Photobleaching](image)

**Figure 12:** Simulated UV exposure for 24 straight hours versus 8 hours “on” 16 hours “off” exposure for 24 hours.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>T0 (unbleached)</th>
<th>Nighttime Simulation (24 hours)</th>
<th>24 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>3.525</td>
<td>3.042</td>
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Table 5: Comparison of absorbance values after 24 hours straight UV exposure versus 24 hours exposure incorporating nighttime darkness for near shore patch reef sample

As can be seen from the data, the absorption values for the simulated nighttime sample were consistently higher (less bleached) than the sample that was exposed for 24 hours.
straight. This is significant because the majority of research studying CDOM photobleaching is performed using straight exposure without accounting for lack of exposure during the night time. This data shows that it may be advantageous to take nighttime dark hours into consideration because straight exposure may overestimate the amount of photobleaching that can occur in that time period.

**Conclusion**

**CDOM and Coastal Management**

In addition to sedimentation, pollution, and bacterial infection, bleaching can impact large areas of a reef with limited recovery, and may be initiated by various factors such as temperature and salinity extremes, as well as UV light. Photobleaching of CDOM and transport of near-shore water out over the reefs may play a key role in controlling UV penetration to the reef surface (Anderson et al., 2001). Additionally, climatic factors such as regional shifts in precipitation frequency and intensity over the Everglades, can strongly affect the amounts of CDOM that enter Hawk Channel from Florida Bay. This study suggests that even in summer months, there can be significantly deeper UV penetration into the water column with up to a 20% increase in UVB (305nm) exposure at 4m and up to 40% increase in UVA (380nm) exposure at 4m. The overall photobleaching for natural waters is lower than freshly leached seagrasses and mangroves; however it can still play a large role in UV exposure at lower depths and potentially in increased UV exposure of corals. Increasing our knowledge about spatial and seasonal distribution of CDOM in the Florida Keys would help to manage and regulate coastal environments and coral reef ecosystems.
References


6. “Executive Order 13089”
   http://www.gsa.gov/Portal/gsa/ep/contentView.do?pageTypeId=8199&channelId=-13339&P=PLAE&contentId=16567&contentType=GSA_BASIC


