

## Spatial and temporal variability of solar ultraviolet exposure of coral assemblages in the Florida Keys: Importance of colored dissolved organic matter

Richard G. Zepp,<sup>1</sup> G. Christopher Shank,<sup>2</sup> Erik Stabenau,<sup>3</sup> Karen W. Patterson,<sup>4</sup> and Mike Cyterski  
Ecosystems Research Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia 30605-2700

William Fisher

Gulf Ecology Division, National Human Health and Ecological Research Laboratory, Gulf Breeze, Florida

Erich Bartels

Mote Marine Laboratory, Tropical Research Laboratory, Summerland Key, Florida

Susan L. Anderson

University of California Davis, Bodega Marine Laboratory, Bodega Bay, California

### Abstract

Solar ultraviolet (UV) radiation can have deleterious effects on coral assemblages in tropical and subtropical marine environments, but little information is available on UV penetration into ocean waters surrounding corals. Here we provide an extensive data set of optical properties in the UV domain (280–400 nm) that were obtained during 1998–2005 at sites located in the Lower and Middle Keys and the Dry Tortugas. Absorption coefficients of the colored component of the dissolved organic carbon (DOC; colored dissolved organic matter [CDOM]) were 6× to 25× larger than particulate absorption coefficients in the UV region, indicating that CDOM controls UV penetration in the inshore coastal waters and reef tract. CDOM absorption coefficients ( $a_{\text{CDOM}}$ ) and DOC were highly correlated to diffuse attenuation coefficients ( $K_d$ ) in the UV spectral region. Measurements using moored sensors showed that UV penetration at the reef tract in the Lower Keys varies significantly from day to day and diurnally. The diurnal variations were linked to tidal currents that transport CDOM over the reef tract. Summertime stratification of Case 1 bluewaters near the reef tract during periods of low wind resulted in higher temperatures and UV penetration than that observed during well-mixed conditions. This result suggests that higher UV exposure accompanying ocean warming during low-wind doldrums conditions significantly contributes to coral bleaching. Modeling results indicate that changes in underwater sunlight attenuation over the coral reefs can affect UV-induced deoxyribonucleic acid (DNA) damage and inhibition of coral photosynthesis much more strongly than changes in the stratospheric ozone layer.

Solar radiation is intimately involved in the physiology of corals. Photosynthetic symbionts (zooxanthellae) in host coral tissues are dependent upon sunlight, especially the visible component known as photosynthetically active radiation (PAR), to drive carbon fixation. However,

absorption of the ultraviolet (UV) component of sunlight by corals can inhibit photosynthesis (Fitt and Warner 1995; Shick et al. 1996; Lesser 2000) and influence other processes, such as larval settlement and growth rates of juveniles (Gleason and Wellington 1995; Gleason et al.

<sup>1</sup> Corresponding author: (zepp.richard@epa.gov).

<sup>2</sup> Present address: University of Texas at Austin Marine Science Institute, Port Aransas, Texas.

<sup>3</sup> Present address: Everglades National Park, South Florida Natural Resources Center, Daniel Beard Center, 40001 State Road 9336, Homestead, Florida 33033.

<sup>4</sup> Present address: Naval Oceanographic Office—Code N35, 1002 Balch Blvd., Stennis Space Center, Mississippi 39522-5001.

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2006). Exposure to solar UV radiation has also been implicated in a phenomenon known as coral bleaching, where symbiotic zooxanthellae are expelled from host coral tissues (Gleason and Wellington 1993; Shick et al. 1996; Anderson et al. 2001) followed by the subsequent emergence of the white color of the coral skeleton. In some instances, bleaching can lead to the death of the coral colony. Mycosporine-like amino acids (MAAs) help provide UV-B protection to coral assemblages (Shick et al. 1996; Shick and Dunlap 2002) and the inverse dependence of MAA concentrations on depth has been attributed to changes in UV exposure (Gleason and Wellington 1995; Lesser and Lewis 1996; Lesser 2000). Other calcifying organisms such as benthic foraminifera that dwell close to the reefs also have experienced bleaching that has been suggested to be linked to UV exposure (Hallock et al. 2003; Talge and Hallock 2003). Unprecedented increases in coral bleaching on a global scale have occurred in recent years (D'Elia et al. 1991) and have been closely linked to concurrent changes in climate and light exposure (Shick et al. 1996; Hoegh-Guldberg 1999).

Although the responses of coral assemblages to changes in light and temperature have received a great deal of attention, comparatively little is known about factors that control coral exposure to solar radiation, especially solar ultraviolet (UV) radiation. Corals live predominately in the tropics and subtropics where high intensities of solar UV radiation prevail (Herman et al. 1996; Shick et al. 1996; Madronich et al. 1998). It has been known for some time that UV radiation can penetrate deeply into clear tropical ocean waters and that penetration depends on water type (Jerlov 1950; Jokiel 1980; Smith and Baker 1981). Modeling studies of the effects of downwelling UV-B radiation on corals DNA damage (Dunne and Brown 1996; Shick et al. 1996) and photosynthesis inhibition (Lesser 2000) have appeared. Evidence continues to grow that the colored component of the DOC (CDOM) contributes significantly to UV attenuation in coastal and open ocean waters (Blough and Del Vecchio 2002; Nelson and Siegel 2002; Morel et al. 2007a) but comparatively few data are available for tropical and subtropical waters where coral assemblages are located (Otis et al. 2004).

Seasonal fluctuations in UV penetration have been observed in midlatitude regions (Blough and Del Vecchio 2002; Nelson and Siegel 2002; Zepp 2003a), and increased UV penetration into the ocean during the summer has been attributed in part to photodegradation of CDOM (Vodacek et al. 1997; Del Vecchio and Blough 2004; Tzortziou et al. 2007). In the Florida Keys, pronounced decreases in the penetration of PAR can accompany the transition from summer to winter in ocean waters over coral reefs (Porter et al. 2004), and seasonal changes in UV and photosynthetically-active radiation (PAR) also occur over coral reefs in tropical regions such as Puerto Rico (Torres et al. 2007). Seasonal variations in light exposure may contribute to the seasonal changes that have been observed in tissue biomass and densities of zooxanthellae in coral reefs (Fitt et al. 2000). The known enhancement of CDOM photobleaching under stratified conditions suggests that UV penetration

into the tropical ocean may be enhanced during the doldrums that are widespread during El Niño events (Gleason and Wellington 1993; Gleason 2001). During these events, increased ocean warming combined with elevated UV irradiance levels at depth has the potential to damage corals and to initiate bleaching episodes.

In this study, our objectives were to determine the geographic, interannual, seasonal, and diurnal variations in the penetration of solar UV and visible radiation into waters surrounding the coral ecosystems of the Middle and Lower Keys and Dry Tortugas. We focused on providing new information about the dynamics of UV penetration into Florida Keys coastal waters and on elucidating the role of various seawater constituents in driving variations in the optical properties of this region. Finally, another objective was to use these data in an optical model to evaluate how changes in UV-attenuating substances such as CDOM over the coral reefs alter biologically relevant UV exposure.

## Methods

*Underwater irradiance measurements*—Depth profiles of underwater irradiance were measured during 1998–2006 on cruises by the RV *Anderson* and on trips from a base at Mote Marine Laboratory in Summerland Key, Florida. The sampling sites were located in the Lower Keys, Middle Keys, and Dry Tortugas with emphasis on stations that were located in the Lower Keys (Fig. 1). Many sites coincided with stations that are part of Florida International University's Water Quality Monitoring Network (Southeast Environmental Research Center; Boyer 2008). The study included over 1200 depth profiles, each of which included 25 UV measurements per meter. At the reef tract sites, UV measurements were performed at >200 depths per cast. The profiling took place throughout the year in the Lower Keys but was limited to summer in the Dry Tortugas and Middle Keys. Downwelling irradiance measurements and upwelling radiance measurements were obtained primarily using a Satlantic Free-Fall MicroPro profiling instrument. The MicroPro was equipped with an OCR-504UV downwelling irradiance sensor with UV channels at 305 nm, 325 nm, 340 nm, and 380 nm (spectral bandwidth 2 nm and 10 nm (at 380 nm)), an OCR-504I downwelling irradiance sensor equipped with visible channels at 412 nm, 443 nm, 490 nm, and 555 nm (spectral bandwidth 10 nm), and an OCR-504R upwelling sensor equipped with visible channels at 412 nm, 443 nm, 490 nm, and 555 nm (spectral bandwidth 10 nm). The irradiance sensors were calibrated annually at Satlantic Inc. against free-electron laser (FEL) standard lamps traceable to National Institute of Science and Technology (NIST) standards using procedures that are described elsewhere (Hooker et al. 1999). Additional profiling was conducted using a hybrid biospherical profiling reflectance radiometer/profiling ultraviolet radiometer (PRR/PUV) instrument equipped with 305 nm, 320 nm, 340 nm, 380 nm, 412 nm, 443 nm, 490 nm, 510 nm, 555 nm, 656 nm, and PAR channels (most channels with band-

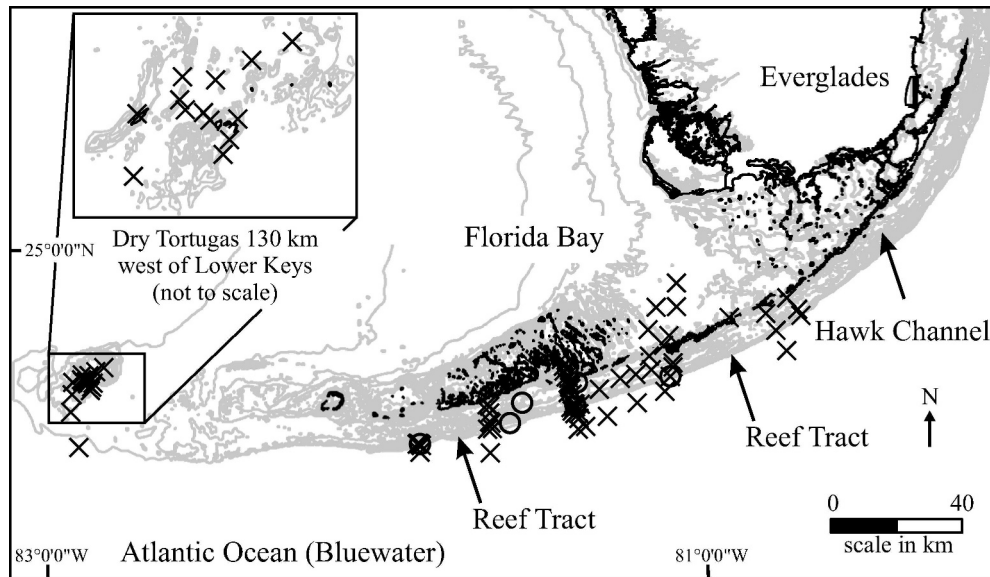


Fig. 1. Map illustrating locations of sites used in this study. X denotes locations where optical profiling occurred; O indicates tower sites where moored measurements of UV irradiance were conducted.

width of 8 nm to 10 nm). Because the spectral bandwidth for the Satlantic instrument is significantly narrower than the bandwidth of the PRR/PUV, data obtained by the former provided more accurate values for UV attenuation, especially at 305 nm, where the solar spectral irradiance decreases rapidly with decreasing wavelength. A direct comparison of the relative performance of the two instruments was not made in this study. Typically, 5–6 casts were conducted at each profiling station. The maximum profiling depths typically ranged up to 75 m at the Case 1 ocean water (bluewater) sites south of the reef tract down to 1–2 m at shallow sites in Florida Bay. The free-falling velocity of the MicroPro was adjusted to 0.3–0.4 m s<sup>-1</sup> in coastal-shelf waters which permitted irradiance acquisition at depth intervals of 5–7 cm, ideal for the turbid coastal-shelf waters in Hawk Channel near the reefs. In the bluewater south of the reef tract, the free-falling velocity was adjusted up to 0.8–0.9 m s<sup>-1</sup>. The descent rate of the PRR/PUV instrument was ~0.2 m s<sup>-1</sup>. The MicroPro was also equipped with a pressure sensor (for depth measurements), a water-temperature sensor, and a tilt-angle sensor. Calibrations indicated that the accuracy of the cosine response of the OCR-504UV instrument for irradiance incident within 0–60° of normal were 8% and 3% for the OCR-504I. Downwelling atmospheric irradiance was also simultaneously measured at these same wavelengths on the ship deck by OCR-504UV and OCR-504I sensors. Data were logged using Satlantic's Satview software and processed using Satlantic's ProSoft software (McLean 2008). The  $K_d$  values were computed for irradiance that was >10% of the surface value. Data for the PRR/PUV were logged using Biospherical software. Diffuse attenuation coefficients  $K_d(\lambda)$  (in m<sup>-1</sup>) were computed using Lambert-Beer's law (Smith and Baker 1978; Gordon 1989) using

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

where  $E_d(z, \lambda)$  is the irradiance at depth  $z$  and wavelength  $\lambda$  (in W cm<sup>-2</sup> nm<sup>-1</sup>) and  $E_d(0, \lambda)$  is the irradiance at the surface. The  $K_d$  values for the PRR/PUV were derived from plots of irradiance vs. depth on a log-linear scale and a least-squares line was fit to all valid data points between the surface and the deepest measurement.

In addition to the depth profiling measurements, downwelling irradiance in the UV region was continuously measured using pairs of Satlantic OCR-504UV sensors equipped with a 305 nm channel (no bioshutters) or with 305 nm, 325 nm, 340 nm, and 380 nm channels and BioShutters for control of fouling. The 305 sensors were deployed during 2002–2004 at Sombrero Tower, Florida (24°37.501'N, 81°6.095'W). The sensors equipped with BioShutters were mounted on two separate navigational markers that were located near Looe Key ~10 km south of the Summerland Key, Florida (24°32.909'N, 81°23.844'W) and near Pelican Shoals ~10 km south of Sugarloaf Key, Florida (24°30.318'N, 81°35.966'W). The sensors were separated by 1–2 m with the upper sensor 1.5 m below the water surface. Data were logged hourly from 09:00 h to 20:00 h over a 10-s observation period and were downloaded during bimonthly service visits to the tower.

*UV-visible spectra*—UV-visible spectra were measured in duplicate for filtered (0.2 μm) water samples collected concurrently with profiling casts. Samples were collected at ~1 m depth using a Van Dorn water sampler. Spectral scans were analyzed over the wavelength range of 250–800 nm on a Perkin Elmer Model Lambda 35 UV-visible Spectroscopy System in 10.00-cm quartz cells. The instrument was zeroed with Nanopure® water in both cells.

Absorption coefficients ( $a_\lambda$  in  $\text{m}^{-1}$ ) were calculated using  $a_\lambda = 2.303 D_\lambda L^{-1}$ , where  $D_\lambda$  is the measured absorbance at wavelength  $\lambda$ , and  $L$  is the pathlength of the quartz cell (in meters). The spectra were corrected for baseline offsets (Green and Blough 1994). Spectral slope coefficients were calculated by fitting absorption coefficients using

$$a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0)e^{-S(\lambda - \lambda_0)}, \quad (2)$$

where  $a_{\text{CDOM}}(\lambda_0)$  is the absorption coefficient at  $\lambda_0$  (i.e., 325 nm), and  $S$  is the spectral slope coefficient (Blough and Del Vecchio 2002), using a nonlinear least squares method (Sigma Stat, SPSS Inc.). For these calculations we only used absorption coefficients that exceeded peak-to-peak baseline noise by 5-fold ( $0.02 \text{ m}^{-1}$ ). Slope coefficients were generally calculated both over the 290–440 nm and 325–440 nm spectral regions where acceptable absorption spectra were observed for all water types included in this study. However, in agreement with previous observations (Yentsch and Reichert 1962; Blough and Del Vecchio 2002; Nelson et al. 2004), we observed a decrease of  $S$  in going from the 290–320 nm region to wavelengths  $>320$  nm; this was particularly apparent in Case 1 ocean water (blue-water). Because the decrease in absorption coefficients was not cleanly exponential over the 290–440 nm region, we chose to report spectral slope coefficients only for 325–440 nm where excellent fits (regression coefficients  $r^2 > 0.99$ ) to the exponential equation were observed in all cases.

*Determination of the particulate absorption coefficients*—Water samples (5 L) also were collected. Suspended particulate matter from water samples (5 L) from a subset of the profiling sites was collected on 0.7- $\mu\text{m}$  glass-fiber filters (GFFs), and spectral characteristics were analyzed on the Perkin Elmer Model Lambda 35 UV-visible Spectroscopy System dual beam spectrophotometer based on the quantitative filter technique (QFT) described in Roesler (1998) and Mitchell et al. (2002). Wetted filters were mounted on a thin quartz plate in the spectrophotometer, and spectral absorbance scans were conducted from 200 nm to 800 nm. A blank wetted filter was used as the reference. Particle scans were conducted in triplicate, and filters were removed and then replaced on the quartz plate to ensure that each scan analyzed a unique part of the filter. The increase in pathlength due to light scattering within the filter ( $\beta$ ) was estimated at 2 as reported in Roesler (1998), and absorption coefficients were calculated using

$$a_p(\lambda) = 2.303(D_s - D_b)/(\beta * L), \quad (3)$$

where  $D_s$  is the absorbance of the GFF containing particles,  $D_b$  is the average absorbance of the particle filter from 745 nm to 755 nm (assumed null absorbance by particles at 750 nm), and  $L$  is the pathlength ( $\text{m}^{-1}$ ) equal to the volume of water filtered divided by the area of the GFF. All particle spectral scans were analyzed within a few hours of collection.

*Dissolved organic carbon*—The dissolved organic carbon content of filtered samples (0.2  $\mu\text{m}$ ) collected concurrently

with profiling casts was measured using a Shimadzu TOC-5050A total organic carbon analyzer. The analyzer was calibrated with potassium biphthalate immediately before each set of analyses.

*Statistical treatment*—Multiple comparison procedures were performed with the MiniTab software package to test for statistically significant differences in diffuse attenuation coefficients among sets of samples grouped by site, by season, or by wavelength. The General Linear Model of Minitab was used to test for differences in mean values of the different groups. Coefficients of variation were tested using the MiniTab Homogeneity of Variance test.

*Modeling studies*—To model potentially damaging UV irradiance levels reaching the coral reef surface, we used simulated solar spectral irradiance reaching the water surface, data from this study to estimate the depth dependence for downwelling spectral irradiance and biological weighting functions for UV damage. The TUV model of Madronich (1993) and Madronich et al. (1998) was used to simulate the solar spectral irradiance reaching the water surface as a function of total ozone and other atmospheric parameters. The underwater downwelling spectral irradiance as a function of depth was computed using Eq. 1. Downwelling spectral irradiance just under the water surface ( $E_d[0, \lambda]$ ) was computed from the solar spectral irradiance at the water surface using Fresnel's Law to estimate reflective loss as the radiation passes through the air-water interface. Values of  $K_d(\lambda)$  derived from this study were used in Eq. 1 to estimate  $E_d(z, \lambda)$ . To estimate  $K_d(\lambda)$  for unmeasured regions of the spectrum that were required for the modeling studies, we used exponential fits of measured values of the measured  $K_d(\lambda)$  vs. wavelength ( $r^2 = 0.98$  typically for fits in the 325–442 nm region).

Using the modeled downwelling irradiance values, the weighted irradiance for UV damage ( $\text{UV}_{\text{int}}$ ) was then computed for a given depth using

$$\text{UV}_{\text{int}} = \int E_d(z, \lambda)(W_\lambda)d\lambda, \quad (4)$$

where  $W_\lambda$  is the biological weighting function (i.e., action spectrum).  $\text{UV}_{\text{int}}$  was integrated over all relevant wavelengths. Action spectra ( $W_\lambda$ ) for DNA damage were obtained from Setlow (1974) and action spectra for photosynthesis inhibition of *Montastraea faveolata*, a common Florida Keys coral species, were taken from Lesser (2000).

## Results and discussion

*Spatial and temporal variability in UV penetration*—UV penetration, quantified as  $K_d(\lambda)$  values, was determined using data from over 1200 underwater depth profiles that were measured at sites located in the Lower Keys along the fringing reef tract, 7 km outside the reefs in Case 1 oligotrophic bluewater, in the nearshore region (Hawk Channel) between land and the offshore reef tract, and in the western part of Florida Bay (Fig. 1). Florida Bay is highly colored and shallow, and it is strongly affected by

runoff from the Everglades and CDOM released by decaying seagrasses (Stabenau et al. 2004). The colored water in Hawk Channel is primarily derived from transport of water from Florida Bay through channels between the Keys. The reef tract in the Lower and Middle Keys is in a transition zone between the colored Case 2 waters to the north and the clear blue Case 1 waters to its south. The ocean water rapidly drops off to depths >75–150 m immediately south of the reef tract. In addition to the Lower Keys, UV penetration also was determined in the Dry Tortugas and Middle Keys during the summer.

UV penetration was lowest in the nearshore regions, especially in Florida Bay, and it increased rapidly in north-to-south transects from Hawk Channel, across the reef tract and into the deeper Case 1 waters (Fig. 2A). Attenuation in the UV region generally decreased with increasing wavelength and in most regions of the Lower Keys the  $K_d(\lambda)$  values were highest during the winter (Fig. 2B). The greatest coefficient of variation (CV) for the  $K_d(\lambda)$  values was computed for the reef tract where Case 1 waters from the deeper ocean periodically exchange with the colored water from Hawk Channel (Table 1). Letters in the “group” column in Table 1 indicate these differences. The CV for Florida Bay is not significantly different than the CVs for bluewater or Hawk Channel, thus its group designation is AB. It shares a group letter with both bluewater, group A, and Hawk Channel, group B. The CV for reef tract, uniquely designated as group C, is significantly larger than the CVs for all other sites.

Variability in light-attenuating properties between nearshore and offshore regions contributes to large fluctuations in UV exposure along the reef tract in the Lower Keys as tides and wind patterns deliver water from different sources to these reefs. To better understand the temporal nature and degree of these changes, pairs of UV sensors were mounted for extended periods at towers located near the fringing coral reefs and programmed to automatically measure UV radiation once an hour during daylight.  $K_d$  values computed using data obtained by the moored sensors (Fig. 3A) further revealed high hourly and daily irradiance variability. Tidal movements of the more-opaque Hawk Channel waters and clearer offshore waters across the reefs cause very large diurnal changes in UV penetration at the reefs. The highest  $K_d$  values corresponded to low tide, when the more opaque waters of Hawk Channel were transported out over the reef line (Fig. 3B), while  $K_d$  values were lowest when UV-transparent blue-water moved over the reef and enhanced underwater UV irradiance. Additional, similar, tidal-related diurnal variations have been described at Sombrero Tower (Zepp 2003b), and tidal-related fluctuations in UV penetration have been reported for waters near the coral reefs at Lee Stocking Island in the Bahamas (Otis et al. 2004).

Water-column UV irradiance was also measured during the late spring and summer over the period from 1998 to 2005 at the Dry Tortugas, a coral-rich cluster of islands that is located about 113 km west of Key West. The large spatial variability in CDOM that was observed in the Lower Keys is not evident in the Dry Tortugas and thus, UV attenuation around these reefs is not nearly as variable

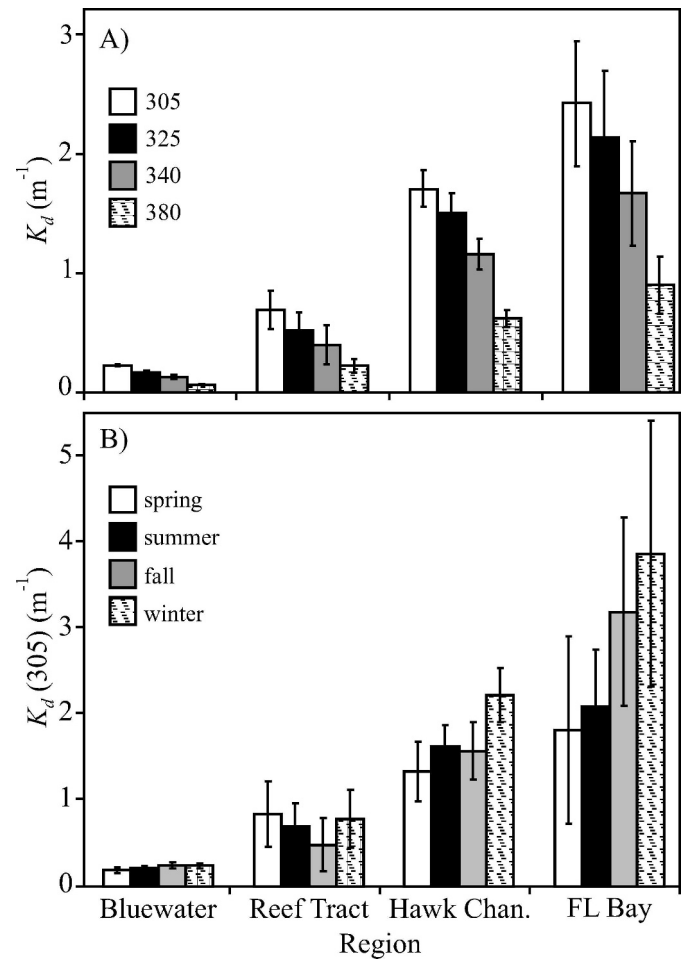


Fig. 2. (A) Spectral and (B) seasonal changes for diffuse attenuation coefficients determined by optical profiling in various regions of the Florida Keys. Ninety-five percent confidence intervals are shown as vertical lines on top of the bars for mean attenuation coefficients by sampling location.

on a diurnal and on a monthly basis. However, significant variability has occurred over a longer time frame. To illustrate the results of these studies, we present averages of our optical profiling data over all Dry Tortugas sites shown in Fig. 1 although there was some site-to-site variability (Fig. 4). During the period from 1998 to 2005 attenuation was highest in the late spring of 1998. This period of relatively high attenuation coincided with the extensive inflow of CDOM-rich shelf waters that occurred during

Table 1. Ninety-five percent confidence intervals for the CV (coefficient of variation = standard deviation divided by the mean) of attenuation coefficients by region in the Lower and Middle Florida Keys, grouped across all seasons and all wavelengths. See text for discussion.

	Lower bound	Upper bound	Group
Bluewater	0.40	0.58	A
Florida Bay	0.54	0.81	AB
Hawk Channel	0.70	0.76	B
Reef tract	0.83	1.10	C

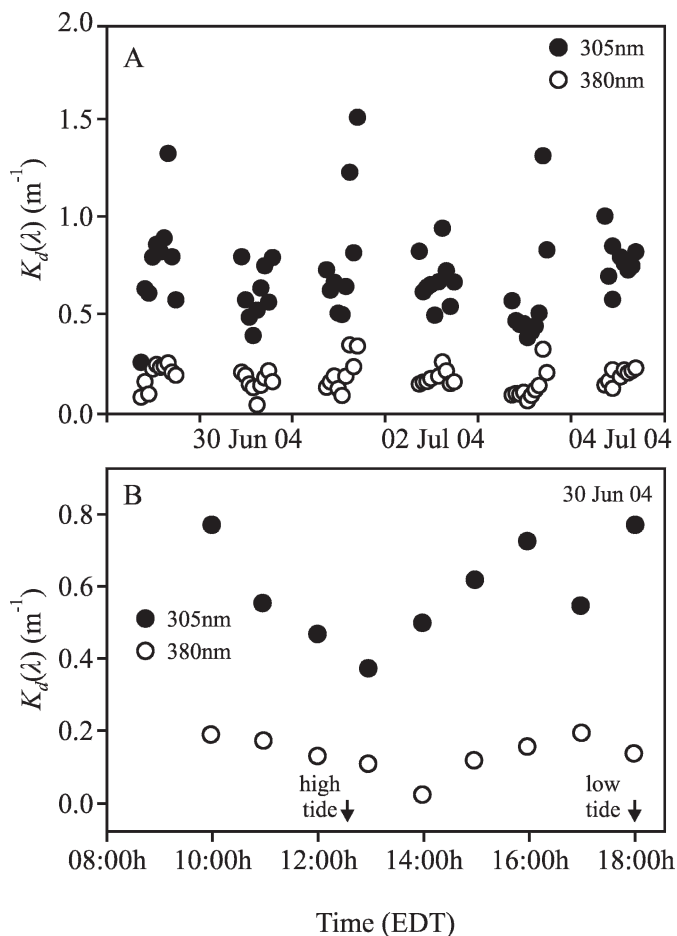


Fig. 3. (A) Diffuse attenuation coefficients during 29 June 2004 to 04 July 2004 near Looe Key Reef, Florida Keys and (B) throughout the day at Looe Key during 30 June 2004. The  $K_d$  values were derived from underwater measurements of UV-B (305 nm) and UV-A (380 nm) solar radiation by sensors moored close to the reef tract.

mid-1998. This change in CDOM may have been related to a local gyre in the region (Lee et al. 1995). UV attenuation dropped significantly by late summer of 1998 and by late summer of 1999 it dropped even further. After 1999, attenuation during the late summer leveled out and remained in a relatively narrow range through 2005.  $K_d$  values in the UV region determined in other studies in the Dry Tortugas during summer of 1995 and 1996 fell within the same range that we observed (Lesser et al. 2000). However, the seasonal variability observed elsewhere in this study indicates that the narrow range exhibited by the results for late summer after 1999 likely does not typify results throughout the year. For example, coastal runoff of a dark plume from the Everglades in South Florida affected the Dry Tortugas during 2003 (Hu et al. 2004). Comparisons with data for the Case 1 deep waters around the Florida Keys (Figs. 2, 3) show that the waters over the Tortugas reefs are significantly more UV-opaque. Unlike the Case 1 waters south of the reef tract in the Lower Keys, there are several local sources of CDOM in the Dry Tortugas such as seagrass detritus (Stabenau et al. 2004) and mangroves (Scully et al. 2004; Shank et al. unpubl.).

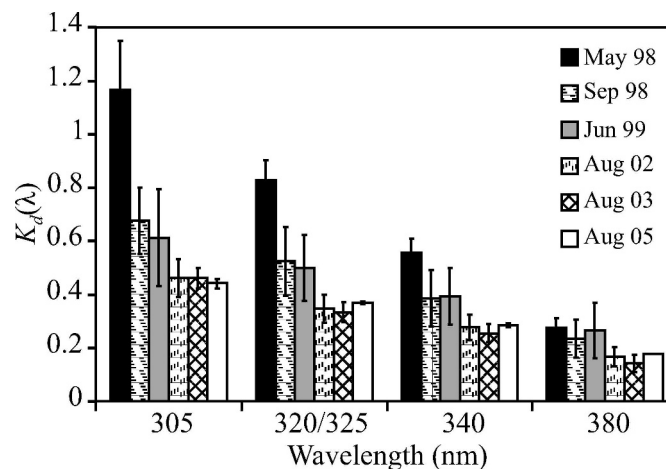


Fig. 4. Diffuse attenuation coefficients in the UV region determined during summer by optical profiling in the Dry Tortugas. Data were averaged over all sites shown in Fig. 1.

*Comparisons to other studies in the tropics and elsewhere*—A recent review of UV penetration into natural waters provides a useful overview of the variability from one water type to another (Hargreave 2003). The clearest natural waters have diffuse attenuation coefficients that fall in the  $0.1 \text{ m}^{-1}$  to  $0.2 \text{ m}^{-1}$  range at 310 nm and close to  $0.03 \text{ m}^{-1}$  for the UV-A region (380 nm). Much lower values ( $<0.05 \text{ m}^{-1}$ ) have been reported for 310 nm in the hyperoligotrophic waters in the South Pacific gyre (Morel et al. 2007b). The studies of Dunne and Brown (Dunne and Brown 1996) observed  $K_d$  values in the  $0.4 \text{ m}^{-1}$  to  $0.8 \text{ m}^{-1}$  range for 310 nm and the  $0.18 \text{ m}^{-1}$  to  $0.258 \text{ m}^{-1}$  range for 380 nm at two sites in the Indian Ocean and Andaman Sea. A closed-in site close to a pier was more opaque, with  $K_d$  values of close to  $1.5 \text{ m}^{-1}$  at 320 nm and  $0.76 \text{ m}^{-1}$  at 380 nm; the 310 nm value was likely higher than the 320 nm value. Although Gleason and Wellington (Gleason and Wellington 1995) did not report diffuse attenuation coefficients for their data sets, we compute that the  $K_d$  values reported for their UV-B dose rates were  $\sim 0.25 \text{ m}^{-1}$ . Based on calculations presented later in this paper as well as those of others for DNA damage to coral reefs (Dunne and Brown 1996; Otis et al. 2004), the dose rates for DNA-damaging UV radiation peaks at  $\sim 303\text{--}304 \text{ nm}$ . Diffuse attenuation coefficients estimated for ocean waters near Lee Stocking Island in the Bahamas were  $0.14 \text{ m}^{-1}$  at 310 nm and  $0.07 \text{ m}^{-1}$  at 380 nm during ebb tide (Otis et al. 2004). During flood tide the diffuse attenuation coefficients increased to  $0.40 \text{ m}^{-1}$  at 310 nm and  $0.18 \text{ m}^{-1}$  at 380 nm. Our data set for  $K_d$  values showed large variation at the reef tract of the Lower Keys. The 95% confidence interval throughout the year was  $0.53 \text{ m}^{-1}$  to  $0.85 \text{ m}^{-1}$  at 305 nm and  $0.17 \text{ m}^{-1}$  to  $0.28 \text{ m}^{-1}$  at 380 nm. At times, however, oligotrophic bluewater ( $K_d = 0.21\text{--}0.24 \text{ m}^{-1}$  at 305;  $K_d = 0.06\text{--}0.07 \text{ m}^{-1}$  at 380 nm) moved over the reef tract. For the Dry Tortugas during late summer in 2002–2005 and 1995 and 1996 (Lesser et al. 2000), the  $K_d$  values ranged from  $0.40 \text{ m}^{-1}$  to  $0.50 \text{ m}^{-1}$  at 320 nm and from  $0.14 \text{ m}^{-1}$  to  $0.18 \text{ m}^{-1}$  at 380 nm.

Taken together, these results indicate that the  $K_d$  values for the Lower Keys reef tract fall in almost the same range as that reported for the Indian Ocean and Andaman Sea. The Dry Tortugas values are similar to those reported for the Indian Ocean. UV penetration is significantly higher in the Bahamas, and the  $K_d$  values during ebb tide at sites near Lee Stocking Island are close to those reported for the clearest oligotrophic ocean waters. However, the clarity of these waters drops during flood tide. UV penetration reported for a site in the Upper Keys was similar to that of the oligotrophic Case 1 waters south of the reef tract in the Lower Keys.

The Florida Keys also have patch reefs located in the Hawk Channel region. Our results show that the  $K_d$  values in the UV domain for waters over these reefs are about three times larger than the values for the reef tract. This result indicates that DNA-damaging UV exposure of patch reefs at a depth of 3 m is at least six times lower for the patch reefs than at the reef tract (*see* discussion below). The stony coral cover for the patch reef habitat type was significantly greater than for other habitat types in the Florida Keys National Marine Sanctuary (Beaver et al. 2004). The greater coral cover observed for reefs in Hawk Channel could possibly be attributable in part to the shielding from damaging UV radiation although factors such as MAA content also clearly play an important role as well (Gleason and Wellington 1995; Lesser 2000; Shick and Dunlap 2002).

*Control of UV exposure by CDOM— $K_d(\lambda)$*  is an apparent optical property that depends in part on the geometry of the light field at various depths. Although an apparent optical property, the Lambert–Beer law can be applied to  $K_d(\lambda)$ , and it can be analyzed in terms of various constituents of the water that contribute to light attenua-

tion (Gordon 1989). Studies in coastal regions have shown that the primary constituents that contribute to  $K_d$  variability are CDOM, suspended particulate matter, phytoplankton and covarying detrital material, and water itself (Baker and Smith 1982; Vodacek et al. 1997; Degrandpre et al. 1996). For coastal areas absorption by water is negligible compared to the other constituents.

DOC and  $a_\lambda$  were measured in the UV region for filtered-water samples collected from the same stations where the profiling occurred. In addition,  $a_p$  were measured for a subset of sites located in the Lower Keys and in the Dry Tortugas. Several results indicated that CDOM predominantly controls UV penetration at the reef tract and inshore sites: (1) A close correlation was observed between the diffuse attenuation coefficients and DOC (Table 2) and the CDOM absorption coefficients in the UV spectral region (Fig. 5). Such statistical correlations do not necessarily demonstrate that CDOM attenuation is predominant. Light attenuation by suspended particulate matter could also account for the correlation if the particulate and CDOM absorption coefficients were strongly correlated. (2) However, other results that compare CDOM and particulate absorption coefficients (Fig. 6) show that  $a_{\text{CDOM}}$  is generally much larger than  $a_p$  and predominantly accounts for the total absorption coefficient of these waters. These results indicate that the UV attenuation is primarily caused by CDOM. The CDOM contribution to UV absorption decreases somewhat with increasing wavelength. Similar results have been reported for the Mid-Atlantic Bight (Degrandpre et al. 1996) and for ocean waters near coral reefs in the Bahamas (Otis et al. 2004).

In the case of the Case 1 bluewaters included in the study, the correlation with DOC was nonexistent (Table 2). Also, although there was statistical significance for linear

Table 2. Linear regression coefficients for  $K_d$  values ( $\text{m}^{-1}$ ) vs. dissolved organic carbon ( $\mu\text{mol C L}^{-1}$ ) in different geographic regions of the Lower Keys ( $K_d = b + m \times \text{DOC}$ ).

		305	325	340	380
Bluewater	m	0.0003	0.0005	0.0004	0.0001
	b	0.176	0.1003	0.0735	0.0482
	$r^2$	0.0388	0.1313	0.1209	0.0261
	adj. $r^2$	0.000	0.0644	0.0533	0.000
	p value	0.4816	0.1845	0.2041	0.5649
Reef tract	m	0.0141	0.0105	0.0071	0.0033
	b	-0.6495	-0.4766	-0.276	-0.0748
	$r^2$	0.3813	0.3799	0.3292	0.2233
	adj. $r^2$	0.3544	0.3001	0.30007	0.1894
	p value	0.001	0.0027	0.0027	0.0171
Hawk Channel	m	0.0204	0.0164	0.0122	0.0062
	b	-0.9135	-0.7419	-0.4927	-0.1745
	$r^2$	0.5359	0.5014	0.4411	0.3055
	adj. $r^2$	0.52954	0.494605	0.433416	0.29602
	p value	<0.0001	<0.0001	<0.0001	<0.0001
Florida Bay	m	0.0204	0.018	0.0138	0.008
	b	-0.755	-0.8167	-0.6094	-0.3851
	$r^2$	0.7602	0.7473	0.7431	0.7353
	adj. $r^2$	0.7453	0.7315	0.7271	0.7188
	p value	<0.0001	<0.0001	<0.0001	<0.0001

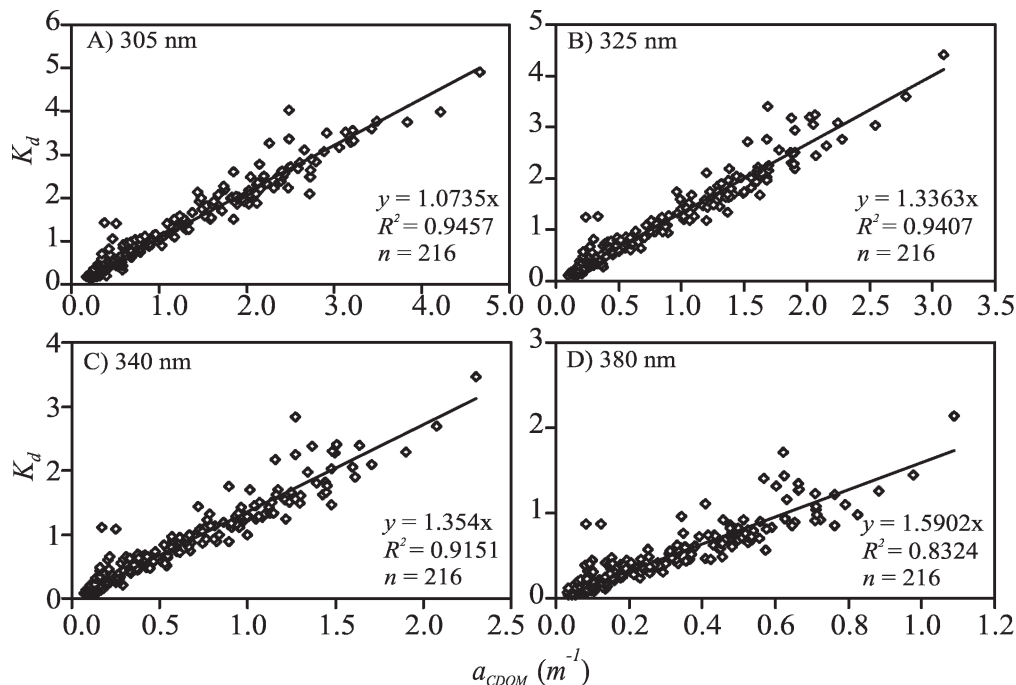


Fig. 5. Comparison of diffuse attenuation coefficients ( $K_d$ ) and absorption coefficients ( $a_{CDOM}$ ) for filtered water samples obtained at all Florida Keys sampling sites.

correlations between  $K_d$  and CDOM absorption coefficients for 305 nm and 325 nm in the bluewaters; the correlation was weak (Table 3).

Although other recent studies in ocean waters have indicated that CDOM is an important determinant of  $K_d(\lambda)$  in the UV spectral range (Nelson and Siegel 2002; Zepp 2003a; Otis et al. 2004), this study provides the first extensive evidence of the importance of CDOM in screening coral reefs from UV exposure in subtropical waters. In addition to its important role in attenuating UV,

our data show that CDOM absorbs substantially in the blue region of PAR; a mean value of >40% of 442-nm radiation was absorbed by the CDOM (Fig. 6). Thus, our results reinforce previous reports that CDOM can significantly interfere with the remote sensing of ocean color and can strongly affect the penetration of PAR in the blue spectral region (Kirk 1994; Blough and Del Vecchio 2002; Siegel et al. 2002).

*Variability of CDOM*—As was the case for  $K_d$  values (Fig. 2), absorption coefficients of filtered water samples increased sharply along the north-to-south transects, and the largest change often occurred over the narrow region representing the interface between the green-yellow waters in Hawk Channel and the blue Atlantic Ocean water. This interface is characterized not only by variability in CDOM concentrations, but also by changes to the shape of the CDOM's UV-visible absorption spectrum. These changes can be described in terms of spectral slope coefficients (defined by Eq. 2) that were determined for water samples collected concurrently during the irradiance profiling

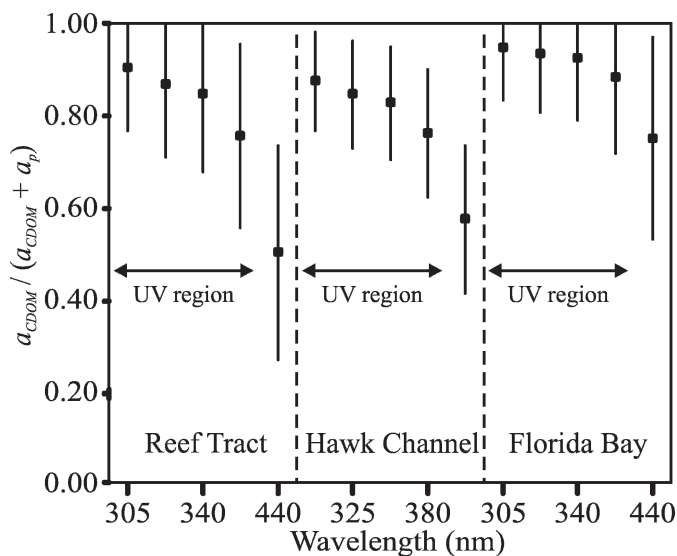


Fig. 6. Ratios of  $a_{CDOM}$  to total absorption coefficients ( $a_{CDOM} + a_p$ ) for different regions of the Lower Keys. Vertical bars indicate ninety-five percent confidence intervals ( $n = 107$ ).

Table 3. Linear regression coefficients for  $K_d$  values ( $m^{-1}$ ) vs. absorption coefficients ( $m^{-1}$ ) of filtered water samples from bluewater (Case 1) sites of the Lower Keys ( $K_d = b + m \times a_\lambda$ ) ( $m^{-1}$ ).

	305	325	340	380
$m$	0.321	0.486	0.300	0.166
$b$	0.137	0.081	0.084	0.057
$r^2$	0.179	0.223	0.095	0.029
adj. $r^2$	0.145	0.191	0.057	0.000
$p$ value	0.0312	0.0148	0.1263	0.4058

Table 4. Seasonal variations in spectral slope coefficients (325–440 nm) for sites in the Lower Florida Keys.

	Winter (Jan–Feb)	Spring (Mar–May)	Summer (Jun–Aug)	Fall (Sep–Nov)
Florida Bay	0.0199±0.0006	0.0181±0.0011	0.0178±0.0011	0.0187±0.0014
Hawk Channel	0.0196±0.0011	0.0192±0.0007	0.0181±0.0012	0.0179±0.0023
Reef tract	0.0192±0.0036	0.0203±0.0029	0.0187±0.0029	0.0193±0.0028
Bluewater	0.0203±0.0025	0.0192±0.0025	0.0196±0.0023	0.0207±0.0027

(Table 4). Because *S* values change in the UV-B region, particularly for the samples from Case 1 waters (Yentsch and Reichert 1962; Blough and Del Vecchio 2002; Nelson and Siegel 2002), we did not include this region in the calculations. The *S* values (325–440 nm) for the Case 1 bluewater samples were generally higher than the mean spectral slope coefficients measured for samples collected closer to land in locations including Hawk Channel. This was especially true during the wet summer months when *S* values decreased in Hawk Channel and Florida Bay.

The spectral slope coefficients can be used to help infer the nature and source of the UV-absorbing substances in the water. Typically, open ocean waters have higher spectral slope coefficients than coastal ocean waters due to differing sources and chemical characteristics of their CDOM pools (Blough and Del Vecchio 2002; Nelson and Siegel 2002) and this also is the case in the Florida Keys (Table 4). Observed spectral slope coefficients of CDOM in our Florida Keys samples were similar to those reported for other ocean environments (Blough and Del Vecchio 2002). However, our data indicate not only that the magnitude of CDOM does vary considerably over the reefs, but also that the sources of CDOM change. Recent studies have shown that seagrass detritus is an important source of CDOM over the Florida Keys coral reefs (Stabenau et al. 2004). The observed seasonal changes in *S* from the dry winter period to the wet summer season suggest that runoff of CDOM or CDOM sources from land also may be involved. Other potential CDOM sources in our study region include the extensive mangrove patches surrounding the Keys and large mats of floating *Sargassum* colonies.

*Stratification effects on UV exposure*—Prevailing south-easterly winds during summer in the Florida Keys induce frequent transport of Case 1 water from offshore over the reefs. Hence, seasonal changes in the surface waters of the Case 1 waters south of the reef tract are an important determinant of light exposure to corals along the reef tract. Pronounced water column stratification in the Florida Keys during the summer months can result from extended periods of decreased winds. Under these conditions, a poorly-mixed thermocline blocks upward transport of cooler, deep waters to the surface layer. Stratification is a common phenomenon in deep sub-tropical ocean waters during the summer months.

Irradiance vs. depth profiles measured during January (winter) and August (summer) 2003 at a deep site located ~8 km south of the fringing reefs are illustrated in Fig. 7. The depth dependence of both UV penetration and temperature differs between warm summer months and cold winter months. In the winter profile, the temperature was nearly uniform and the depth dependence of the downwelling irradiance was close to exponential. However, much more complex temperature and light profiles (detectable at >340 nm) developed during the summer months. The profile exhibited sharp changes in slope near 30–40 m depth, where the thermocline occurred. For example, irradiance measurements indicated that  $K_d$  (340 nm) of the warmer water in the upper 40 m was three times lower than that of the deep, cooler water below the thermocline. The  $K_d$  (340 nm) measured below 40 m during this summer profile was close to wintertime surface water  $K_d$  values. Similar seasonal changes in CDOM fluorescence

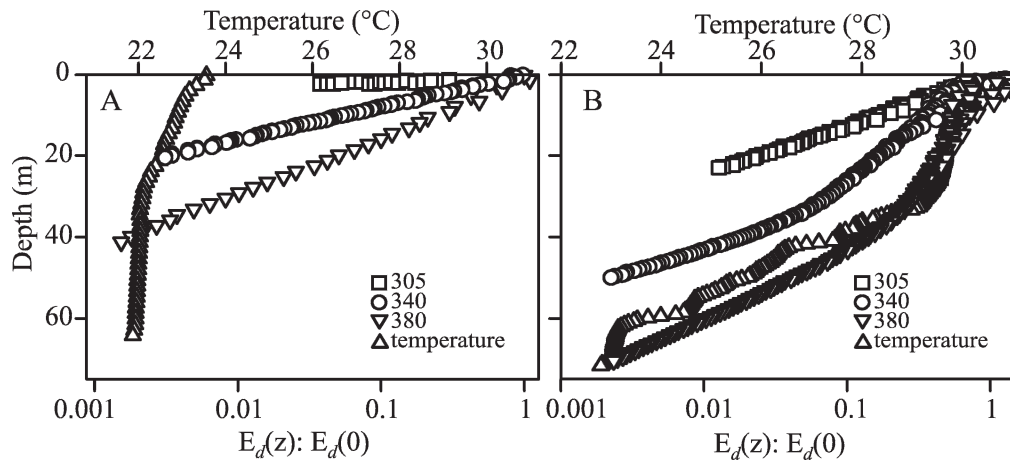


Fig. 7. Seasonal variation in temperature and UV vs. depth profiles at a site near Looe Key coral reef, Florida Keys. The 3-fold higher UV transparency of the surface waters during the summer is attributable to stratification of the water coupled with CDOM loss caused by photobleaching and microbial degradation. The  $K_d$  values at 325 nm and 340 nm for the deeper water (below the thermocline at 35 m) changed little between summer and winter. (A) Mid-January 2003; (B) mid-August 2003.

have also been observed in the Mid-Atlantic Bight off the east coast of the United States (Vodacek et al. 1997) and also in CDOM of lakes in the mid-Atlantic region of the United States (Morris et al. 1995).

It is likely that stratification resulted in a significant reduction in CDOM levels in the offshore surface waters of the Florida Keys due to the combined effect of photobleaching and subsequent microbial degradation of CDOM in the upper water column (Vodacek et al. 1997; Moran et al. 2000; Del Vecchio and Blough 2004). ‘Photobleaching,’ also observed in other ocean regions, refers to the decrease of absorption coefficients and fluorescence of CDOM in the UV and visible spectral regions that occurs during extended irradiation (Zepp 2003a; Stabenau et al. 2004; Tzortziou et al. 2007). Substantial losses of CDOM coupled with reduced inputs of more opaque deep water are likely to have caused the surface waters to become markedly clearer during the summer prior to our profiling. This photobleaching pathway for depletion of CDOM in stratified surface layers of water bodies has been found to be important in the Mid-Atlantic Bight (Del Vecchio and Blough 2004). These results support previous suggestions that increased UV exposure of corals may result from clarification of the seawater during the doldrums that accompany El Niño events (Gleason and Wellington 1993; Shick et al. 1996; Gleason 2001). In a broader context, increased UV penetration related to growing stratification in the oceans and freshwaters is one potentially important consequence of climate change (Zepp et al. 2007).

Other factors can contribute to an increase in CDOM with depth. Algal detritus collects at the thermocline in marine waters and decomposition of the detritus can result in CDOM production at depth (Chen et al. 2004; Nelson et al. 2004). This process can have particularly important effects on CDOM depth profiles during springtime algal blooms in the Sargasso Sea (Nelson et al. 2004) and in the Louisiana Bight near the Mississippi River Plume (Chen et al. 2004), but is not likely to be important during summer in the Case 1 waters south of the Florida Keys. Another interesting process that affects CDOM depth distribution involves the tidal transport of CDOM-rich plumes from high-salinity, near coastal waters into deeper offshore waters (Otis et al. 2004). This pathway is important near the Bermuda Banks where CDOM has a significant effect on UV exposure of the corals.

*Estimated UV exposure damage*—We used our extensive database detailing the optical characteristics of the water column near the Florida Keys reefs to compare fluctuations in corals UV exposure related to changing CDOM concentrations with the potential effect of atmospheric ozone variability in this region. These estimates first 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 and Zepp 1997; Neale and Kieber 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 and Kieber 2000), as originally

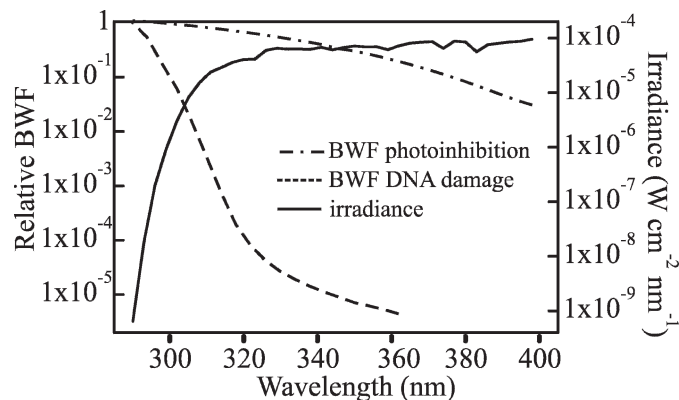


Fig. 8. Comparison of biological weighting functions (BWF) for DNA damage (Setlow 1974) and for photosynthesis inhibition of *Montastraea faveolata* (Lesser 2000) with midday July 2004 solar spectral irradiance for Looe Key Reef, Florida.

described by Rundel (1986). Unlike action spectra measured using monochromatic radiation (Coohil 1991); the Rundel approach takes into account that there are interactions between various parts of the spectrum, such as photorepair of UV-B damage by UV-A radiation.

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 photoinhibition of corals photosynthesis can be induced by solar radiation throughout the UV region (Lesser and Lewis 1996; Lesser 2000). The BWF for growth inhibition of *Symbiodinium* spp. (J. E. Rogers pers. comm.) is similar to that for DNA damage reported by Setlow (1974). The BWF for these two types of damage are compared with midday July 2004 (solar spectral irradiance at Looe Key Reef in Fig. 8). The weighted irradiance for UV damage at a certain wavelength is the cross product of the biological weighting function and the irradiance (Eq. 4). 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 was computed using Eq. (1) and measured diffuse attenuation coefficients for the time and location of interest. To complete such computations, surface irradiance was estimated using the Tropospheric Ultraviolet-Visible Model (TUV) of Madronich et al. (1998) and reflective loss at the air–water interface was computed using Fresnel’s Law (Miller et al. 2002; Zepp 2003). The estimated spectral dependence of DNA-damaging and photosynthesis-inhibiting UV dose rates as a function of depth for Looe Key Reef (Fig. 9) indicates that DNA damage decreases much more rapidly with depth than does photosynthesis inhibition. The diffuse attenuation coefficients used for the estimates in Fig. 9 were mid-range for this location, approximately halfway between those observed at high and low tides. Weighted UV irradiances computed with different action spectra have

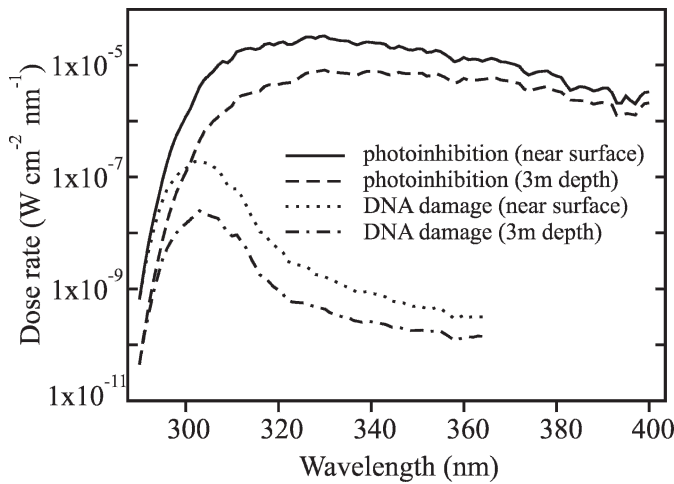


Fig. 9. Estimated spectral dependence of DNA-damaging and photosynthesis-inhibiting UV dose rates as a function of depth for Looe Key Reef in the Florida Keys. Assumptions discussed in text.

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 (Madronich et al. 1998)

$$(UV_{int})_2 / (UV_{int})_1 = [(O_3)_1 / (O_3)_2] RAF, \quad (5)$$

where  $(UV_{int})_2$  and  $(UV_{int})_1$  are the UV exposures that correspond to total ozone amounts  $(O_3)_1$  and  $(O_3)_2$ , respectively. 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 (Fig. 9). These calculations indicate that changes in underwater spectral irradiance as it downwells through the water column reduce the RAF compared to near-surface

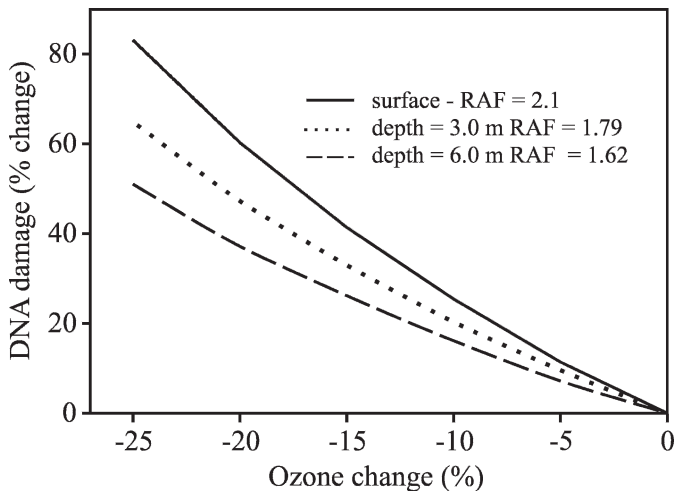


Fig. 10. Computed dependence of DNA damage and the associated radiation amplification factors on depletion of total ozone at different depths at Looe Key Reef. Comparison of estimated DNA damage and photosynthesis inhibition of *Montastraea faveolata* by depletion of total ozone.

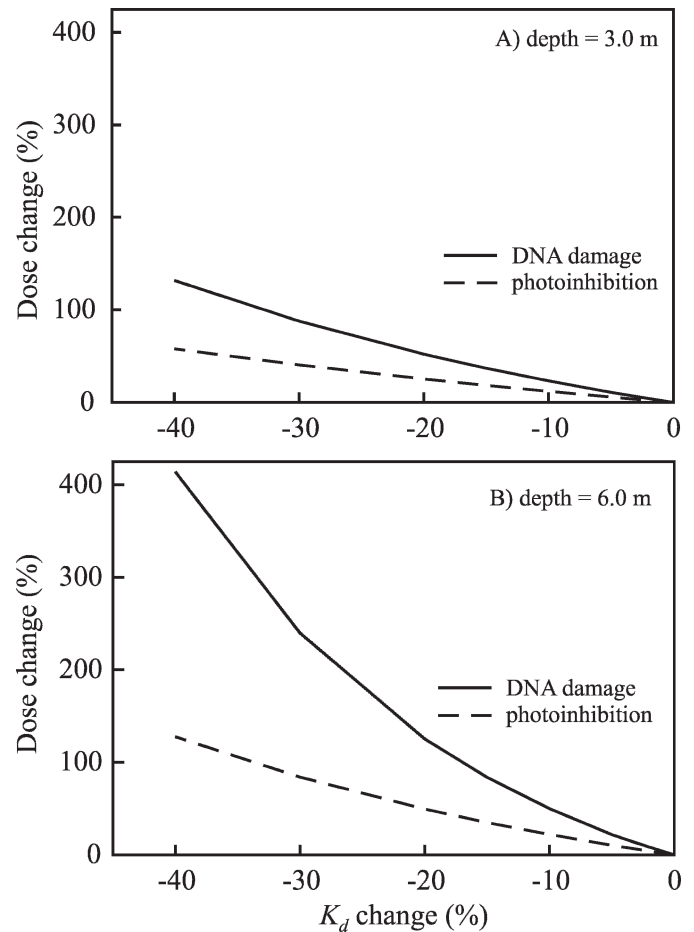


Fig. 11. Modeled effects of changing CDOM concentrations on UV-induced DNA damage (solid line) and inhibition of *Montastraea faveolata* (dashed line) at depths of (A) 3.0 m and (B) 6.0 m at Looe Key reef. At 6.0 m radiation amplification factor were 3.26 for DNA damage and 1.65 for photosynthesis inhibition.

conditions (Fig. 10). These results are consistent with earlier modeling studies of the depth dependence of ozone depletion effects on a marine diatom and dinoflagellate in the Antarctic (Cullen et al. 1992). As previously shown by Lesser (2000), the RAF for photosynthesis inhibition is quite low compared to that for DNA damage because photoinhibition is induced primarily by UV-A radiation which is insensitive to ozone changes.

The effects of changing UV attenuation coefficients on underwater UV exposure can be described in a similar manner:

$$(UV_{int})_2 / (UV_{int})_1 = [(K_{d,UV})_1 / (K_{d,UV})_2] RAF, \quad (6)$$

where  $(UV_{int})_2$  and  $(UV_{int})_1$  are the exposures at a certain depth that correspond to UV diffuse attenuation coefficients  $(K_{d,UV})_1$  and  $(K_{d,UV})_2$ , respectively. The computed dependence of  $UV_{int}$  for DNA damage and for photosynthesis inhibition on attenuation coefficients at depths of 3.0 m and 6.0 m at Looe Key Reef is shown in Fig. 11. For these calculations, the dose rates for DNA damage and for photosynthesis inhibition were computed assuming various

across-the-board reductions in the UV-diffuse attenuation coefficients for Looe Key. Both these results and earlier studies of Dunne and Brown (1996) have shown that DNA damage potentially is quite sensitive to attenuation within the water column over coral reefs. In addition, the present studies show that, unlike the case of atmospheric ozone changes, UV attenuation coefficient changes in water over the reefs have substantial effects on both DNA damage as well as photosynthesis inhibition. To illustrate the significance of changes, the results in Fig. 11 indicate that a 30% decrease in  $K_d$  (not uncommon at the reefs where UV variability was greatest, see Table 1) can result in an equivalent increase in UV-induced photosynthesis inhibition and an even larger enhancement in DNA damage for a typical reef depth of 3 m. The magnitude of the RAFs is a function of depth as well (Fig. 11); 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 in the water column than atmospheric ozone, especially inhibition of the photosynthetic system.

In summary, the modeling results indicate that UV-induced DNA damage as well as photosynthesis inhibition of a coral species are highly sensitive to changes in the UV attenuation coefficients of the overlying ocean waters. Radiation amplification factors for changes in  $K_d$  values are as high or higher than those computed for the effects of ozone depletion on DNA damage. These results, coupled with other observations of the high variability of UV attenuation in ocean waters over the reefs in the Florida Keys, suggest that variability in ocean UV attenuation linked with climate change or other human perturbations may be a considerably more potent stressor of coral reefs than has been previously realized.

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