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UV Exposure of Coral Assemblages in the Florida Keys

by

Richard G. Zepp

Ecosystems Research Division
U.S. Environmental Protection Agency
960 College Station Road
Athens, GA 30605-2700

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Notice

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Foreword

The overall degradation of coral reefs, measured by declining coral abundance and species diversity as well as increases in macroalgae and reef skeletal erosion, has been documented in the Florida Keys and elsewhere around the world. A widely-recognized aspect of the deterioration of coral reefs is the phenomenon of coral bleaching. Coral bleaching may be the symptom of coral reef degradation that is most closely linked to climate change. Records of coral bleaching from 1870 to the present indicate that the severity, locality, and frequency have reached unprecedented levels. Only three bleaching events were reported between 1876 and 1979, compared to more than 60 bleaching episodes from 1980 to 1993. Most recently, the El Niño Southern Oscillation (ENSO) conditions during 1997-98 induced worldwide bleaching from the Western Atlantic to the Great Barrier Reef. EPA's Global Change Research Program is addressing potential vulnerabilities due to interactive components of global change that could adversely affect coral reef ecosystems including: (1) climate variability and change; (2) changes in UV radiation; and (3) land use change. This research is designed to complement other EPA research on coastal environment processes, improvements in environmental indicators of coastal conditions, coastal monitoring designs, and assessments that document U.S. conditions and trends in the coastal ocean. Targeted research and assessment efforts supported by the program will support the development of coral reef ecosystem management and protection strategies in the context of a varying and changing climate.

Bleaching, through interactions with other factors such as sedimentation, pollution, and bacterial infection, can contribute to the destruction of large areas of a reef with limited recovery, and it may be induced by a variety of stressors ranging from exposure to unusually warm temperatures, salinity, and solar radiation. Recent research has implicated both the UVR (280 – 400 nm) and PAR (400-700 nm) components of solar radiation in various responses of coral reefs to global change. Changes in solar UV reaching the coral reefs have been caused by human alterations of atmospheric composition such as depletion of the ozone layer. In addition, changes in the composition of the water over the reefs can have important effects on the penetration of UV and visible light to the reef surface. Such changes can be caused by shifts in runoff of UV-absorbing substances from land, clarification of the water under doldrum conditions associated with global warming and changes in organisms that live near coral reefs that produce sunlight-absorbing substances. This report provides a review of past work that has been conducted on light exposure of coral reefs, in particular in the UV region. The report then describes a case study of factors that are affecting UV exposure of the coral reefs in the Florida Keys. The intended audience of this report is coral ecologists, optical oceanographers and managers and EPA environmental scientists and ecologists who must routinely analyze and estimate stressors for ecological or human health exposure assessments.

Rosemarie C. Russo, Ph.D.
Director
Ecosystems Research Division
Athens, Georgia

Abstract

Recent studies have indicated that solar radiation can be a significant stressor of coral assemblages in tropical and subtropical marine environments. Here the scientific literature related to the interactions of solar radiation with coral reefs is reviewed, with emphasis on harmful effects of solar UV radiation (UVR). Results of a case study of corals' UV exposure in the Florida Keys also are presented in the report. UV exposure was quantified using diffuse attenuation coefficients that were determined using downwelling vertical profiles of UV and visible radiation from sites located at the Upper, Middle and Lower Keys and the Dry Tortugas. For comparison, absorption and fluorescence spectra of the filtered water samples from these sites were measured. Absorption and diffuse attenuation coefficients were highly correlated in the UV-B (290-315 nm) spectral region and ratios of absorption to diffuse attenuation coefficients were > 0.9 throughout this spectral region. Absorption coefficients in the 300 to 500-nm spectral region could be closely described by a nonlinear exponential function. These results indicated that the penetration of solar UV into waters over the coral reefs in the Florida Keys is controlled by the chromophoric component of dissolved organic matter (CDOM) in the water. Analyses of the dependence of underwater UV irradiance on changes in atmospheric ozone or in the UV attenuation coefficients of the water over the reefs indicate that: (1) the dependence on ozone or UV attenuation coefficients can be quantified using radiation amplification factors (RAF); RAFs can be computed using a power relationship for direct UV damage to DNA or for other UV damage to the photosynthetic system of the zooxanthellae associated with corals; (3) UV damage of both types is more sensitive to changes in water UV attenuation coefficients than total ozone, especially damage to the photosynthetic system; (4) RAFs for direct DNA damage to corals caused by changes in ozone are reduced by UV light attenuation in the waters overlying the reefs.

Continuous measurements of solar UV-B irradiance (305 nm) at a location close to the reef tract (Sombrero Tower) demonstrated that diffuse attenuation coefficients undergo large diurnal and seasonal variations in response to fluctuating CDOM concentrations that are linked to currents and CDOM transformations. Other results further indicated that light exposure in the waters around the Florida Keys strongly varies with time and location. Generally, diffuse attenuation and absorption coefficients increased sharply along south-to-north transects from the deep bluewaters of the Florida Straits into Hawk Channel, the shallow coastal shelf region between the reef tract and the Keys. The largest change occurred over a narrow region that represented the interface between the green-yellow waters in Hawk Channel and the blue Atlantic water. Analyses of the results obtained at the deep stations just south of the coral reefs also indicated that the depth dependence of both the light and temperature differs greatly between the warm summer months and cold winter months. We found that the upper ocean water close to the coral reefs was generally much more opaque to UVR and photosynthetically active radiation (PAR) during the cold winter months than during the summer. During the summer, stratification of the water results in clarification of the waters over the coral reefs and much greater UV and PAR exposure of the reefs. This effect is attributable in part to UV-induced decomposition of the CDOM in the water over the reefs. These results suggest that the extensive stratification which occurs under El Niño conditions may be greatly increasing exposure of the reefs to UV and PAR, thus exacerbating corals bleaching. Other research during the case study indicated that decomposing phytoplankton detritus and decaying litter from seagrasses and mangroves are the major sources of UV-absorbing substances over the coral reefs in the Florida Keys. Management strategies designed to protect seagrasses and mangroves should also play an important role in reducing coral reef exposure to harmful effects of solar radiation.

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1. Background

Several recent reports have summarized the potential nature and consequences of global change on coastal areas and marine resources, including coral assemblages (Boesch et al. 2000; Scavia et al. 2002). Potential changes may occur in: (1) ocean temperature, freshwater inflow, coastal storms, sea level change, and ocean circulation; (2) shorelines, developed areas, coastal wetlands, estuaries, coral reef ecosystems, ocean margin ecosystems and fisheries' resources. These reports discuss adaptation and coping strategies for shorelines, wetlands, mangroves, estuaries, coral ecosystems and fisheries resources. Additional reviews of this area can be found in the Intergovernmental Panel on Climate Change, Third Assessment report (IPCC, 2001) and in program descriptions related to material flux and "human dimensions" of change being addressed by the Land Ocean Interactions in the Coastal Zone Program element of the International Geosphere Biosphere Program.

1.1 Coral Bleaching: Impacts of Warming and Light

Photosynthetic coral symbionts, members of the dinoflagellate genus *Symbiodinium*, provide both color and energy to a wide variety of coral taxa. When these symbionts (zooxanthellae), or their pigments, are expelled or lost from the host coral tissues, the white color of the coral skeleton emerges, leaving a bleached appearance. Bleaching also can involve direct degradation of the pigments in the zooxanthellae. The descriptive term 'bleaching' reflects a breakdown of the symbiosis. Records of coral bleaching from 1870 to the present indicate that the severity, locality, and frequency have reached unprecedented levels (D'Elia et al., 1991; Glynn, 1993) Coral bleaching may be the symptom of coral reef degradation that is most closely linked to climate change (Hoegh-Guldberg, 1999). Although bleaching has been correlated with increased temperatures, many studies have concluded that light exposure may also be implicated as a stressor producing additive or synergistic effects (Shick et al. 1996). Research on the effects of solar radiation have examined photosynthetically active radiation (PAR, 400 - 700 nm spectral range) and ultraviolet radiation (UVR). UV-B radiation (280 - 315 nm spectral range) and UV-A radiation (315 - 400 nm spectral range) are two important components of UVR.

Several possible causal mechanisms can account for interactive effects of temperature and solar radiation in bleaching. One possible mechanism that has received much recent attention considers that warmer temperatures contribute to light-induced bleaching by interfering with the complex photoinduced electron transfer processes that occur in photosynthetic fixation of CO_2 (Jones et al. 1998, Hoegh-Guldberg 1999). As a consequence, reactive oxygen species (ROS) are produced that cause cellular damage if not immediately removed. This effect is exacerbated by increased PAR or UVR exposure that introduces more light energy and further increase production of ROS. These stresses combine to create cellular damage and expulsion of the zooxanthellae symbionts (bleaching).

Other mechanisms are possible for the combined effect of temperature and light on bleaching, especially when UV radiation is involved (Shick et al. 1996, Vincent and Neale 2000, Moran and Zepp 2000, Anderson et al. 2002). For example, UV-B radiation can directly damage DNA and both UV-A and UV-B radiation can directly induce the formation of damaging ROS in cell tissues. Bleaching of pigmented cells is a common effect of UV radiation (Vincent and Neale 2000). Observed interactions between UV and increased temperature could potentially involve reduced production of UV-protective substances by the cells (Shick et al. 1996), increased or reduced efficiency in enzymatic repair of DNA damage with increased temperature (Pang and Hays 1991, Li et al. 2002), or reduced production of cellular antioxidants that protect sensitive cellular constituents from ROS. Wavelength studies of light-induced damage to corals are not widely available, but several studies have indicated that UVR plays an important role in bleaching (Gleason and Wellington 1993, Drollet et al. 1994, 1995, Fitt and Warner 1995, Shick et al. 1996, Glynn 1996, Gleason 2001, Anderson et al. 2001) and in photosynthesis inhibition (Lesser and Lewis 1996; Lesser 2000). A few studies have shown that UV-B radiation does not readily bleach certain species of corals, presumably because they are well protected by mycosporine-like amino acids (Fitt and Warner 1995, Shick et al. 1996, Lesser 2000).

Other indirect pathways involving interactions of warming and light may impact corals' health. Coral larvae avoid UV radiation (Gleason 2003) and thus increased UV exposure could adversely affect the efficiency of decolonization of coral reefs during spawning events. Moreover, atmospheric inputs of iron have been proposed to contribute to coral bleaching (Barber 2001) and the biological availability of iron in the sea is enhanced by exposure to solar UV radiation (see Zepp 2002 for a recent review). Warmer temperatures and UV exposure also interactively affect microbial populations in the sea (Moran and Zepp, 2000) possibly including microorganisms that are involved in coral diseases. UV exposure and warmer temperatures can enhance the biological availability of refractory forms of organic carbon and nitrogen, thus possibly impacting nutrient cycling dynamics in coral reefs. Finally, changes in atmospheric and oceanic composition caused by global climate change can result in significant changes in the exposure of coral reefs to UVR and PAR.

1.2. Interactions of Climate Change and Light in the Ocean

Coral reefs are located in tropical and subtropical oceans that are exposed to the most intense solar radiation on Earth (Shick et al. 1996, Herman et al., 1996, Madronich et al. 1998). Stratospheric ozone depletion has enhanced UV-B radiation with minimal effects on UV-A (315- 400 nm) radiation and PAR. However, these effects have been most pronounced in mid- and high-latitude regions of the Earth and changes in the ozone layer over the tropics has been minimal (Shick et al. 1996, Herman et al., 1996, Madronich et al. 1998). Although international action has been taken to restore the ozone layer by limiting releases of ozone-depleting compounds, recovery of the ozone layer to pre-1980 ("unperturbed") levels may require up to 50 years (WMO 1998). Changes in cloud cover and haze can affect the level of solar radiation reaching the Earth's surface. Future trends in these effects are uncertain (WMO 1998, Hartman 2002), although recent data indicate that it has been getting less cloudy in the tropics (Wielicki et al. 2002).

The exposure of coral assemblages to UV radiation depends not only on the UV irradiance at the sea surface, but also on attenuation of the UV radiation as it passes through the air-sea interface and then downwells through the water (Haeder et al. 2003; Kerr et al. 2003; Zepp et al. 2003a). The penetration is highly variable (Kirk, 1994; Degrandpre et al., 1996), ranging from meters in coastal regions to tens of meters in the open ocean. To further complicate matters, UV penetration at a given location varies with time, especially in coastal areas that are heavily impacted by runoff from land (Degrandpre et al., 1996; Morris and Hargreaves, 1997; Vodacek et al., 1997). This variability is attributable to changes in the composition of the water. Water itself is quite transparent to UV-B radiation, but UV-absorbing organic matter in most natural waters, especially the colored (chromophoric) dissolved organic matter (CDOM), strongly absorbs UV radiation. CDOM has also been referred to as "gelbstoffe" or "yellow substance," "gilvin," and "humic substances." Attenuation coefficients of many types of ocean water in the UV region can be computed from concentrations of CDOM (Degrandpre et al., 1996; Siegel and Michaels 1996; Vodacek et al., 1997). The intense color and UV attenuation of CDOM is attributable to light absorption by a chemically complex and poorly-characterized mixture of anionic organic oligoelectrolytes known to contain phenolic moieties and exhibit surface active properties. Changes in the concentration of CDOM are driven not only by variations in its input, but also to the photochemical bleaching and photochemically-enhanced microbial degradation of the CDOM (Morris and Hargreaves, 1997; Vodacek et al., 1997; Moran and Zepp 1997; Miller and Moran, 1997).

Several parameters are used to quantify and model the transmittance of light through sea water at a particular wavelength (λ). For a region of uniform composition in the sea the transmittance can be described in terms of a diffuse attenuation coefficient, K_d (λ) (Kirk 1994; Siegel and Michaels 1996; Smith and Baker 1981, Vodacek et al. 1997). The diffuse attenuation coefficients are calculated from underwater UV measurements using eq. 1.

$$E_d(\lambda,z) = E_d(\lambda,0)\, e^{-K_d(\lambda)\, z} \qquad (1)$$

Where $E_d(\lambda,z)$ is the spectral irradiance at wavelength λ and depth z, $E_d(\lambda,0)$ is the spectral irradiance immediately below the water surface, and $K_d(\lambda)$ is the diffuse attenuation coefficient of the water at wavelength λ. Because the irradiance immediately beneath the surface can be related to that reaching the surface (e.g., using equations that describe reflective loss and refraction of light at the air-sea interface), eq. 1 is of great importance in quantitatively relating the irradiance reaching the sea surface to underwater solar spectral irradiance reaching the surface of a coral reef. Under normal conditions the magnitude of $K_d(\lambda)$ can change somewhat with increasing depth due to changes in the geometry of the light field, but these changes are quite small in the UV region where a large fraction of the irradiance is derived from the sky. In addition to these experimental approaches, recent research has resulted in the development of a variety of numerical models that can simulate changes in spectral irradiance with increasing ocean depth; these have been reviewed in some detail by several authors (Kirk 1994; Mobley 1994; Mobley et al. 1993). These models use inherent optical properties for absorption and scattering of light in seawater in their computations.

Absorption coefficients $a(\lambda)$ of ocean water samples are computed using eq. 2:

$$a(\lambda) = 2.303\, A(\lambda) / l \qquad (2)$$

Where $A(\lambda)$ is the absorbance of the filtered water sample measured in UV-visible spectrophotometer and l is the pathlength of the cell (usually expressed in meters) used for the absorbance measurement. Absorption coefficients, scattering coefficients, and attenuation coefficients (the sum of absorption and scattering coefficients) can be used to model the transmittance of solar radiation into the sea.

Underwater measurements to determine K_d indicate that shorter wavelength UV light is attenuated most rapidly, and that the rate of attenuation decreases with increasing wavelength. Values for K_d not only vary with wavelength, but exhibit wide variation across marine environments. Coastal and estuarine marine systems typically have high K_d (i.e., limited light penetration), while open ocean waters have low K_d. Coral reefs generally live in regions with K_d values that fall in the range of open ocean waters, such that reduction of UV-B irradiance to 1% of surface values can be over 20 meters (clear sea water) compared to 2-3 meters for a typical coastal system (with suspended sediments and dissolved organic matter). Attenuation in the UV-B region is generally higher than that for PAR. For example, at a depth of 20 meters in the clearest open ocean water (e.g., Sargasso Sea), UV-B irradiance (305 nm) is attenuated to 1.8% of the surface value (Smith and Baker 1981) whereas PAR is attenuated to only 15% of a surface (Smith et al. 1989).

Various global environmental changes can impact UV exposure of coral reefs through effects on the composition of the water. Climate and land use change affect the movement of UV-attenuating dissolved and particulate substances from land into water. Such substances, particularly CDOM, control the penetration of UV-B into many aquatic environments. Microorganisms that are exposed to UV-B radiation can develop cellular UV-protective substances such as mycosporine-like amino acids that absorb in the UV region (Shick and Dunlap 2002). Such organisms or detritus derived from them can contribute significantly to UV attenuation in ecosystems that have low concentrations of dissolved organic carbon (DOC). Observed seasonal changes have provided evidence for the important influence of climatic change on UV penetration into freshwaters and the ocean. Droughts, for example, reduce terrestrial inputs of CDOM and sediments into aquatic environments. In contrast, increased precipitation may reduce UV penetration by enhancing runoff. Shifts in soil moisture content and related changes in oxygen content affect the microbial production of soil humic substances and thus can alter inputs of this important source of CDOM in near coastal regions. Global changes may influence the growth of phytoplankton, seagrasses, and mangroves that provide UV- and PAR-absorbing compounds and control light penetration into the sea water over coral reefs. Moreover, global warming, through changes in atmospheric circulation, precipitation patterns, temperature, and length of warm seasons, can affect stratification and vertical mixing dynamics in freshwaters and the sea. Stratification can result in increased UV penetration and exposure in the upper water column, a phenomenon that is driven in part by UV-induced decomposition of UV-absorbing substances in the surface water. Reductions in oceanic primary productivity over the past decade have been attributed to increased stratification of the upper ocean and this effect may be caused in part by increased UV penetration.

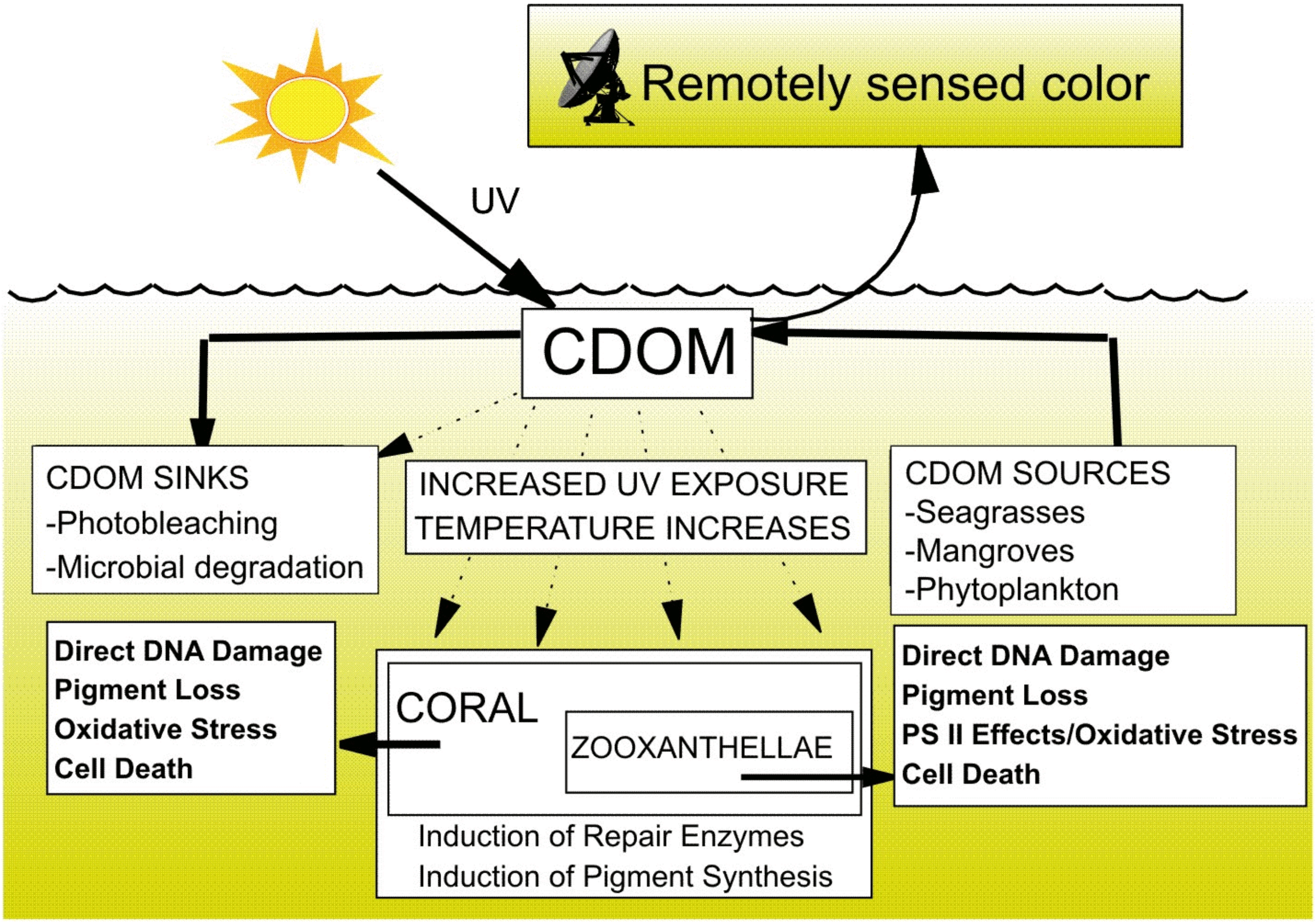
The interactions of bacteria, organic matter, temperature and UV changes are complex and it is impossible at this point to predict how climate warming might affect UV penetration to coral reef surfaces. However, recent observations have shown that the warm upper layers of freshwaters and the ocean that develop under stratified conditions are generally much more UV transparent than deeper, cooler waters. Increased stratification of the water column, often a consequence of 'doldrum' conditions brought on by El Niño events, has been proposed to result in clarification and increased light penetration into sea water, especially in the UV spectrum (Wellington and Gleason 1993, Shick et al.1996, Gleason 2001, Anderson et al. 2001).

In addition to its important role in attenuating UV-B radiation, the CDOM also strongly absorbs solar radiation in the visible spectral region (Kirk, 1994) and thus interferes with the remote sensing of ocean color. Ocean color measurements have been used to estimate marine productivity. Analyses of remote sensing data have shown that CDOM makes an important contribution to ocean color in the eastern tropical Atlantic (Monger et al., 1997), the English Channel (Hochman et al., 1995), the Middle Atlantic Bight (Hoge et al., 1995) and the global ocean (Siegel et al. 2002). On the mid-shelf of the southeastern United States CDOM absorbs 50 - 90% of the incident sunlight in the violet and blue regions (at 412 and 433 nm), depending on the season (Nelson and Guarda 1995); plankton and particulate detrital material absorb the remainder. Thus, research efforts are underway to develop robust algorithms for retrieval of CDOM spectra for correct interpretation of remotely sensed ocean color data in coastal environments (Lee et al., 1994, Blough and Green, 1995; Hoge et al 1995, Hoge and Lyon, 1996, Monger et al., 1997). These algorithms are applied to the analysis of the observed reflectance of sunlight from the upper ocean at selected wavelengths in the visible and near-infrared. Reflectance from coastal regions was measured during a seven-year period during the 1980s by the Nimbus-7 Coastal Zone Color Scanner (CZCS). More recently, the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) started operation in 1998 (Hooker et al., 1993). SeaWiFS collects data at 412 and 490 nm, wavelengths where CDOM strongly absorbs, and thus it has proved to be a useful tool for estimating CDOM absorption coefficients in the ocean. In addition, other techniques such as hyperspectral remote sensing, which can record several hundred spectral image bands at once, may also provide useful information for estimation of CDOM concentrations. These data, coupled with relationships that link CDOM optical parameters in the visible and UV region, can potentially be used to estimate spatiotemporal patterns of the penetration of UV radiation into seawaters over coral reefs.

1.3. Conceptual Model for Interactions of Climate Change, Light and Coral Assemblages

A conceptual model (Figure 1) summarizes the discussions in this Background section. It is hypothesized that increasing sea surface temperatures can result in thermal stratification at many locales. This could result in increased photobleaching of chromophoric dissolved organic matter (CDOM). As the CDOM photobleaches, the UVR and PAR penetration should increase. If coral reefs concurrently experience increased light exposure and warmer seawater temperatures, then the potential for light induced damage in both coral and symbiotic zooxanthellae increases. Factors that contribute to protecting the coral from such damages include pigment protection, induction of mycosporine amino acids, and the induction of DNA repair enzymes. If a significant increase in DNA damage and damage to the photosynthetic apparatus of the zooxanthellae is incurred, then it may be an additive stressor on the corals. Recent research indicates that warming sea surface temperatures can reduce the ability of photosynthetic systems in zooxanthellae to withstand the damaging effects of increased light exposure on the proteins and DNA. In the balance of this report, a case study of the factors affecting corals UV exposure in the Florida Keys is presented to test the hypotheses about light exposure that are presented in the conceptual model. Finally, the various sources and sinks of substances that control light penetration are discussed.

Figure 1. Conceptual model for interactions of climate change, light and coral assemblages.



2. UV Exposure in the Florida Keys

In Section 1 various studies were reviewed that have implicated both the UVR (280 – 400 nm) and PAR (400-700 nm) components of solar radiation in responses of coral reefs to global change. In this section we consider factors that contribute to the exposure of corals to solar radiation, with emphasis on recent results from the Florida Keys (Figure 2). Our research in the Keys examined the geographic, inter-annual, seasonal and diurnal variation in penetration of solar UV and PAR radiation into the ocean waters close to the coral reefs. Results of these studies indicate that variations in the optical properties of the water caused by changes in water composition have pronounced effects on UV exposure. We provide new information about the nature and dynamics of the substances in the Florida Keys water that control UVR and PAR penetration. Our research included measurements of downwelling vertical profiles of UV and visible radiation that were obtained at sites located at the Upper, Middle and Lower Keys and the Dry Tortugas. Absorption spectra of the filtered water samples from these sites also were measured. In addition, we obtained continuous observations of underwater UV-B (305 nm) radiation at a SeaKeys tower (Sombrero) that provided useful insights into the diurnal and seasonal variations of UV penetration that can be directly compared to other meteorological parameters that are measured at this location. Finally, we conducted field and laboratory studies to help elucidate the effects of changes in temperature and solar irradiance on the sources and sinks of light-absorbing substances in the waters over the coral reefs.

2.1. Solar UV Radiation Over the Florida Keys

Solar UV radiation reaching the ocean surface is influenced by changes in solar altitude, cloud cover, aerosols, and, in the case of UV-B radiation, by atmospheric ozone. As illustrated by the data in Figure 3 for 2000-2003, globally-averaged atmospheric ozone in the latitude band that includes the Florida Keys fluctuates between its maximum value during the summer to its minimum during winter (NASA data obtained from the TOMS Web site at http://jwocky.gsfc.nasa.gov). Model calculations by Madronich and co-workers at the National Center for Atmospheric Research (Figure 4), indicate that there was no significant increase in erythemal UV over the Lower Florida Keys during the 1979 - 1992 period. (Computed results obtained from the NCAR Web site http://www.acd.ucar.edu/TUV/). Changes in erythemal (sunburning) UV closely track changes in UV-B radiation. As discussed earlier in this report, these model results are consistent with observations of atmospheric ozone and UV-B radiation during the 1980's and 1990's. Large increases in UV-B occurred over high- and mid-latitudes, due to depletion of atmospheric ozone, but changes in ozone over the tropics and sub-tropics were minimal. Computed spectral irradiance using the TUV model for the Looe Key coral reef and for the Florida Everglades agreed closely with irradiance measurements obtained at the Everglades site of the EPA UV network (Figure 5) (obtained at the EPA UV network Web site http://www.epa.gov/uvnet/).

Observations at the Mote Marine Laboratory, Summerland Key, FL during 2002 - 2003 illustrate the seasonal changes in UV-B and UVR reaching the ground during 2002 - 2003 (Figure 6). The data were obtained using Yankee Environmental Systems UVB and UVA pyranometers. The region measured by the Yankee UVB instrument falls in the 280 - 320 nm range.The UVA instrument actually measures UVR; because UV-A irradiance strongly dominates UVR the irradiance measured by the "UVA" pyranometer is close to that in the UV-A band. Both regions of UV vary seasonally with the highest values in summer and the lowest in winter. The seasonal changes are driven mainly by the decrease in solar altitude during the winter. The ratio of UV-B to UVR increased 15-20 % during the winter at this location, due in part to the thinning of atmospheric ozone, during this season. The reduction in atmospheric ozone during winter tends to increase UV-B irradiance, but has minimal effects on UVR. The envelopes of these sinusoidal curves are described by data obtained under clear skies. Attenuation by clouds and haze dropped the UV irradiance below the envelopes.

Figure 2. Map illustrating locations of sites used in this study.

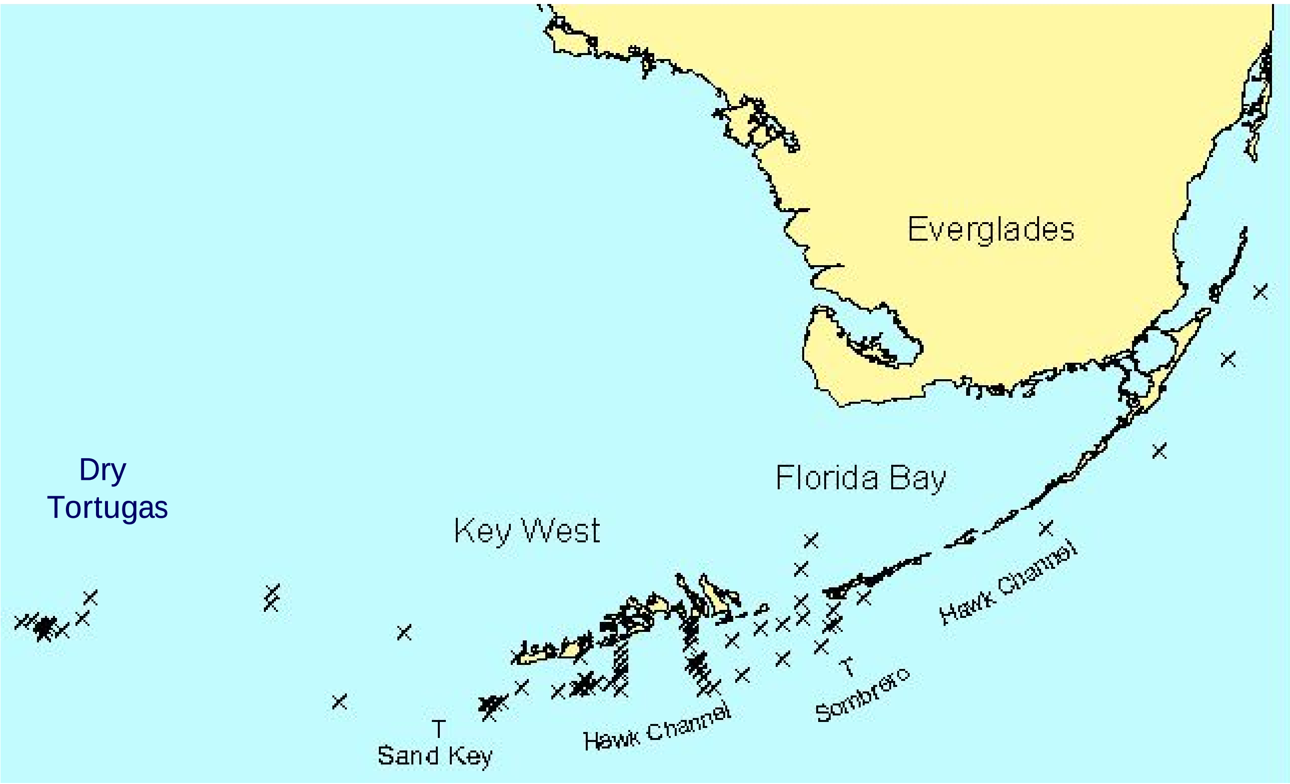


Figure 3. Seasonal changes in monthly averaged atmospheric ozone over the latitude band in the Northern Hemisphere that includes the Florida Keys (latitude 20 °N - 25 °N). Ozone data were measured during January 2000 to September 2003 by the NASA/Goddard Space Flight Center Total Ozone Mapping Spectrometer (TOMS). See http://jwocky.gsfc.nasa.gov for data sets.

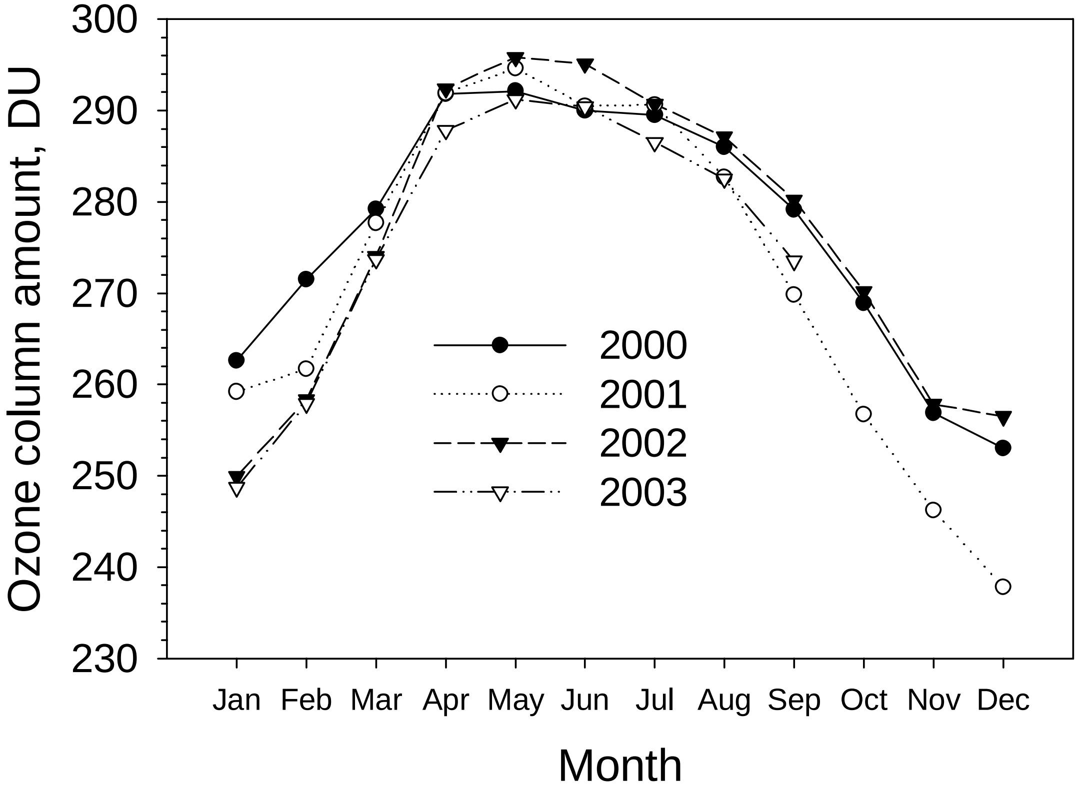


Figure 4. Model calculations of monthly averaged erythemal UV over the Lower Florida Keys (24.5 °N, 81.9 °W) during the 1979 - 1992 period. Calculations were made by Madronich and co-workers at the National Center for Atmospheric Research(Computed results obtained from the NCAR Web site http://www.acd.ucar.edu/TUV/).

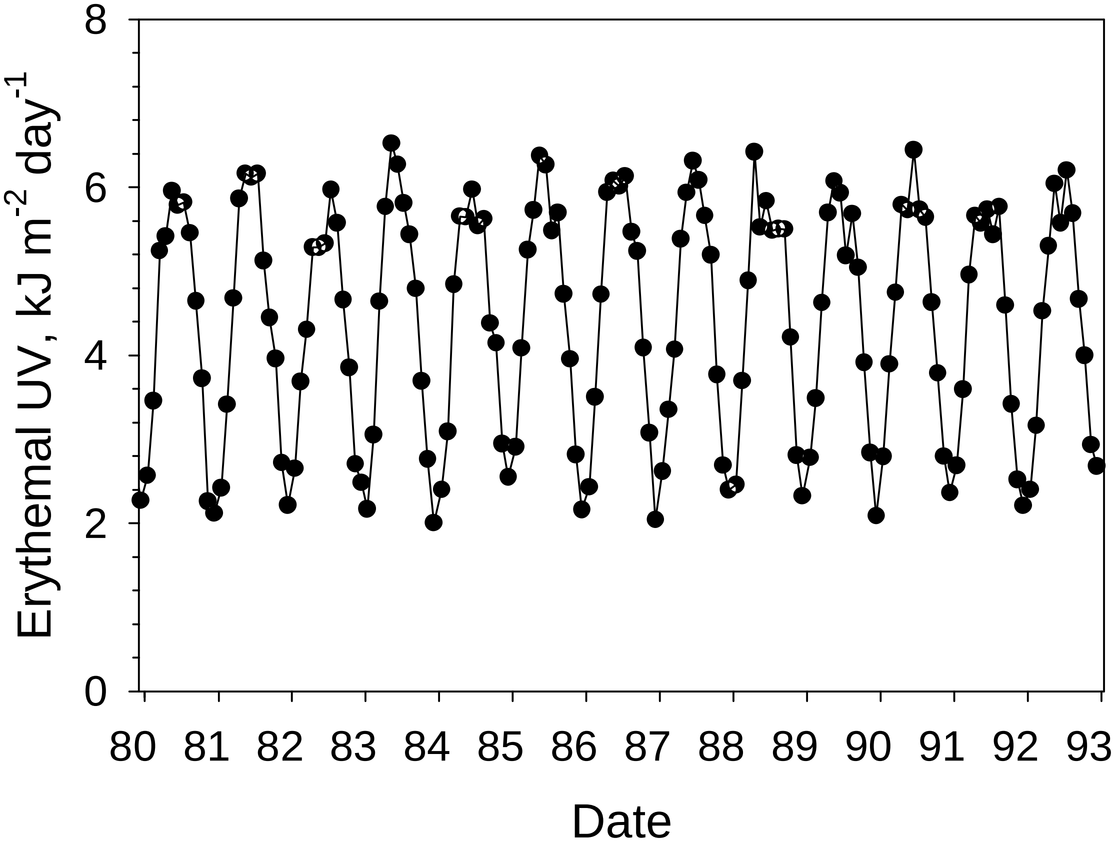


Figure 5. Comparison of model calculations of solar UV irradiance on July 21, 2001 for Looe Key Reef and the Everglades National Park with data observed on July 21, 2001 at the Everglades National Park EPA UV-Net site. Calculations were made using the TUV model that was developed by Madronich and co-workers at the National Center for Atmospheric Research (model is available from the NCAR Web site http://www.acd.ucar.edu/TUV/).

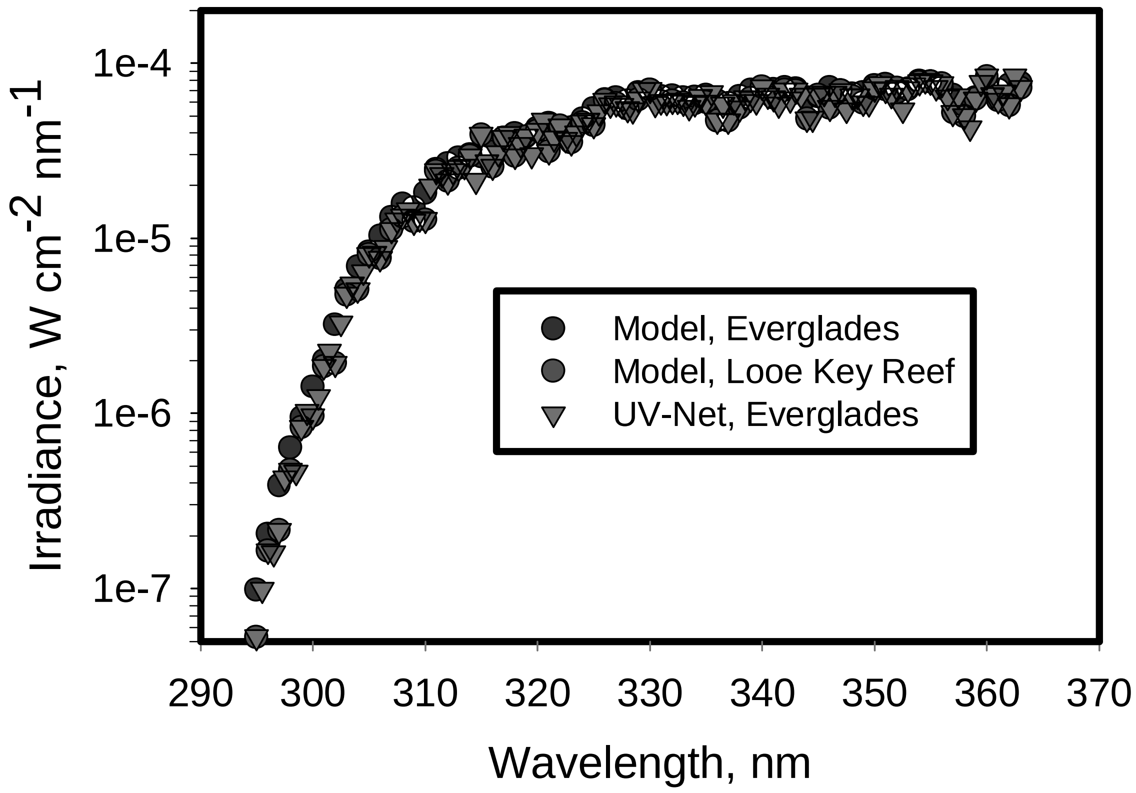
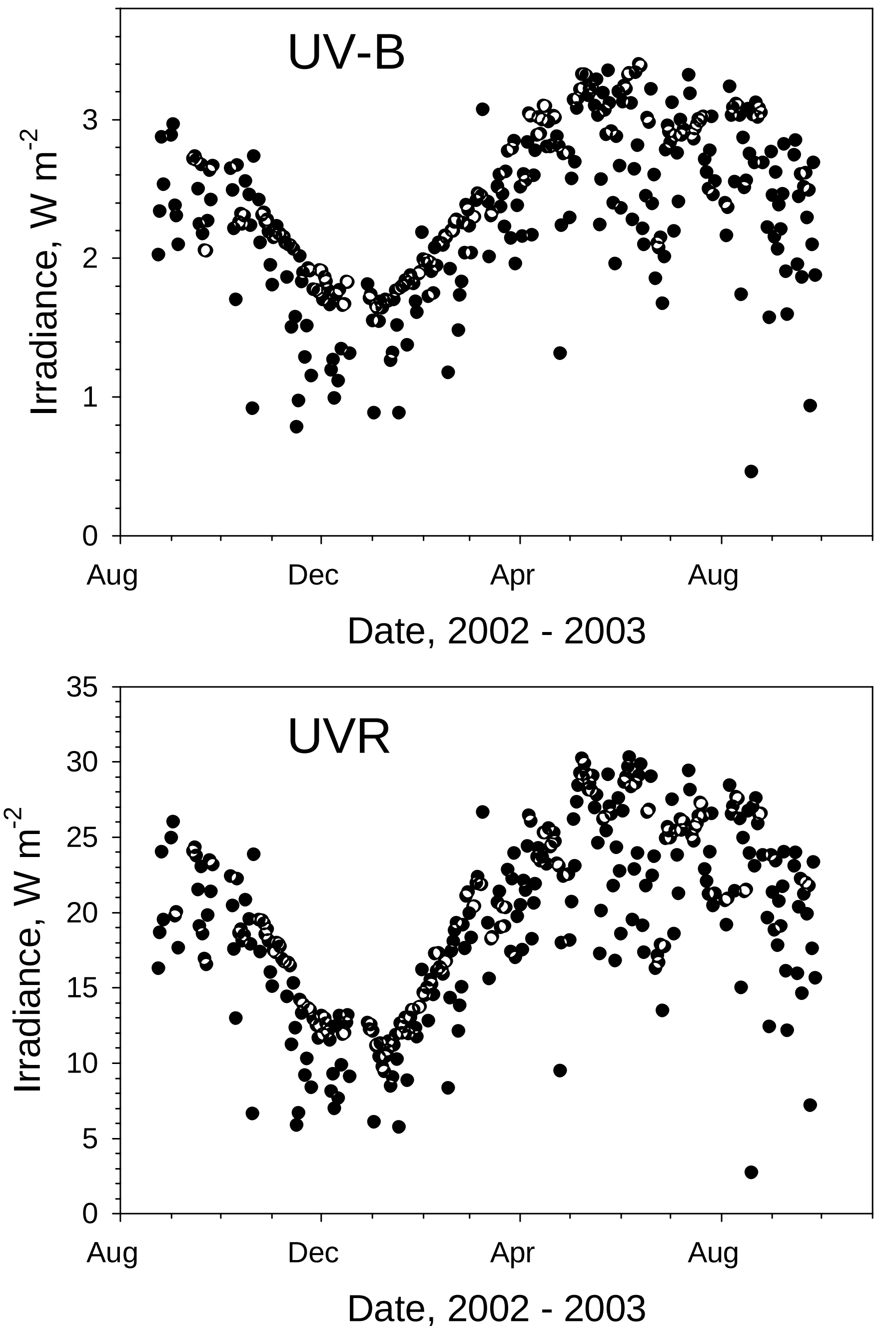


Figure 6. Average daily UV-B and UVR at the Mote Marine Laboratory in the Lower Keys (latitude 24.5 °N, longitude 81.6 °W) during 2002 - 2003. The data were measured by Yankee Environmental Systems UVB and UVA pyranometers at one-minute intervals.



2.2. Optical Properties of Florida Keys Waters: CDOM Control of UVR Penetration

Depth profiles of underwater irradiance were measured on cruises by the RV Anderson and on short trips from a base at Mote Marine Laboratory, Summerland Key, FL. The sampling sites were located throughout the Florida Keys with emphasis on stations that were located in the Lower Keys (Figure 2). Downwelling irradiance measurements and upwelling radiance measurements were obtained primarily using Satlantic OCP-100 and Satlantic Free Fall MicroPro profiling instruments. The free falling velocity of the MicroPro during these casts was typically 0.3-0.4 m/s, which permitted irradiance acquisition at depth intervals of 5-7 cm, ideal for the turbid coastal shelf waters (Hawk Channel) near the Florida Keys reefs. Also, profiling was conducted by K. Patterson using a Biospherical PUV instrument equipped with 305, 320, 340, 380 and PAR channels (Patterson 2000). Diffuse attenuation coefficients were computed using eq. 1 and the irradiance values from the underwater depth profiles in the UVR and visible spectral region located at the reefs, outside the reefs in deep oligotrophic waters, and in the coastal shelf region between land and the reefs. Many of the stations coincided with sites that are part of the Southeast Environmental Research Center (SERC), Florida International University's Water Quality Monitoring Network (see http://serc.fiu.edu/wqmnetwork/) which regularly characterizes water chemistry parameters. Our instrument also concurrently logged the changes in temperature with depth in the water.

The results of these studies indicated that, in the near surface regions near the reefs, the irradiance generally decreased exponentially with increasing depth, as expected. (Figure 7). The results further indicated that UV light attenuation varied greatly from one location to another (Figure 7). To learn more about the nature of the light-absorbing substances in the ocean water around the Florida Keys, we also measured the absorption coefficients for filtered water samples (passed through 0.2 μm polycarbonate membranes) that were collected at the stations where the depth profiling took place. Figure 8 provides a comparison of the diffuse attenuation coefficients and absorption coefficients in the UV-B spectral region (305 nm) for various stations located around the Florida Keys. The close correlation between these two coefficients shows that the dissolved substances in the water generally control the penetration of UV-B radiation. These results are consistent with other recent studies in ocean waters which indicate that, in the UVR spectral region, CDOM is generally the most important determinant of Kd. The wavelength dependence of the absorption coefficients can be used to help infer the nature of the UV-absorbing substances in the water. The UV-visible spectra of seawater samples often can be described by an exponential equation such as $a_s = a_{so} \exp(-S(\lambda - \lambda_o))$, where a_{so} is the absorption coefficient at λ_o (i.e., 290 nm) and S is the spectral slope coefficient (Zepp and Schlotzhauer 1981; Blough and Green 1995). The observed spectral slope coefficients in Florida Keys waters were in the same range as those assigned in other studies to CDOM in the water (Blough and Green 1995; Blough and Del Vecchio 2002). These results are consistent with other recent studies in ocean waters (see Section 1) which indicate that, in the UVR spectral region, CDOM is generally the most important determinant of $K_d(\lambda)$.

Fluorescence data from the Florida Keys waters were also consistent with the hypothesis that CDOM controls UVR attenuation. Because fluorescent functional groups are incorporated into CDOM, measurements of the nature and concentrations of CDOM have been based on its fluorescence spectra and intensity (Coble 1996; Blough and Del Vecchio 2002; Zepp et al. 2003b). In this study, diffuse attenuation coefficients in the UV region (340 nm) correlated with concurrently measured CDOM fluorescence in a transect near Looe Key (Figure 9). The fluorescence was measured using a WET Labs, Inc. CDOM Flash Lamp Fluorometer.

Although dissolved substances play the dominant role in attenuating UV-B radiation in the waters around the Florida Keys, it is clear that other substances can play an important role in light attenuation in the UV-A and PAR region. For example, comparisons between the K_d and absorption coefficient spectra for the turbid mid-Hawk Channel region showed that the K_d values in the long-wavelength and blue region (340-443 nm) were typically considerably larger than the absorption coefficients of the dissolved substances in the water (Figure 10). It is likely that these differences are caused by suspended particles in the shallow Hawk Channel waters. Particles, such as re-suspended bottom sediments and particulate organic matter, also can reduce UVR penetration by absorption and scattering.

Figure 7. Depth profiles for UV-B (305 nm) irradiance at several locations in the Florida Keys. The irradiance at various depths [$E_d(z)$] was normalized to the irradiance just below the water surface [$E_d(0)$] to better compare the relative changes in the irradiance at the various sites.

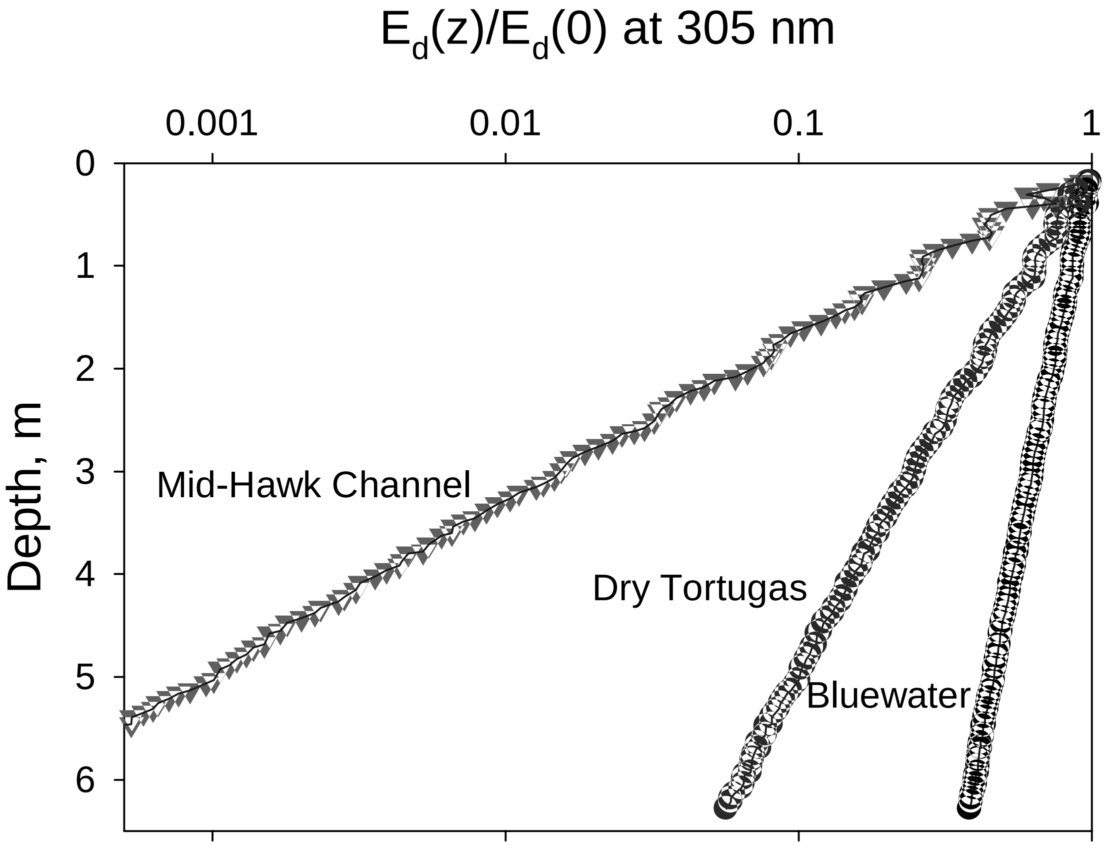
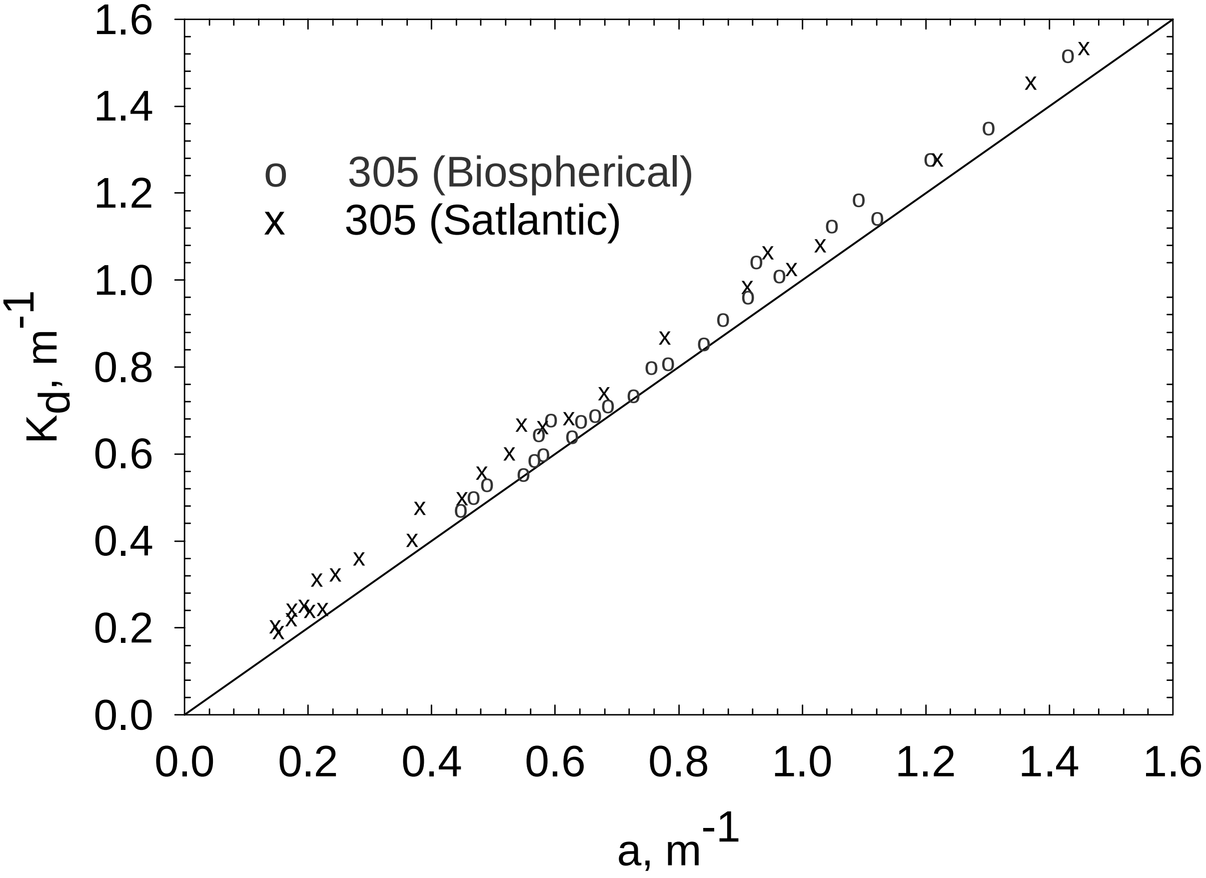


Figure 8. Comparison of diffuse attenuation coefficients and absorption coefficients for filtered water samples obtained at sites in the Florida Keys. The close correlation indicates that CDOM controls UV-B penetration.



2.3. Geographic and Current-induced Change in UV Penetration

The results shown in Figure 8 demonstrate the great variability in diffuse attenuation and absorption coefficients in the UV-B spectral band that we observed at various sites around the Florida Keys. This is further illustrated by the change in absorption spectra that we observed along south-to-north transects from the oligotrophic Atlantic Ocean waters south of reefs in the Lower Keys to the shallow coastal-shelf waters in Hawk Channel (Figure 11). Generally, the absorption of the water increased sharply along these transects, and the largest change often occurred over a narrow region that represented the interface between the green-yellow waters in Hawk Channel and the blue Atlantic water. The increase in UV absorption was accompanied by an increase in CDOM fluorescence along the south-to-north transects.

The tidal movement of the more-opaque Hawk Channel waters over the reefs can cause very large diurnal changes in UV-B penetration at the reefs. This diurnal effect is demonstrated by the change in K_d values for 305 nm light during mid-August. The K_d values were computed from the irradiance data observed using sensors mounted on the Sombrero Tower, a SEAKEYS/C-MAN station in the Florida Keys (Figure 12). The highest values of K_d corresponded to low tide when the more opaque waters of Hawk Channel were transported out over the reef line.

2.4. Seasonal Changes and Stratification Effects

Seasonal changes in K_d values for 305-nm light followed an interesting pattern during the 2002 El Niño year (Figure 13). A 30-day moving average was used to smooth short term fluctuations. The water at the reef tract became more UV-B transparent over the summer and well into the fall. In December with the arrival of the first major cold front, the water rapidly became more opaque to UV-B radiation. The cause of this rapid change is not known, but other results that are discussed below suggest that it was attributable in part to a major breakdown in stratification of the ocean water south of the reefs.

Whatever the cause, these changes in K_d had major effects on underwater UV exposure. Figure 14 illustrates the impact of such changes in K_d values on underwater UV exposure. Because there is an exponential relationship between the diffuse attenuation coefficient and UV transmission, increases in UV exposure can amplify K_d changes. This amplification is discussed in Section 2.5. Irradiance vs. depth profiles were measured at deep sites located south of the coral reefs in the Florida Keys (Figure 15). During most of the time the water from these deep sites is transported over the reefs. Hence, seasonal changes in the surface waters of these deep sites are an important determinant of the light exposure of the reefs. As shown in Figure 15, the depth dependence of both the light as well as temperature differs greatly between the warm summer months and cold winter months. The upper ocean water is generally much colder and more opaque to UVR during the cold winter months than during the summer.

The temperature in the upper ocean was nearly uniform and the depth dependence of the downwelling irradiance was close to exponential during the winter (Figure 15). However, a much more complex depth dependence of temperature and light developed during the warm summer months. The depth dependence of both the temperature and irradiance profiles exhibited a sharp change in slope at a depth of 30 – 40 meters. Analysis of the data in Figure 15 indicated that diffuse attenuation coefficient of the warm water in the upper ocean was 3.2 times lower than that of the deep, cooler water. During high tide and other periods of major bluewater incursions over the Hawk Channel region, the K_d values for the water over the coral reefs were close to those of the warm surface seawater. The K_d value for the deep water was close to that observed for the surface seawater and water over the reefs at this location during the winter. As shown in Figure 14, a 3-fold decrease in the K_d value can result in over an order of magnitude increase in UV light exposure at a depth of 4 meters, a common depth for the coral reefs in that area.

Figure 9. Comparison of diffuse attenuation coefficients in the UV region (340 nm) with fluorescence measured by a Wetlabs CDOM fluorometer.

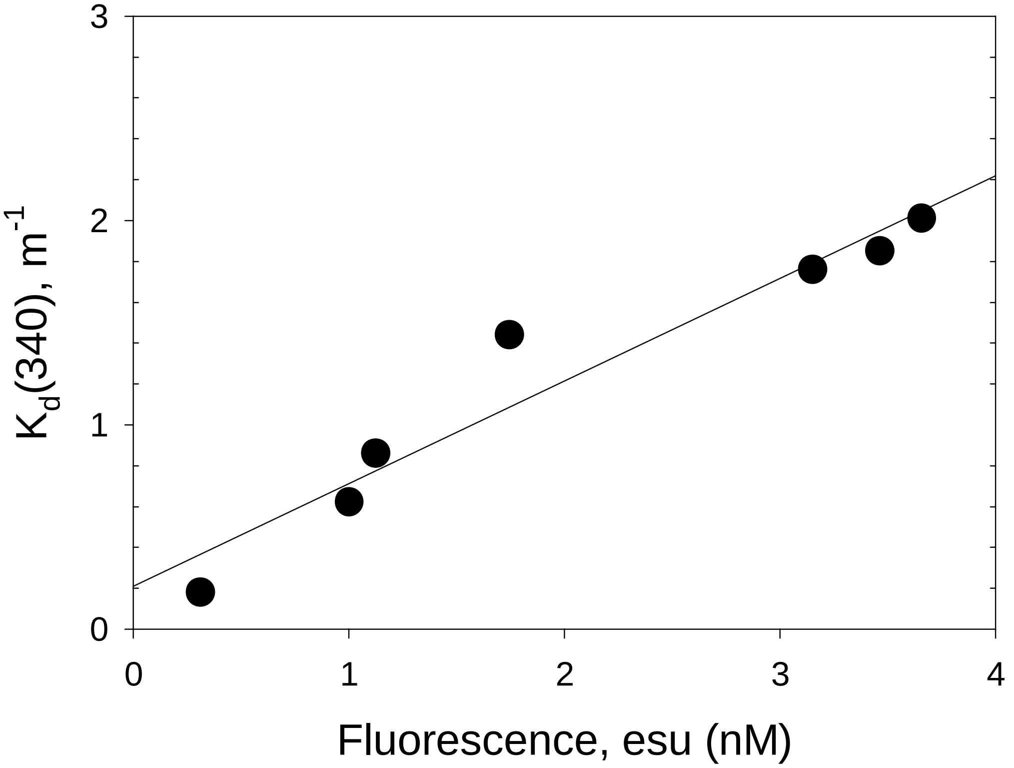


Figure 10. Diffuse attenuation coefficient spectra compared to absorption spectra for mid-Hawk Channel, the coastal, shelf region between land and the reefs in the Florida Keys. The comparison shows that absorption and scattering by suspended particles make a significant contribution to UV-A and PAR light attenuation, but CDOM controls UV-B attenuation.

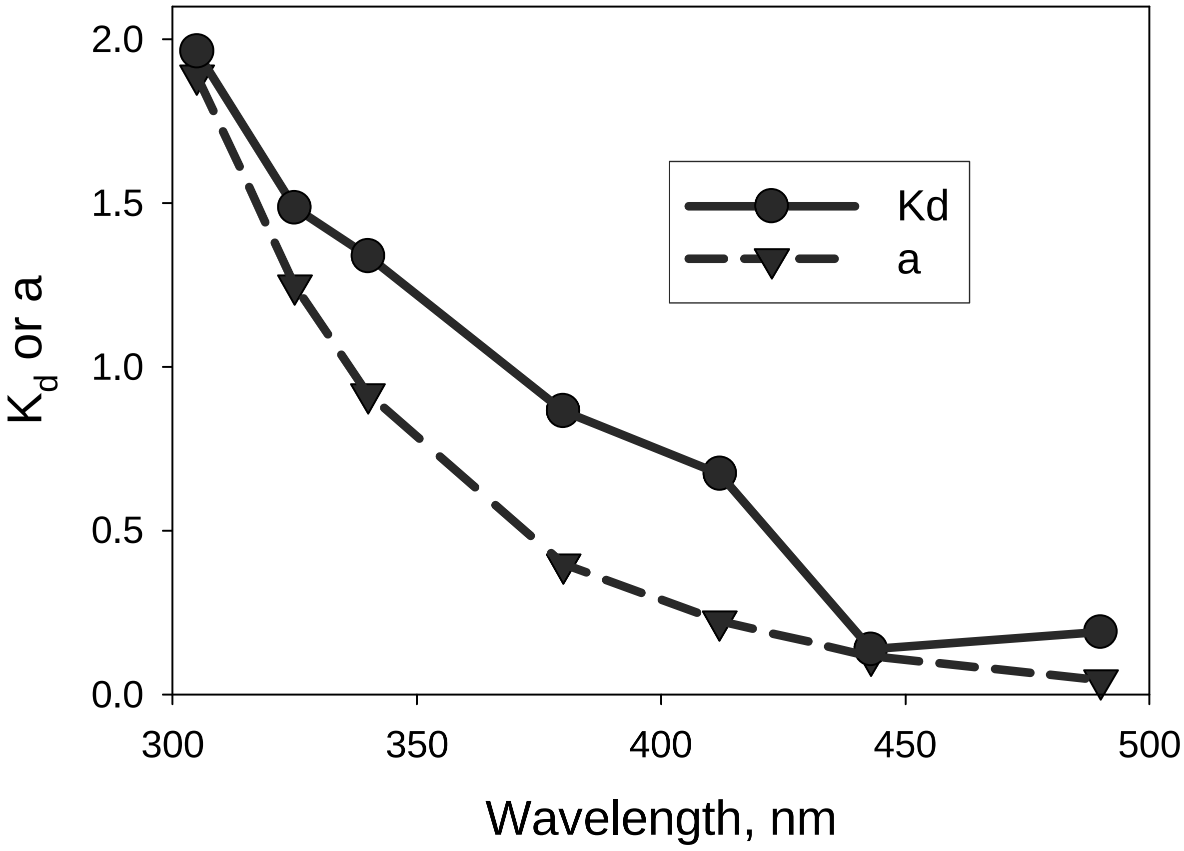


Figure 11. Diffuse attenuation coefficient spectra of water obtained along S – N transect near Looe Key, Florida Keys. The sites were located in the Atlantic Ocean bluewater four miles south of Looe Key Reef (UM215)(●), close to Looe Key Reef (FIU263)(▿), and in mid Hawk Channel region (FIU262)(■) not far from the reef site. Light absorption increases with increasing proximity to land and Florida Bay. These coefficients are based on underwater irradiance data that were measured at low tide when UV penetration is lowest at Looe Key Reef. During high tide the Kd(λ) values are similar to those shown for the bluewater site (●). The mean value for 5 casts is shown for each wavelength.

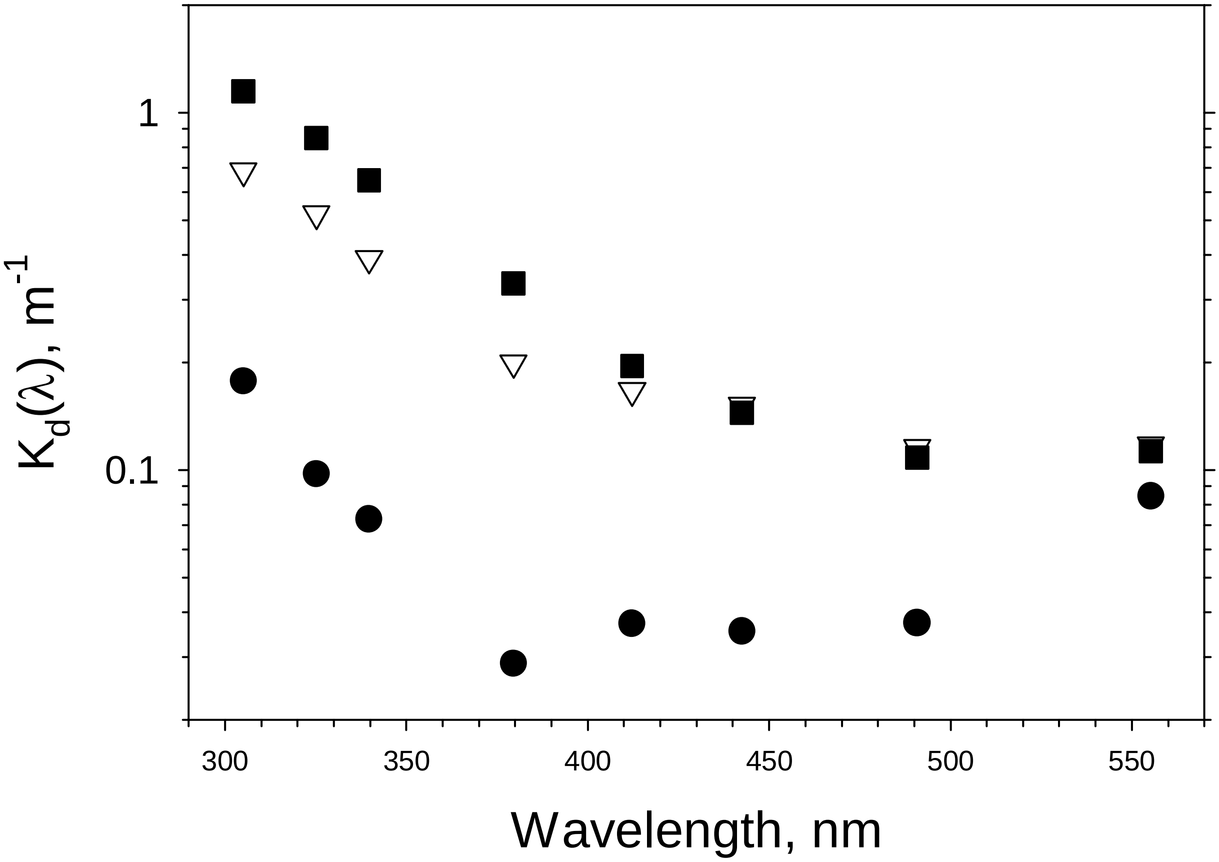


Figure 12. Diurnal variation in UV-B diffuse attenuation coefficient K_d (305 nm) at Sombrero Tower SeaKeys site during August. The results are closely related to tidal currents at the coral reefs. The K_d values were computed using eq. 1 and the irradiance data from two sensors that were mounted with a separation of 1.5 m on one of the tower legs.

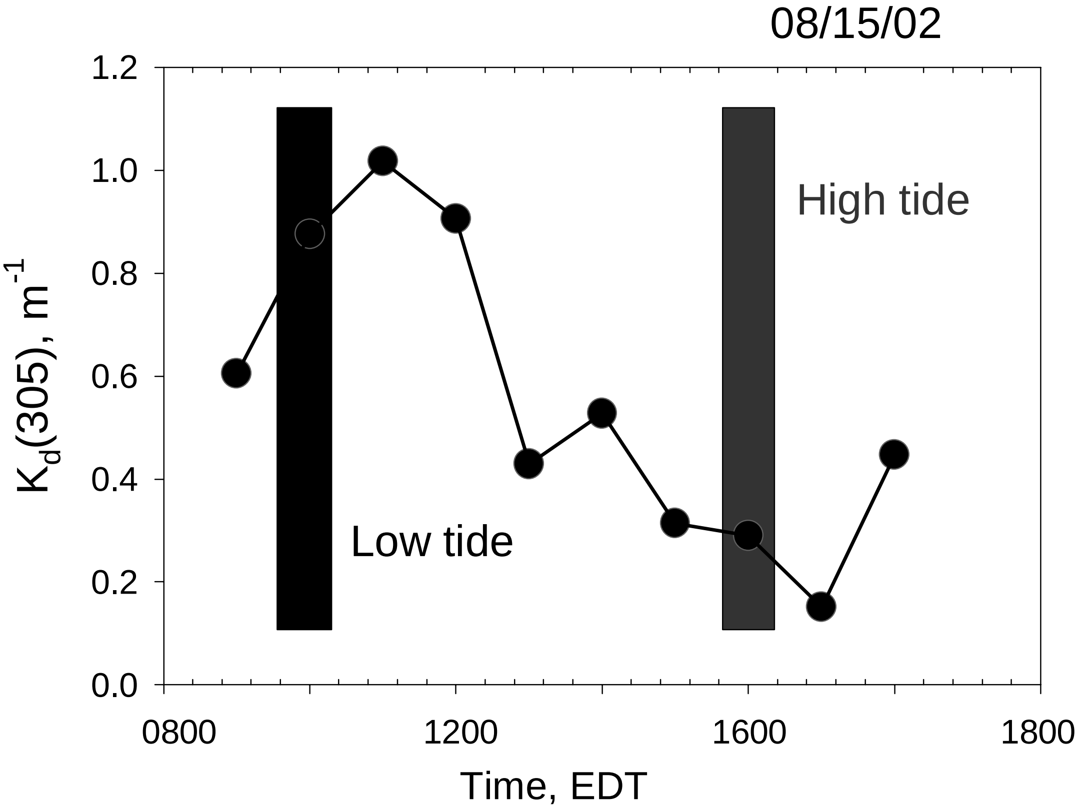


Figure 13. Seasonal change in UV-B diffuse attenuation coefficient K_d (305 nm) at Sombrero Tower SeaKeys site during 2002-2003 at 1100 EST. Thirty-day moving average is shown in gray to smooth out short term volatility.
The large jump near the end of 2003 coincided with the first major cold front to move through the Florida Keys and also with the end of the 2002 El Niño.

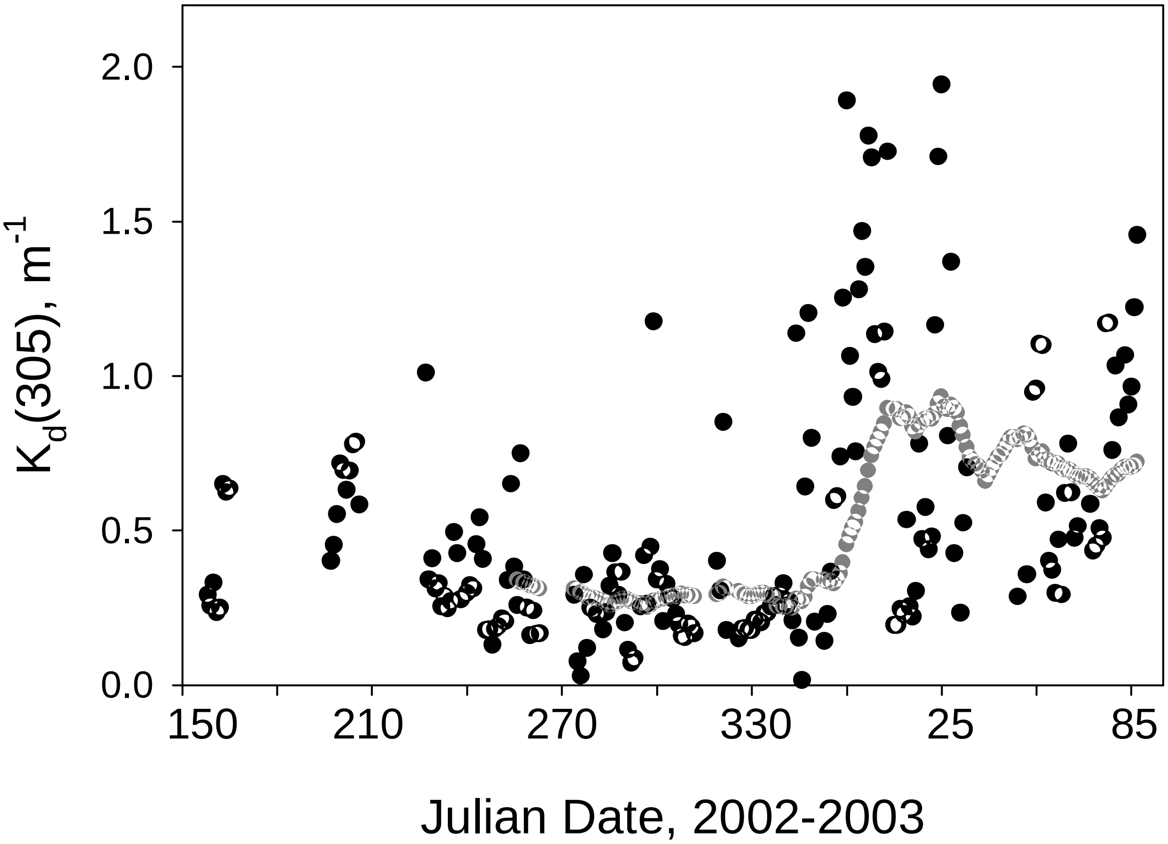
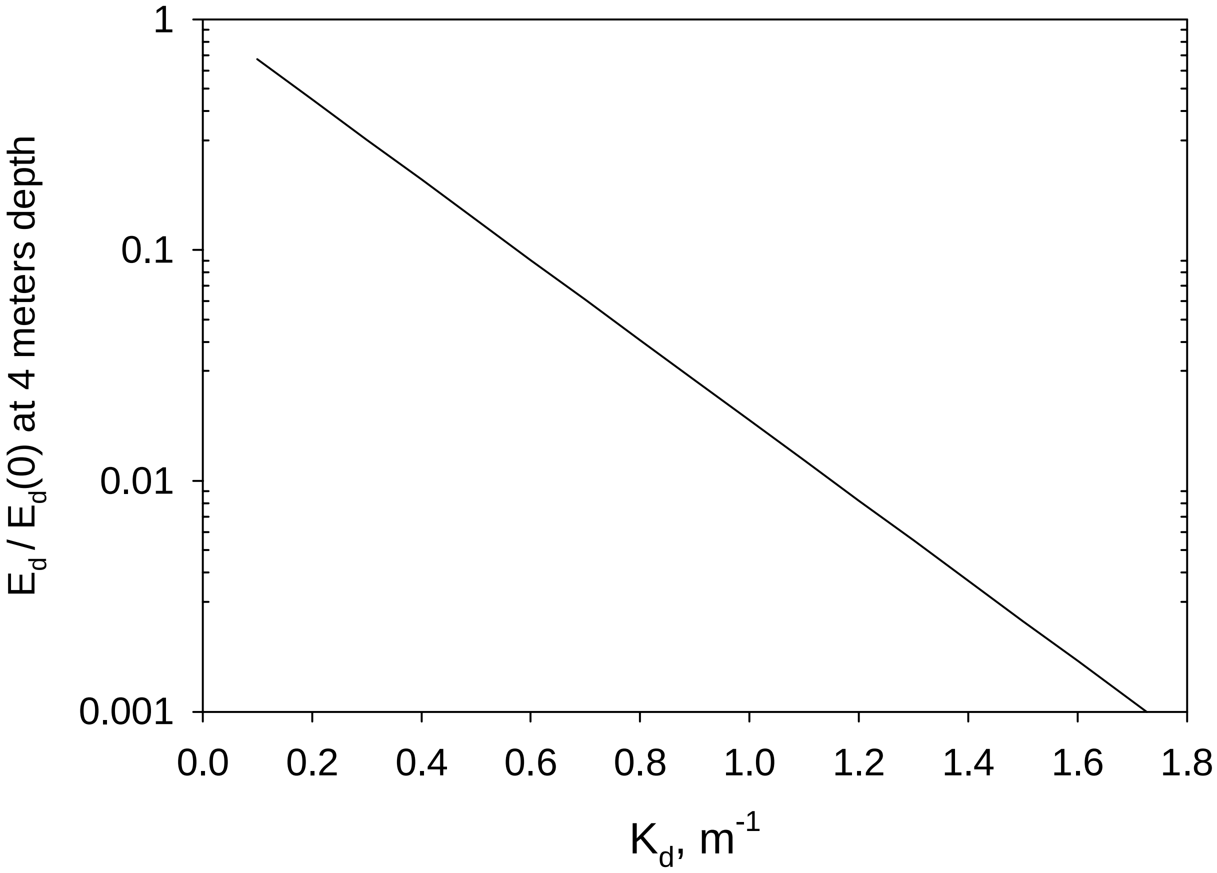


Figure 14. Relationship between fractional drop-off in irradiance with depth [(Ed / Ed(0)] and diffuse attenuation coefficient $K_{d.}$



The temperature profiles during the summer (Figure 15) indicate that the water has stratified; *i.e.*, that it has developed a poorly-mixed thermocline that blocks upward transport of cooler, deep waters to the surface layer. The thermocline is the region where temperatures rapidly decrease with depth. The pronounced stratification effect on the water is accompanied by a substantial increase in UVR penetration in the surface waters above the thermocline compared to that below it. This is evidenced by a change in the slope of log plots of the irradiance versus depth in the vicinity of the thermocline. We attribute this effect to combined photobleaching and microbial degradation of the CDOM, as discussed in Section 1. The term "photobleaching" refers to the decrease of absorption coefficients of the CDOM in the UVR and visible spectral regions in irradiation. To examine this possibility, water samples obtained near the coral reefs were exposed to simulated solar radiation under controlled conditions in the laboratory. In most cases, such as the results shown in Figure 16 for a water sample obtained at Looe Key Reef, the water photobleached. This effect also has been observed at other locations in the ocean (Nelson and Siegel 2002; Nelson et al. 1998; Siegel and Michaels 1996; Vodacek et al. 1997).

These results suggest that the extensive stratification which occurs under the low-wind conditions that accompany ENSO events may be greatly increasing exposure of the reefs to UVR. Indeed, it has previously been suggested that increased UV exposure may result as a consequence of clarification of the seawater during the doldrums conditions that accompany El Niño events (Gleason 2001; Gleason and Wellington 1993; Shick et al. 1996). This possibility appears to be confirmed by the comparison of the inter-annual K_d values for 305 nm radiation at various sites in the Dry Tortugas (Figure 17). During August 2002, a moderate El Niño year, the waters around the Dry Tortugas had significantly lower K_d values than during the early La Niña period of mid 1998 to 1999. Additional research is required to confirm this possibility.

2.5. Estimated UV Exposure Damage

The results of this research can be used to estimate the degree of UV exposure and damage that coral reefs may experience in the Florida Keys and how that damage might vary as a function of time and place and changes in UV-absorbing substances such as the ozone in the atmosphere or CDOM in ocean water. These estimates require knowledge of the action spectra for UV damage. Action spectra describe the wavelength dependency of radiation in producing some biological or chemical response (Coohil 1991, Moran 1997, Neale 2000). The term "biological weighting function" (BWF) has been used to distinguish a type of action spectrum measured using polychromatic UV and visible radiation with a series of cutoff filters (Neale 2000), as originally described by Rundel (Rundel 1986). Unlike action spectra measured using monochromatic radiation (Coohil 1991), the Rundel approach helps take into account the facts that there are interactions between various part of the spectrum, such as photorepair of UV-B damage by UV-A radiation.

The evaluation of action spectra for UV damage also must take into account its dependence on exposure, in particular whether reciprocity applies. The term "reciprocity" applies to systems in which biological or chemical responses to UV depend on cumulative exposure alone, independent of the duration of exposure or the irradiance (Cullen 1994, Neale 2000, Neale 1998). Reciprocity does not apply to organisms that rapidly repair UV damage. Instead, a steady state that reflects a balance between damage and repair is attained with continuous UV exposure (Neale 2000, Banaszak 2001,Lesser 1996). This steady state can be described as a function of weighted irradiance. Elegant procedures for modeling these effects have been developed over the past decade (Neale 2000, Banaszak 2001, Lesser 1996,Cullen 1994).

Figure 15. Seasonal variation in the temperature and UV vs. depth profiles at a site near Looe Key coral reefs, Florida Keys. The 3-fold higher UVR transparency of the surface waters during the summer is attributable to stratification of the water coupled with CDOM loss caused by photobleaching and microbial degradation. A detailed analysis of the deepwater data indicates that its clarity (K_d values) has changed little between summer and winter. A Mid-January; B Mid-August.

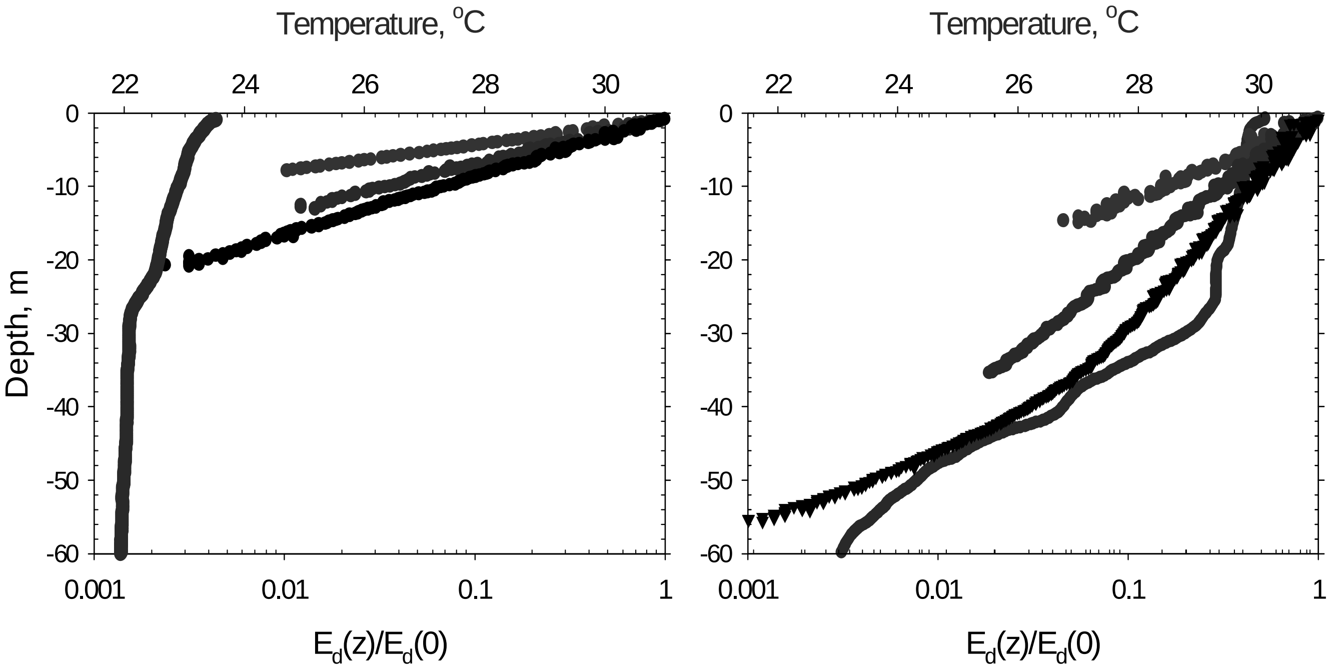


Figure 16. Decrease in absorption coefficients of a water sample obtained at Looe Key Reef in Lower Keys on exposure to simulated solar radiation. The radiation was similar to that provided by mid-afternoon sunlight at this site on a clear day in mid July.

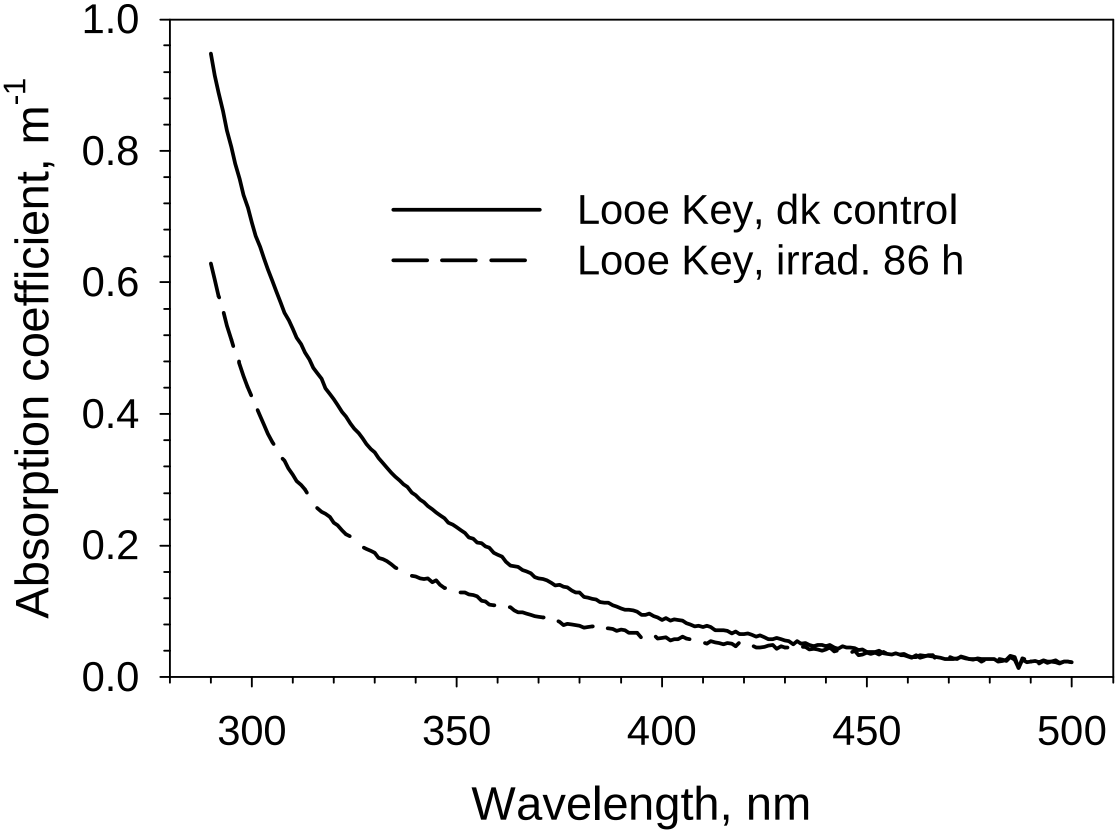
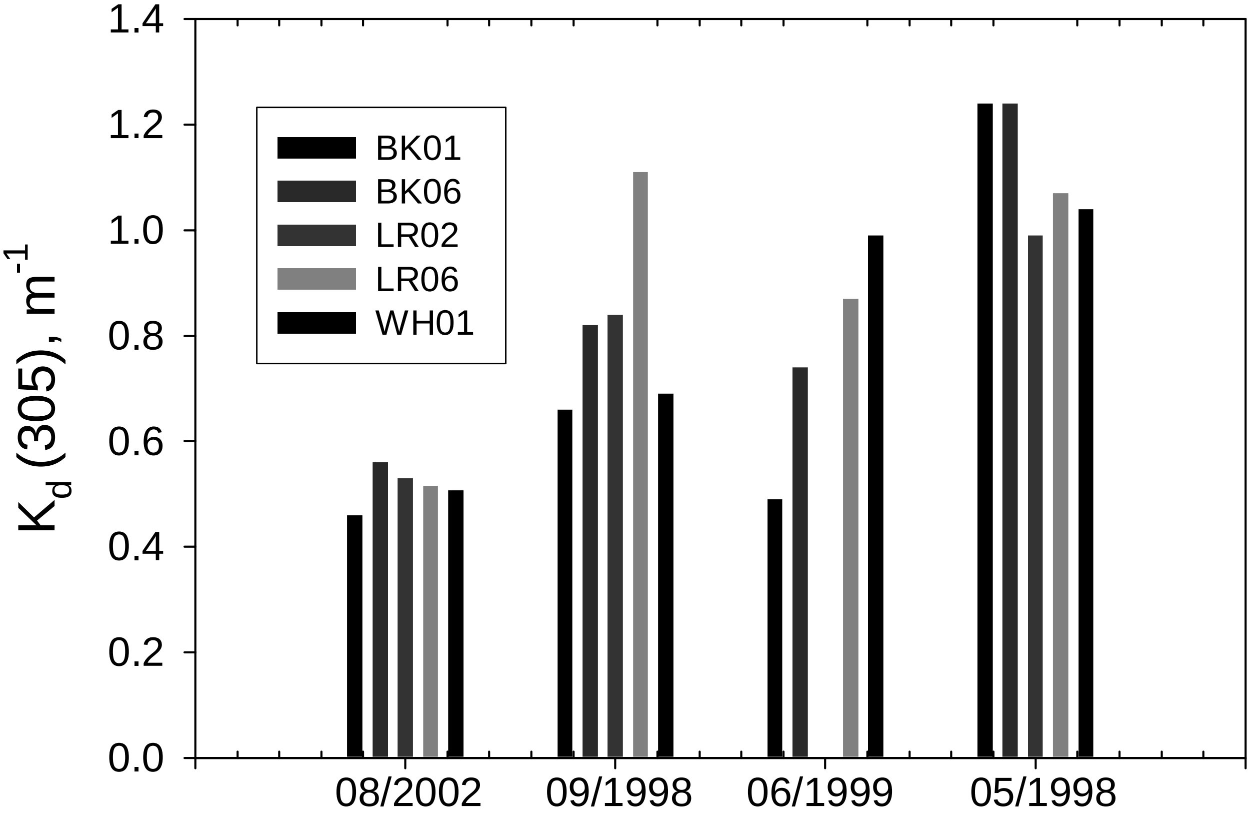


Figure 17. Inter-annual variability in UV-B diffuse attenuation coefficients (305 nm) for corals sites in the Dry Tortugas, a corals site that is not in close proximity to urban areas. Comparison indicates that UV-B attenuation is lower during an El Niño year (2002) compared to early La Niña years (1998-1999).



Solar UV radiation can damage a variety of biological "targets" and thus the action spectra can depend on the biological endpoint of interest. For example, direct damage to DNA is induced primarily by UV-B radiation whereas UV photoinhibition of corals photosynthesis can be induced by solar radiation throughout the UVR region (Figure 18). The weighted irradiance for UV damage at a certain wavelength is the cross product of the biological weighting function and the irradiance. By integrating this cross product over the entire underwater solar spectrum, the effective dose rate or exposure (UV_{int}) is obtained. The depth dependence of exposure of the coral reef to damaging UV can be estimated by conducting such integrations using measured or computed irradiance for various depths and action spectra for UV damage to corals. Underwater irradiance can be computed using eq. 1 and diffuse attenuation coefficients for the time and location of interest. In such computations the surface irradiance can be estimated using the TUV model of Madronich et al. (1995, 1998) and reflective loss at the air-water interface is computed using Fresnel's Law (Miller et al. 2002; Zepp 2002). The computed wavelength dependence for exposure to DNA damaging UV just below the surface and at a depth of 4.0 meters at various sites near Looe Key reef is illustrated in Figure 19. The attenuation coefficients used for the estimates in Figure 19 are those shown in Figure 11 for low tide conditions, a period in which UV penetration at Looe Key was at its lowest point. During high tides the depth dependence at the reef is similar to that illustrated for the bluewater site (UM215). For comparison, the depth dependence for DNA damage, for photosynthesis inhibition, for UV-B radiation and for UVR at Looe Key Reef are shown in Figure 20.

Weighted UV irradiances computed with different action spectra have different responses to changes in atmospheric ozone and CDOM concentrations in the seawater. A widely used measure of this dependence in the case of ozone is the radiation amplification factor (RAF) which is defined by a power function (eq. 3):

$$(UV_{int})_2 \,/\, (UV_{int})_1 = [(O_3)_1/(O_3)_2\,]^{RAF} \qquad (3)$$

Where $(UV_{int})_2$ and $(UV_{int})_1$ are the UV exposures that correspond, respectively, to total ozone amounts $(O_3)_1$ and $(O_3)_2$. The differences in potential responses of corals to ozone change are demonstrated by comparisons of computed UV changes for the action spectra for DNA damage and for photosynthesis inhibition (Figure 21). For the latter, the action spectrum for *Montastraea faveolata* at a depth of 3.0 meters was used. The RAF for DNA damage near the water surface is an order of magnitude higher than photosynthesis inhibition. The spectrum of underwater UV irradiance changes as it penetrates down into the water. The change has important effects on the ozone RAF for DNA damage, reducing the RAF compared to surface conditions (Figure 22). Reductions also occur for the photosynthesis RAF computed for underwater UV.

The effects of changing CDOM concentrations on underwater UV exposure can be described by an equation that is similar to eq. (3).

$$(UV_{int})_2/(UV_{int})_1= [(K_{d,\,uv})_1/(K_{d,\,uv})_2]^{RAF} \qquad (4)$$

Where $(UV_{int})_2$ and $(UV_{int})_1$ are the exposures at a certain depth that correspond, respectively, to UV diffuse attenuation coefficients $(K_{d,\,uv})_1$ and $(K_{d,\,uv})_2$. The computed dependence of UV_{int} for DNA damage and for photosynthesis inhibition on attenuation coefficients at a depth of 4.0 meters at Looe Key Reef is shown in Figure 23. For these calculations, the exposure for DNA damage and for photosynthesis inhibition were computed assuming various across-the-board reductions in the UV diffuse attenuation coefficients for Looe Key (Figure 11). Note that, unlike the case of atmospheric ozone changes, UV attenuation coefficient changes in the water over the reefs have substantial effects on both DNA damage as well as photosynthesis inhibition. The magnitude of the RAFs is a function of depth as well; generally the RAFs increase with increasing depth. These results show that UV damage of both types can be more sensitive to changes in UV attenuation coefficients than atmospheric ozone, especially damage to the photosynthetic system.

Figure 18. Comparison of biological weighting functions for DNA damage (Setlow) and for inhibition of photosynthesis by *Montastraea faveolata* (Lesser 2000)

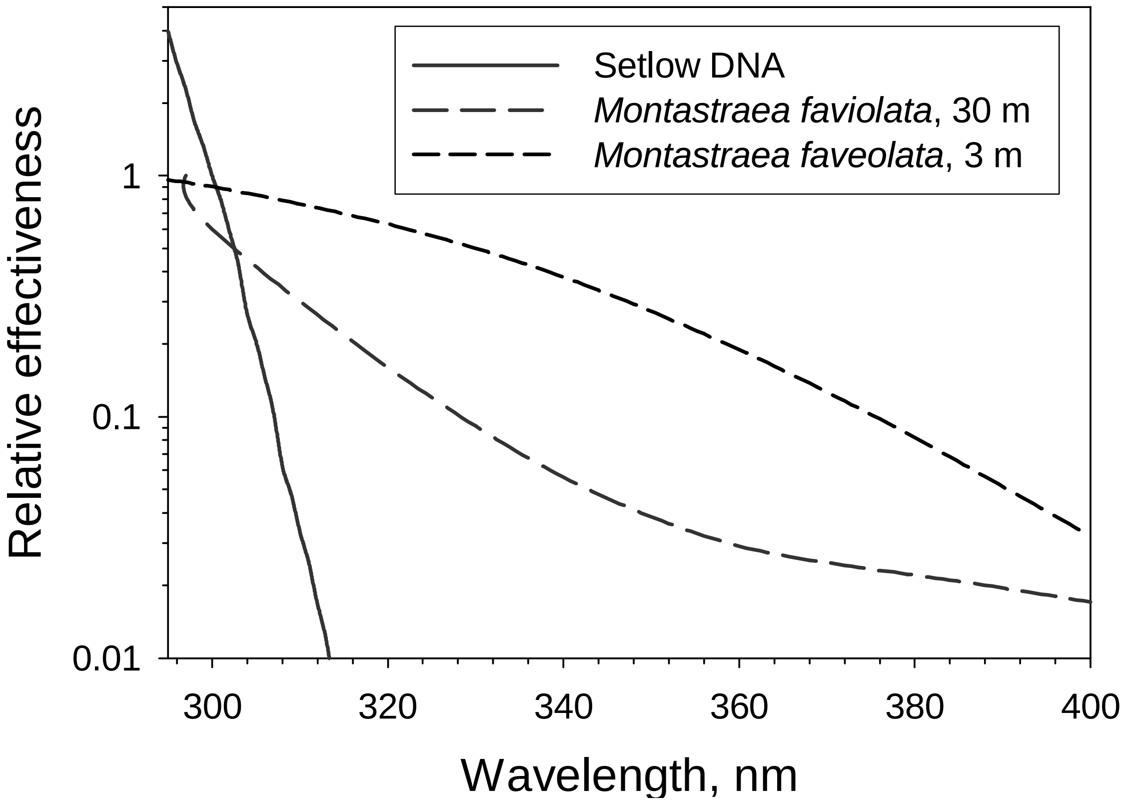


Figure 19. Comparison of estimated dose rate (exposure) of DNA-damaging solar radiation during July at midday at sites around Looe Key Reef. Setlow biological weighting function from Figure 14 and underwater solar UV irradiance data from this report were used for these calculations. At a depth of 4.0 m the dose is reduced less than 50% at the bluewater site, but in mid-Hawk Channel the dose is reduced about 30-fold. The bluewater and mid-Hawk Channel results represent the extremes in UV exposure that are experienced by Looe Key Reef. Typically, the exposure is close to the bluewater result under high tide conditions.

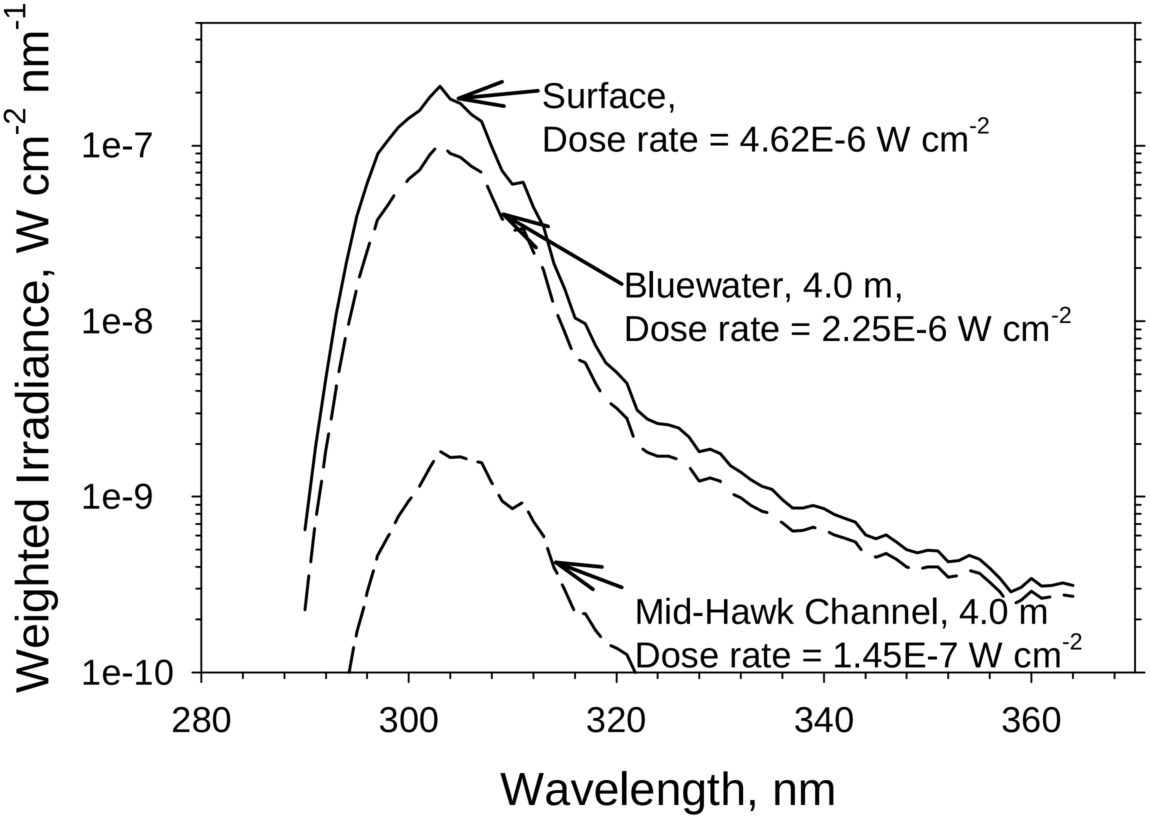


Figure 20. Comparison of the depth dependence for computed UV exposure for DNA damage, photosynthesis inhibition, UV-B and UVR at Looe Key Reef during midday, July at low tide

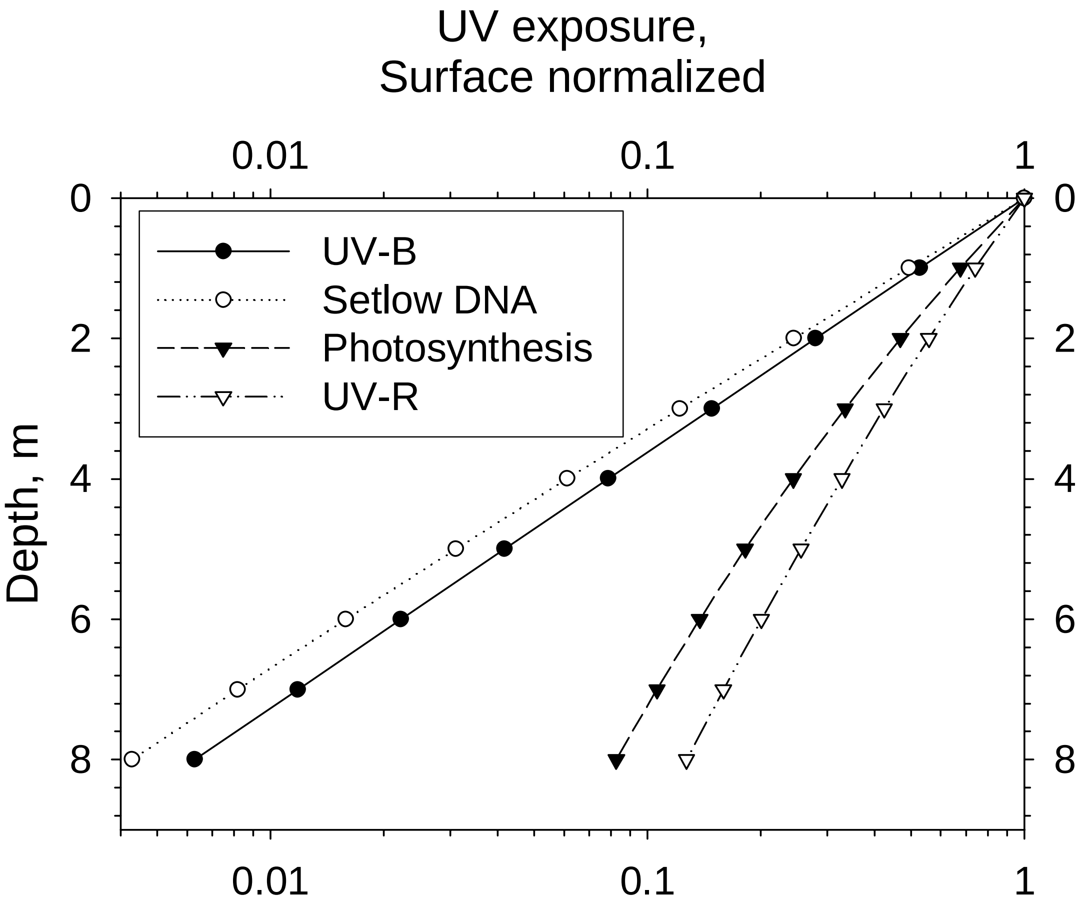


Figure 21. Ozone radiation amplification factors (RAFs) for UV damage to DNA (Setlow action spectrum) and for UV inhibition of corals photosynthesis (Lesser, 2000). The term “RAF” is defined in the text.

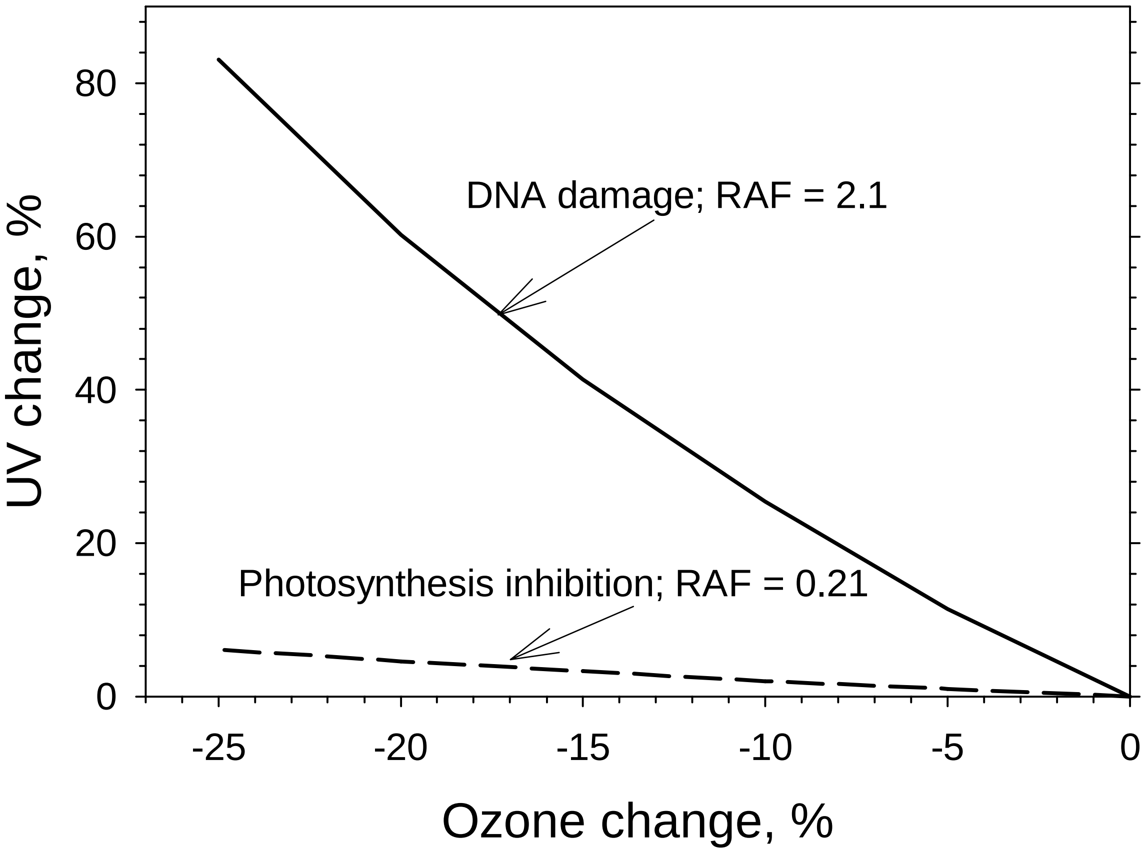


Figure 22. Change in ozone RAF with increasing depth in waters over Looe Key Reef, Florida Keys. The RAF is defined in the text.

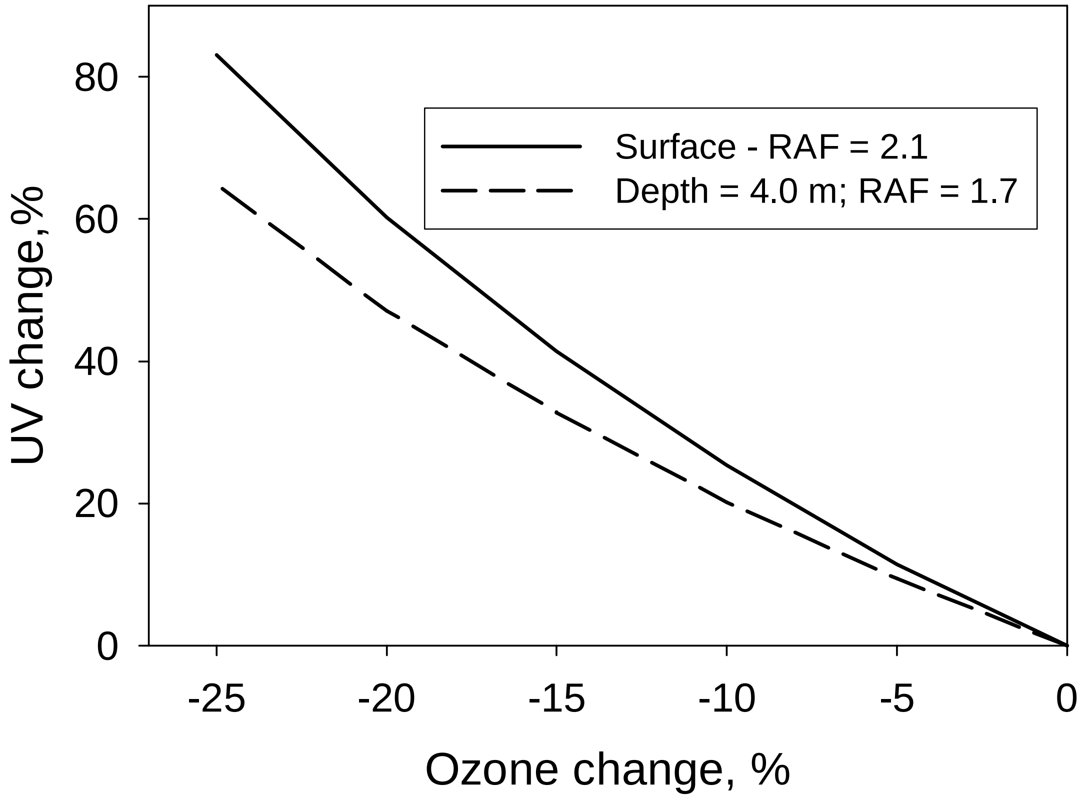


Figure 23. Computed dependence of UV damage to DNA (Setlow action spectrum) and UV inhibition of corals photosynthesis (Lesser, 2000) on change in UV diffuse attenuation coefficients at a depth of 4 meters at Looe Key Reef, Florida Keys. The computed RAFs for CDOM are shown in the figure (see text for definition of RAF).

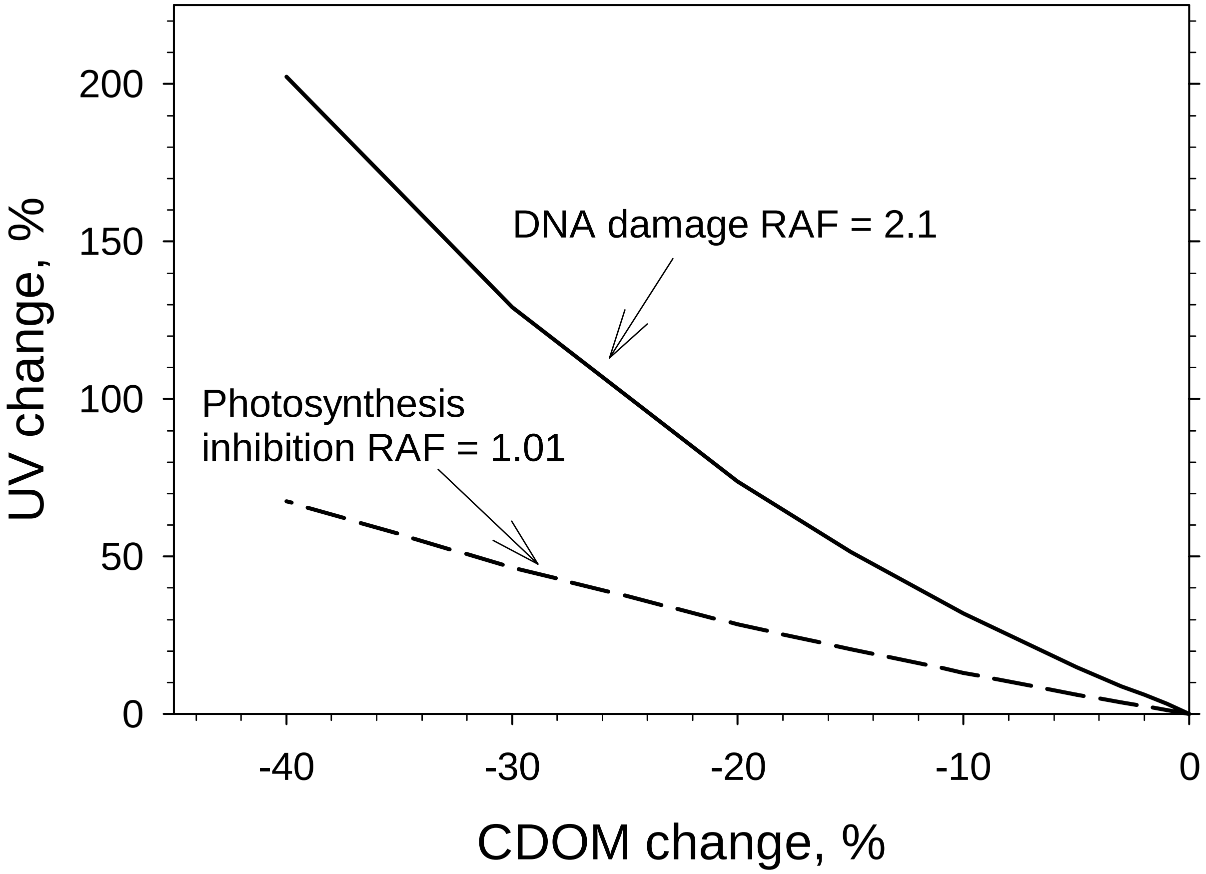
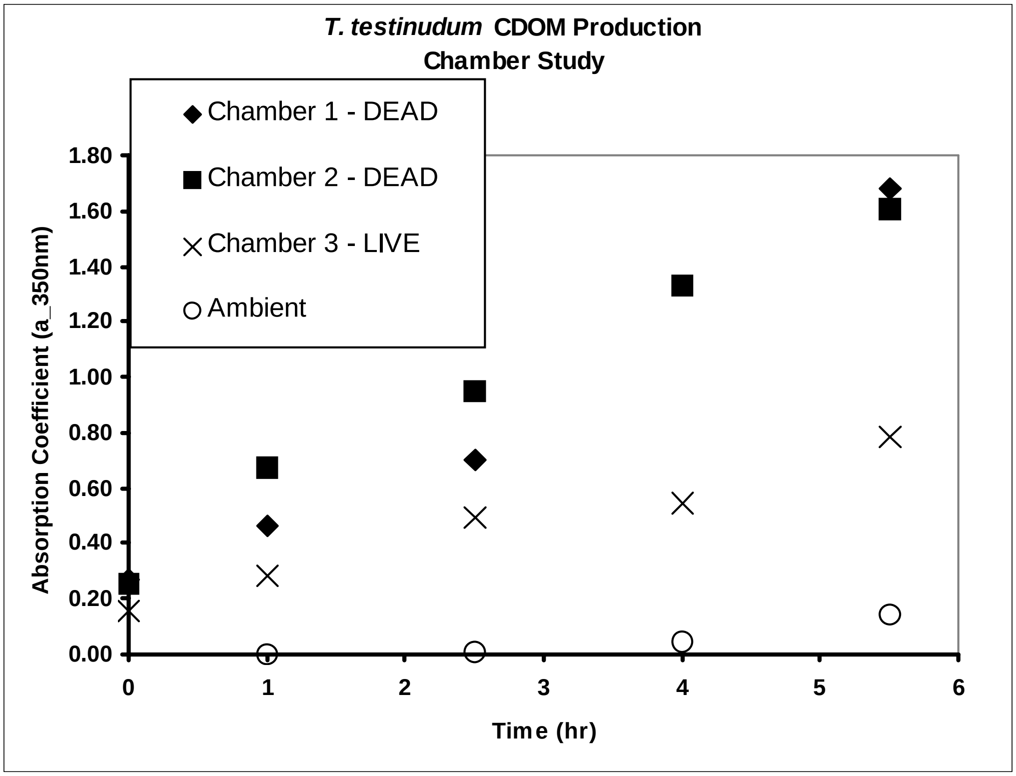


Figure 24. Observed increases in UV absorption coefficients (at 350 nm) in Plexiglas chambers placed over beds of dead seagrass (*Thalassia testudinum*) and living seagrass. The data show that seagrasses are an important source of UV-attenuating CDOM over the coral reefs in the Florida Keys.



2.6. Sources and Sinks of CDOM

In shallow coastal shelf regions such as Florida Bay and Hawk Channel, large amounts of biomass are produced by submerged aquatic vegetation. Around the Florida Keys and other global locations where coral reefs are located, turtlegrass (*Thalassia testudinum*) (Peterson and Fourqurean 2001)and mangroves are major sources of biomass and thus potentially significant CDOM sources.

Our studies using chambers over seagrass beds in the field as well as with dead grass litter suspended in temperature-controlled aquaria indicated that *Thalassia* does indeed produce CDOM that has a featureless exponential absorption spectrum with about the same spectral slope coefficients as that of water samples obtained from Florida Bay and the northern part of Hawk Channel (Figure 24). Within experimental error the absorption spectrum of this CDOM was insensitive to the temperature at which it was produced. The CDOM from various locations in Hawk Channel was susceptible to photobleaching by solar radiation. The time required for absorption coefficients to drop 50% at 350 nm ranged from 25 to 45 hours under irradiation that, based on a simulation using the TUV model of Madronich (Madronich et al. 1998), was equivalent to that derived at mid-afternoon during July in the Florida Keys. During photodegradation the spectral slope coefficient of the CDOM solution also increased. A similar increase in slope is observed in a typical transect from coastal to offshore regions. These results indicate that a portion of the observed increase in spectral slope coefficient in these transects may be attributed to photobleaching of a near shore seagrass derived CDOM during transport offshore.

Mangrove leaves are another potentially important source of CDOM in the Florida Keys. Like the seagrass CDOM, the mangrove derived CDOM also was susceptible to photobleaching by solar radiation. Specific absorption coefficients (absorption coefficients normalized to dissolved organic carbon) for mangrove CDOM solutions were about twice as high as those for the seagrass CDOM solutions.

2.7. Quality Assurance Considerations

A number of quality assurance measures were employed to ensure that high quality data were obtained in these field and laboratory studies. The spectral irradiance of the solar simulator used in the CDOM photobleaching experiments and some of the coral field experiments was measured using an Optronics OL 754 spectroradiometer. An Optronics OL 750 spectroradiometer was used to cross-check the irradiance measurements. Downwelling irradiance measurements and upwelling radiance measurements were obtained primarily using Satlantic OCP-100 and Satlantic Free Fall MicroPro profiling instruments. These instruments rapidly logged UV and visible downwelling and upwelling radiation as they fell freely down through the water column. The downwelling irradiance sensor from the OCP-100 also was used in a moored position close to the reefs to measure UV and visible light reaching the reef surface during other experiments in which thymine dimers were measured. Also, profiling was conducted by K. Patterson using a Biospherical PUV instrument equipped with 305, 320, 340, 380 and PAR channels. These instruments were periodically calibrated against standard light sources to insure accuracy (at least once every 6 months). The temperature and depth sensors on the profiling instruments were periodically calibrated at the factory. Downwelling UV and PAR irradiance was also simultaneously measured on the ship deck by Satlantic OCR-504UV and OCR-504I sensors. The deck sensors were calibrated at the same time as the MicroPro sensors. In addition to the depth profiling measurements, downwelling UV-B irradiance also was continuously measured using two OCR-504UV sensors equipped with UV channel at 305 nm; the sensors were mounted on one of the legs of Sombrero Tower at depths separated by 1.50 meters and were set to log data hourly from 0900 to 2000 over a 10 second observation period. Data were downloaded during bi-monthly service visits to the tower. To check for changes due to fouling the sensors were brought to the surface during the service visits and data were logged with the sensors placed in close proximity. Changes in the ratio of the irradiance measured by the two sensors were used to assess the effects of fouling on relative sensor response.

2.8. Conclusions

Evidence is presented in this section of the report that UV exposure of coral reefs in the Florida Keys is controlled by CDOM in waters overlying the reefs. Diffuse attenuation coefficients were determined using downwelling vertical profiles of UV and visible radiation that were obtained at sites located at the Upper, Middle and Lower Keys and the Dry Tortugas and absorption spectra of the filtered water samples were measured. Absorption and diffuse attenuation coefficients were highly correlated ($r^2 > 0.9$) in the UV-B (290-315 nm) spectral region. These results support the hypothesis that UV attenuation at these sites is predominately attributable to absorption by CDOM. Using the irradiance data, it is shown that UV damage to corals can be more sensitive to changes in CDOM concentrations than atmospheric ozone, especially damage to the photosynthetic system. The absorption spectra of CDOM freshly derived from decaying detritus from seagrasses and mangroves closely matched those of the CDOM in the shallow regions of the study region that were close to land, indicating that these are major CDOM sources in the Florida Keys. The CDOM photobleached with loss of UV absorbance and an increase in spectral slope coefficient when exposed to simulated solar radiation. Under summer conditions with low winds a pronounced stratification effect on UVR transmission occurred in the deep water just outside the reefs, the net effect of which was to substantially increase UV penetration in the surface waters above the thermocline. This effect is ascribed to combined photobleaching and microbial degradation of the CDOM in the upper water column coupled with reduced upwelling of cool, more opaque waters from the deep ocean. Because this surface water is often laterally transported over the reefs by the action of currents, this stratification effect enhances reef UV exposure compared to well-mixed conditions. This result suggests that the extensive stratification which occurs under ENSO conditions may be greatly increasing exposure of the reefs to damaging UV. We conclude that CDOM concentrations and UV penetration over the reefs are modulated by a complex interplay between this stratification effect coupled with transport and photobleaching of CDOM-rich waters from shallow waters close to the reefs. UV damage of both types is more sensitive to changes in CDOM concentrations than total ozone, especially damage to the photosynthetic system.

3. Conclusions and Management Implications

This research has advanced the science of corals as it relates to UV interactions in the following ways:

- It was demonstrated that the UV exposure of coral reefs in the Florida Keys is highly variable and that this variability is linked to climate changes that are occurring over the region. The linkage stems from concurrent changes in physicochemical properties of the waters such as warmer temperatures and increased water clarity.

- We showed that the chromophoric (colored) component of dissolved organic matter (CDOM) in the water over the reefs plays a key role in controlling light exposure. Thus changes in CDOM concentrations caused by climate change and/or land-based human activities can translate into significantly altered UV exposure of coral reefs.

- We identified what may be a major pathway for the large scale impact of El Niño events on mass bleaching of corals. Our results suggest that stratification caused by the prolonged periods of low winds and warm temperatures that accompany El Niño events can result in significant increases in damaging UV radiation over the reefs. We hypothesize that this increased exposure to UV, in concert with warmer waters, places intense stress on the corals that results in extensive bleaching.

- We elucidated possible biological sources of CDOM in waters close to coral reefs. Changes in these biological sources, such as seagrasses and mangroves, caused by climate change and human activities can have long-term detrimental effects on corals by perturbing UV protective substances in the ocean water.

The research has contributed to the management of coral reefs in the following ways:

- By identifying the environmental conditions that lead to enhanced UV exposure to coral reefs, we have laid the groundwork for a remote sensing based "UV/hot spots" system that potentially can be used to alert corals managers that conditions are favorable for extensive corals bleaching (see http://www.osdpd.noaa.gov/PSB/EPS/method.html for a description of the currently used "hot spots" warning system that focuses only on sea surface temperatures). High water temperatures do not always presage major coral bleaching events, but high water temperatures coupled with high UV exposure almost always lead to extensive bleaching. The prediction of major bleaching events by the hotspot network is enhanced by the inclusion of a time factor in its warning procedure. That is, the hotspot must prevail for a period of weeks before a warning of bleaching is issued. A prolonged period of hotspot development is also a good indicator of strong stratification of the ocean at that location. Stratification promotes increased UV exposure over a period of time. However, the exact relationship between length of hotspot development and increased UV exposure is poorly understood. Thus the addition of a remote sensing capability for UV exposure, coupled with the current hotspot method, would likely enhance the ability to forecast bleaching events.

- Our findings that CDOM plays a key role in controlling harmful UV exposure should help managers plan strategies to optimize coral health; e.g., by protecting and enhancing the health of seagrasses and mangroves that produce UV-protective substances.

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