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Effects of Stormwater Nutrient Discharges on Eutrophication Processes in Nearshore Waters of the Florida Keys

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ABSTRACT: Rainfall events cause episodic discharges of groundwaters contaminated with septic tank effluent into nearshore waters of the Florida Keys, enhancing eutrophication in sensitive coral reef communities. Our study characterized the effects of stormwater discharges by continuously (30-min intervals) measuring salinity, temperature, tidal stage, and dissolved oxygen (DO) along an offshore eutrophication gradient prior to and following heavy rainfall at the beginning of the 1992 rainy season. The gradient included stations at a developed canal system (PP) on Big Pine Key, a seagrass meadow in a tidal channel (PC), a nearshore patch reef (PR), a bank reef at Looe Key National Marine Sanctuary (LK), and a blue water station (BW) approximately 9 km off of Big PIne Key. Water samples were collected at weekly intervals during this period to determine concentrations of total nitrogen (TN), ammonium (NH4+), nitrate plus nitrite (NO₃⁻ plus NO₂⁻), total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), and chlorophyll a (chl a). Decreased salinity immediately followed the first major rainfall at Big Pine Key, which was followed by anoxia (DO ≤ 0.1 mg l⁻¹), high concentrations of NH₄+ (\sim 24 μ M), TDP (\sim 1.5 μ M), and chl a (\sim 20 μ g l⁻¹). Maximum concentrations of TDP (~0.30 µM) also followed the initial rainfall at the PC, PR, and LK stations. In contrast, NH₄+ (~4.0 μM) and chl α (0.45 μg l⁻¹) lagged the rain event by 1-3 wk, depending on distance from shore. The highest and most variable concentrations of NH4+, TDP, and chl a occurred at PP, and all nutrient parameters correlated positively with rainfall. DO at all stations was positively correlated with tide and salinity and the lowest values occurred during low tide and low salinity (high rainfall) periods. Hypoxia (DO ≤ 2.5 mg l⁻¹) was observed at all stations following the stormwater discharges, including the offshore bank reef station LK. Our study demonstrated that high frequency (daily) sampling is necessary to track the effects of episodic rainfall events on water quality and that such effects can be detected at considerable distances (12 km) from shore. The low levels of DO and high levels of nutrients and chl a in coastal waters of the Florida Keys demand that special precautions be exercised in the treatment and discharge of wastewaters and land-based runoff in order to preserve sensitive coral reef communities.

Introduction

Protecting water quality and the long-term health of the Florida Reef Tract is an issue of national concern as this outstanding natural resource represents North America's only living coral reef ecosystem. Numerous scientific and management workshops have addressed the effects of expanding human activities on this resource, which led to passage of the Florida Keys National Marine Sanctuary Act by the United States Congress in 1990. While a suite of human impacts have been recognized, water quality degradation resulting from nutrient overenrichment and eutrophication is considered the most significant and widespread problem (National Occanic and Atmospheric Administration 1988; United States Environmental Protection Agency 1993). Cor-

al reefs have low nutrient thresholds for the onset of decline from eutrophication, as noted in Hawaii (Smith et al. 1981), Barbados (Tomascik and Sander 1985, 1987), the Florida Keys (Lapointe and Clark 1992), and the Great Barrier Reef (Bell 1992), thus the concern regarding nutrient overenrichment.

Most studies of coastal eutrophication consider surface runoff as the major pathway of nutrient input, although submarine groundwater discharge accounts for substantial inputs to many coastal systems (Johannes 1980; Valiela et al. 1990). Submarine groundwater discharge results from groundwater percolating up through nearshore sediments, driven by the hydraulic head differential between the receiving water and the water table on the adjacent land mass. Submarine groundwater discharge delivers three to five times as much ni-

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trate to coastal waters as riverine inputs along the north Perth coastline in Western Australia (Johannes and Hearn 1985). It is also an important route of anthropogenic nutrient input in the Florida Keys, where high groundwater tables and transmissive limestone substrata occur along with the widespread use of septic tanks, cesspits, and injection wells for on-site sewage disposal systems (Lapointe et al. 1990; United States Environmental Protection Agency 1992). Although the importance of watershed rainfall as a major factor regulating riverine nutrient inputs and primary production has been recognized for temperate estuaries (Mallin et al. 1993), the relationship of rainfall to episodic nutrient enrichment via submarine groundwater discharge and its ecological effects have not been assessed in the coastal waters of the Florida Keys.

One pervasive impact resulting from the widespread use of on-site disposal systems in the Florida Keys is the reduction of dissolved oxygen (DO) concentrations in nearshore waters (Lapointe and Clark 1992). Such reductions in DO result from the contamination of groundwaters and surface waters with untreated or partially treated wastewater effluents that have high levels of biochemical oxygen demand (BOD) (Mitchell 1974; Bicki et al. 1984). In addition, submarine groundwater discharge of nutrient-enriched groundwaters increase phytoplankton biomass (chlorophyll a), light attenuation, and community respiration, all of which reduce DO levels, particularly during warm, cloudy periods (Odum and Wilson 1962; Valiela et al. 1990; Lapointe et al. 1994). Most pollution studies make single-point measurements of DO during daylight hours; however, the minimal daily DO occurs during pre-dawn hours, so midday measurements alone lead to misconceptions of ecosystem status (Johannes 1975; Lapointe and Clark 1992).

This study tested the hypothesis that rainfall-driven stormwater inputs to nearshore waters of the Florida Keys results in "pulsed" submarine groundwater discharge of wastewaters that subsequently cause transient periods of nutrient enrichment, development of widespread phytoplankton blooms, and reduced DO. To address this hypothesis, our study characterized nutrient concentrations, chlorophyll a (chl a), DO, salinity, and tidal stage along an offshore transect from Big Pine Key to Looe Key National Marine Sanctuary (LKNMS) during the transition period from the dry season to the wet season. Our previous research on effects of land-based wastewater nutrient enrichment on productivity and trophic structuring of seagrass communities along this transect demonstrated its use as a eutrophication gradient (Lapointe et al. 1994). As noted by Ketchum (1967), if the total nutrient concentration of lower salinity coastal water is higher than that of more offshore, higher salinity waters, then a land-based source of nutrients is indicated.

Materials and Methods

ENVIRONMENTAL SETTING

The Florida Keys, a 220-mile-long archipelago of low-lying carbonate islands stretching from Key Largo to Dry Tortugas, are flanked by the Gulf of Mexico and Florida Bay to the north and west and the Straits of Florida and Atlantic Ocean to the south and east. Channels between the Keys allow for the net transport of water from the Gulf of Mexico and Florida Bay seaward toward the offshore bank reefs and the Straits of Florida (Smith 1994; Fig. 1). The climate of the Keys is typical of the "wet and dry" tropics, with over 80% of the annual rainfall falling between June and October (average annual rainfall is ~54 inches yr⁻¹; Mac-Vicar 1983). Tides in Monroe County are semidiurnal on the Atlantic coast and mixed on the Gulf of Mexico coast. Mean sea level varies by 24 cm through the year, with maximum tides occurring between May and October (Marmer 1954).

Human development of the Florida Keys over the past several decades has significantly increased wastewater nutrient discharges to coastal waters. During the 1950s and 1960s, extensive canalization (utilizing dredge and fill operations) of the Keys provided greater boating access for residential and tourism development. Freshwater recharge of groundwaters in the Florida Keys has been increased by human development as a result of potable water supplies being pumped into the Florida Keys from well fields on the South Florida mainland (current freshwater flows into the Florida Keys are ~14 million gallons per day; United States Environmental Protection Agency 1992). With the exception of the two incorporated areas in the Keys-Key West and Key Colony Beach-that have centralized wastewater collection and secondary treatment, the remaining areas of the Keys rely on on-site disposal systems. The extensive canal systems in the Keys, as well as contiguous nearshore waters, are mixing zones where groundwater nutrients derived from on-site disposal systems discharge into nearshore waters (Lapointe et al. 1990; Lapointe and Clark 1992). Approximately 65% of the domestic wastewater in the Florida Keys is disposed of by on-site sewage disposal systems (OSDS), which include ~25,000 septic tanks (regulated by Chapter 10D-6 of the Florida Administrative Code as administered by the Florida Department of Health and Rehabilitative Services) and ~11,000 illegal cesspits (George Garrett, Monroe County personal communication). The re-

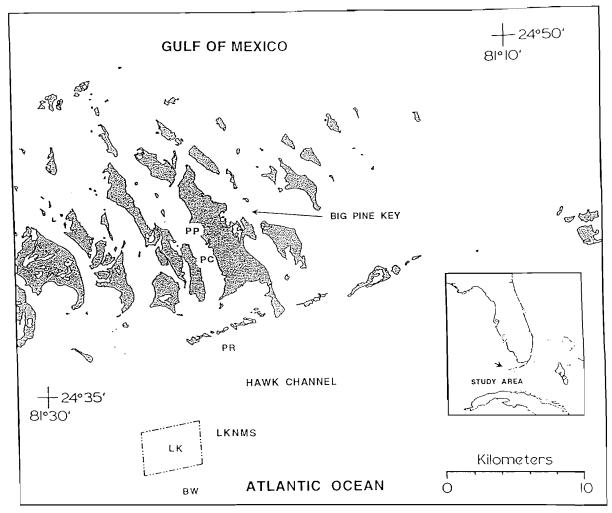


Fig. 1. Map of the study area in the lower Florida Keys adjacent to Big Pine Key showing the water quality monitoring stations. LOOE KEY (LK), N 24°32′84.1", W 81°24′43.8"; PATCH REEF (PR) N 24°36′79.0", W 81°23′67.0"; PINE CHANNEL (PC), N 24°42′07.4", W 81°24′52.1"; PORT PINE (PP), N 24°43′39.5", W 81°23′94.4"; BLUE WATER (BW), N 24°31′29.8", W 81°24′23.3".

maining wastewater from the OSDS's is disposed of by \sim 1,000 aerobic treatment units that discharge into shallow (20–30 m) injection wells regulated by the Florida Department of Environmental Protection (United States Environmental Protection Agency 1992, 1993).

HYDROLAB MONITORING

Our eutrophication gradient extended from inshore waters of Big Pine Key to ~9 km offshore (south) and included four continuously monitored stations: a canal system directly impacted by septic tank discharges (Port Pine Canal, PP), a seagrass meadow in a tidal channel (Pine Channel, PC), a patch reef inshore of Hawk Channel (PR), and an offshore bank reef at Looe Key National Marine

Sanctuary (LK, Fig. 1; Table 1). A fifth station (BW) was located 12 km offshore and 3 km south of Looe Key National Marine Sanctuary in blue water and was monitored at weekly intervals for nutrients and chl a. Hydrolab Data Sonde 3 multiplesensor water quality data-logging instruments were deployed simultaneously at each of the four stations in 1-2 m water depth, and remained in place between April 9 and August 6, 1992, to provide continuous monitoring along the nearshore portion of the eutrophication gradient. This sampling regime allowed us to assess short-term (diel and individual storm events) as well as longer term, seasonal variability in water quality parameters. By initiating sampling during the dry season (April and May) and continuing through the wet season in

TABLE 1. Descriptive statistics for five Hydrolab Datasonde parameters.

Location	Parameter	Number	Minimum	Maximum	Mean	Standard Error	Standare Deviation
Port Pine			<u> </u>				
	Temperature (°C)	4,343	21.12	32.86	29.28	0.04	2.64
	pН	4,343	7.52	8.37	8.04	0.00	0.16
	Salinity (‰)	4,343	29.3	39.5	36.33	0.03	1.83
	Dissolved oxygen (mg 1-1)	4,343	0	8.22	2.98	0.03	1.92
	Tide (m)	4,343	1.17	1.82	1.40	0.00	0.12
Pine Channel							
	Temperature (°C)	4,345	20.37	34.14	28.56	0.04	2.53
	Hq	4,345	7.81	8.99	8.25	0.00	0.13
	Salinity (‰)	4,345	29.8	39.5	35.94	0.03	2.09
	Dissolved oxygen (mg l ⁻¹)	4,345	1.39	12.01	5.68	0.03	1.76
	Tide (m)	3,347	1.26	2.14	1.73	0.00	0.14
Patch Reef							
	Temperature (°C)	4,345	22.7	33.31	28.33	0.04	2.33
	pH	4,345	7.86	9.42	8.21	0.00	0.10
	Salinity (‰)	4,345	33.5	38.6	36.55	0.02	1.29
	Dissolved oxygen (mg l-1)	4,345	1.44	11.45	6.02	0.02	1.43
	Tide (m)	4,345	3.3	4.34	3.83	0.00	0.17
Looe Key							
	Temperature (°C)	4,344	23.28	32.13	27.94	0.03	2.25
	pH	4,334	7.1	8.5	8.18	0.00	0.09
	Salinity (‰)	3,030	33.4	37.6	36.40	0.01	0.53
	Dissolved oxygen (mg 1-1)	4,343	1.65	12.98	6.12	0.02	1.35
	Tide (m)	3,323	1.17	2.2	1.68	0.00	0.18

June and July, we characterized the effects of the "first flush" on water quality parameters and eutrophication processes. Rainfall was monitored with a gauge at PP throughout the study; rainwater samples for nutrient analysis were collected in clean high-density polyethylene containers.

The Hydrolabs provided continuous records of water quality parameters, including temperature, specific conductance, salinity, DO, and depth. Concrete mooring systems were constructed to stabilize the Hydrolabs; a PVC shield was included to reduce physical damage, sedimentation, and light that contribute to fouling of the sensors. Preliminary experiments showed that the Hydrolabs provided accurate data for only 5-6 d due to biofouling of the sensors. Accordingly, we deployed the Hydrolabs for five consecutive 3-wk periods by cleaning the sensors at 4-d intervals; to achieve this, over 100 individual maintenance missions were performed during the study. The Hydrolabs were programmed to collect ambient water quality data at 30-min intervals. Prior to each 3-wk deployment, the specific instrument checks and calibration protocols described below were carried out.

Temperature

The temperature sensor was factory set and required no calibration or maintenance; however, at each calibration, temperature was checked against a laboratory thermometer (Walter H. Kessler

#2056 mercury thermometer) as a check for accuracy.

Specific Conductance/Salinity

The Hydrolabs were recalibrated for specific conductance/salinity with conductivity/salinity standards prior to each deployment. Ambient seawater in the sampling area has an average conductance of 50 mS cm⁻¹, hence we used a conductivity standard that "bracketed" that value. A YSI 3165 Conductivity Calibrator Solution (100 mS cm⁻¹) was mixed (1:1 volume/volume) with deionized water to yield a conductivity standard of 50 mS cm⁻¹. The salinity of a sterilized, filtered standard seawater sample was also determined with a factory-calibrated SeaBird CTD and used for intercalibration of salinity measurements.

Dissolved Oxygen

DO calibration of the Hydrolabs began with replacement of the DO membrane. One day prior to instrument deployment, a new low-flow membrane was installed on the DO probe, stretched, and conditioned in deionized water overnight. The following day barometric pressure was recorded and entered into the DO calibration system while the new, relaxed membrane was fully saturated. The air calibration method described in the Hydrolab Operating Manual was used as well as a common bath in which all four instruments were immersed simultaneously. Pre- and postdeployment cross-cali-

bration checks were performed with a Seabird CTD and by Winkler titration (using a Hach Digital Titrator) to detect any significant instrument drift and to insure accurate DO measurement. Time series DO data derived from the Hydrolab deployments were analyzed along with tide and salinity data using the distance-weighted least squares method. This allowed us to produce a three-dimensional statistical representation of the interaction among DO, tide, and salinity.

Depth

Calibration of the depth sensor was accomplished by entering zero for the standard at the water surface. This system was checked at the study sites by use of a standard tape measure as depths were within 2–3 m of the surface.

NUTRIENTS AND CHLOROPHYLL A

Water samples were collected for determination of ammonium (NH₄⁺), total nitrogen (TN), nitrate plus nitrite (NO₃⁻ plus NO₂⁻), total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), and chlorophyll a (chl a) at each of the four Hydrolab stations and the offshore BW station at approximately 1-wk intervals between April 27 and July 30, 1992. Our study focused on concentrations of NH₄⁺ due to its predominance in groundwaters contaminated by septic tank effluent (Lapointe et al. 1990) and in surface waters of the Florida Keys (Lapointe and Clark 1992). TDP was measured because this nutrient pool includes dissolved organic phosphorus (DOP), the major dissolved phosphorus pool that supports macroalgal blooms in coastal waters of the Florida Keys via alkaline phosphatase hydrolysis of organic phosphorus monoesters (Lapointe 1989; Lapointe et al. 1994). Chl a concentrations were measured as an index of phytoplankton biomass, the best overall parameter for monitoring eutrophication on coral reefs (Laws and Redalje 1979).

Duplicate water samples were collected adjacent to the Hydrolab units (~2 m depth) and at the BW station (2 m depth) into clean, high-density polyethylene bottles and kept on ice in the dark during return to the laboratory. One aliquot of each sample was filtered through a 0.45-µm GF/F filter. The filter was analyzed for chl a using a modified dimethyl sulfoxide (DMSO)-acetone method (Burnison 1979) for extraction followed by measurement of fluorescence on a Turner Designs Model 10 fluorometer calibrated with known concentrations of reagent-grade chlorophyll. The filtrate of each water sample was frozen until analysis for NH₄+ (Slawk and MacIsaak 1972) and TDP on a Technicon Autoanalyzer II; TDP was determined

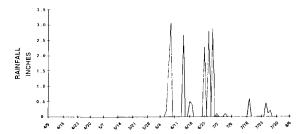


Fig. 2. Weekly rainfall during the study period.

by persulfate digestion followed by the molybdenum-blue method for SRP (Menzel and Corwin 1965). Whole, unfiltered water samples were predigested with persulfate then analyzed for TN (D'Elia et al. 1977) and TP (Menzel and Corwin 1965).

Results

RAINFALL

The spring and early summer of 1992 were typical of the transition from the dry to wet season in the Florida Keys. Between April 9 and the end of May, there was no significant rainfall and this period provided a dry season baseline for our study. The wet season began in the first week of June when a total of 5.0 inches of rain fell; 3.6 inches fell the second week, 5.0 inches the third week, and 3.0 inches the last week, totaling 16.6 inches for the month. During July, 2.5 inches of rain fell (Fig. 2).

HYDROLAB MEASUREMENTS

The Hydrolab records at all four stations illustrated the transition from the cooler, drier spring months to the warmer, wetter summer months. The minimum, maximum, and mean values of the five parameters measured with the Hydrolabs are provided in Table 1.

Port Pine Canal

A mid-spring cold front in late April, which reduced water temperatures to 21.1°C at PP, was followed by a continuous warming trend in June and July, and a temperature peak of 32.9°C in August. Salinity at this station increased steadily during the spring dry season, to a maximum of 39.5‰ at the end of May; it decreased with the onset of the rainy season and reached a minimum value of 29.3‰ in early July, after which it increased (Fig. 3).

The DO concentrations at PP averaged 2.9 ± 1.9 mg I^{-1} (n = 4,343) during the study (Table 1). The maximum DO values, up to 8.8 mg I^{-1} , occurred during midday in the cooler, drier period in April and May. DO values decreased to hypoxic (<2.5 mg I^{-1}) and anoxic (DO < 0.1 mg I^{-1}) levels with

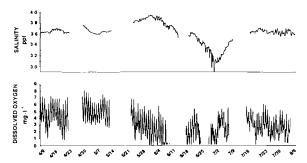


Fig. 3. Dissolved oxygen (mg 1^{-1} ; n = 4,343) and salinity (parts per thousand, n = 4,343) between April 9 and August 6, 1992, at the Port Pine Canal station on Big Pine Key, Florida.

the onset of the rainy season in early June (Figs. 3 and 4). Low DO levels at PP began on May 30 concurrent with the beginning of the rainy season and reduced salinity; persistent anoxia began on June 8 when the first heavy rainfall (>3 inches) of the season occurred (Fig. 4). Over the course of this study, DO levels correlated negatively with temperature (p < 0.001) and positively with salinity (p < 0.001) and tide (p < 0.001). Reduced salinity from rainfall and ebbing tides interacted to reduce DO levels at PP (Fig. 5).

Pine Channel

The mid-spring cold front in late April reduced water temperatures to 20.4°C at PC, followed by a continuous warming trend through June and July, and a water temperature peak at 34.1°C in August. Salinity at this station increased steadily during the dry season in April and May, and peaked at 39.5% at the end of May. Salinity decreased with the onset of the rainy season and reached a minimum value of 29.8% in late June and early July, after which it increased (Fig. 6).

The DO concentrations at PC averaged 5.7 ± 1.8

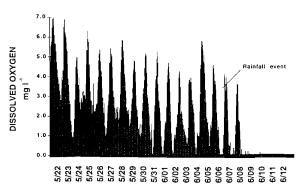


Fig. 4. Time series dissolved oxygen (mg l⁻¹) at Port Pine Canal between May 22 and June 12, 1992, showing anoxia following the initial rainfall event.

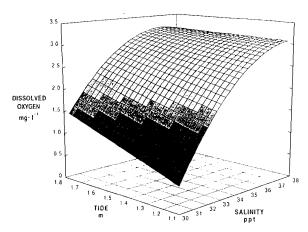


Fig. 5. Surface response curve of dissolved oxygen (mg 1^{-1} , n=4,343) versus tide (meters, m; n=4,343) and salinity (parts per thousand, n=4,343) at Port Pine Canal during the study period.

mg l⁻¹ (n = 4,345) during the course of the study. The maximum DO values, up to 12.0 mg l⁻¹, occurred during midday in the cooler, drier period in May and decreased with the onset of the rainy season; the minimum value of 1.4 mg l⁻¹ followed the first major rainfall on June 6. Substantial diurnal variability in DO occurred in the seagrass meadows at PC, with hypoxic values ranging from <2.0 mg l⁻¹ before dawn to >6.0 mg l⁻¹ at midday (Fig. 6). DO at PC correlated negatively with temperature (p < 0.001) and positively with salinity (p = 0.004) and tide (p < 0.001).

Patch Reef

The mid-spring cold front in late April reduced water temperatures to 22.7°C at PR, followed by a continuous warming trend through June and July, and a water temperature peak at 33.3°C in August. Salinity at PR increased during the dry season in April and May and peaked at 38.6‰ in early June.

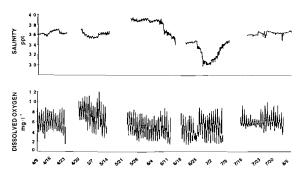


Fig. 6. Dissolved oxygen (mg l^{-1} ; n=4,345) and salinity (parts per thousand, n=4,345) at Pine Channel during the study period.

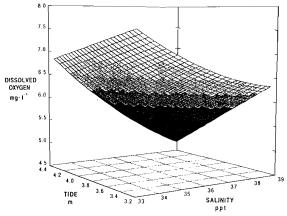


Fig. 7. Surface response curve of dissolved oxygen (mg l^{-1} ; n=4,345) versus tide (meters, m; n=4,345) and salinity (parts per thousand, n=4,345) at the Patch Reef during the study period.

Salinity decreased with the onset of the rainy season and reached a minimum value of 33.5‰ in early July, after which it increased.

The average DO concentration at PR was 6.0 ± 1.4 mg l⁻¹ (n = 4,345) during the study. The maximum DO values, up to 11.5 mg l⁻¹, occurred during the cooler, drier period in May. DO concentrations began decreasing after May 30 and reached a minimum value of 1.4 mg l⁻¹ in late July. The reduced DO concentrations at this site began after June 6 when salinity decreased following the onset of the rainy season. Over the course of the study, DO at PR correlated negatively with temperature (p < 0.001) and positively with salinity (p < 0.001) and tide (p < 0.001). Reduced salinity (resulting from rainfall) and ebbing tides interacted to reduce DO levels at PR (Fig. 7).

Looe Key

The mid-spring cold front in late April reduced water temperatures to a low of 23.3°C at LK, followed by a continuous warming trend through June and July, and a water temperature peak at 32.1°C in August. Salinity at LK increased steadily during the dry season in April and May and peaked at 37.6‰ in early August. Salinity dropped sharply in early June with the onset of the rainy season and reached a minimum value of 33.4‰ in early July, after which it increased (Fig. 8).

The DO concentrations at LK averaged 6.1 ± 1.4 mg 1^{-1} (n = 4,343) during the study. The maximum DO values, up to 12.9 mg 1^{-1} , occurred during the cooler, drier period in May. DO concentrations decreased following the onset of rainfall, and minimum values of 1.65 mg 1^{-1} occurred between June 9 and 12 (Fig. 9). Following the onset of the

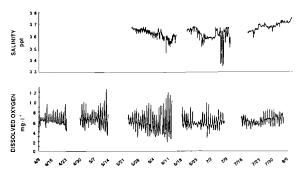


Fig. 8. Dissolved oxygen (mg 1^{-1} , n = 4,345) and salinity (parts per thousand, n = 3,030) at Looe Key National Marine Sanctuary during the study period.

rainy season in Junc, there was a trend of increased diel variability in DO concentrations indicated by lower minima and higher maxima (Fig. 9). Over the course of the study, DO at LK correlated negatively with temperature (p < 0.001) and positively with salinity (p < 0.001) and tide (p < 0.001); reduced salinity and ebbing tides interacted to reduce DO levels at LK (Fig. 10).

Blue Water

A water column profile of DO and salinity on July 24 showed the presence of lower salinity, lower DO water from the surface to a 20-m depth at BW (Fig. 11).

NUTRIENTS AND CHLOROPHYLL A

The TN and TP concentrations of rainfall collected on June 12 and June 24 at PP averaged 14.9 \pm 5.6 μM and 0.03 \pm 0.0 μM , respectively. Concentrations of NO₃ plus NO₂ averaged 9.9 \pm 0.0 μM and NH₄ averaged 6.2 \pm 0.3 μM . SRP concentrations in rainfall were <0.03 μM on both samplings.

NH₄⁺ concentrations increased at all stations following the initial rainfall in early June. For exam-

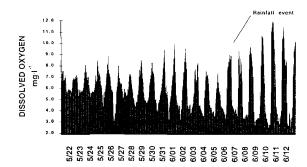


Fig. 9. Time series dissolved oxygen (mg l⁻¹) at Looe Key National Marine Sanctuary between May 22 and June 12, 1992, showing hypoxia following the initial rainfall event.

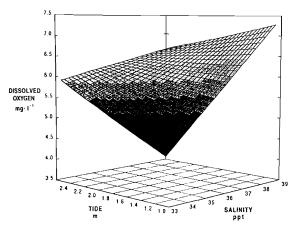


Fig. 10. Surface response curve of dissolved oxygen (mg l^{-1} , n = 4,343) versus tide (m, n = 4,343) and salinity (parts per thousand, n = 4,343) at Looe Key National Marine Sanctuary.

ple, NH_4^+ concentrations at PP during May were $<2.0 \mu M$ and increased to over 20 μM concurrent with the onset of rainfall and reduced salinity on June 10 (Fig. 12). Maximum NH_4^+ concentrations

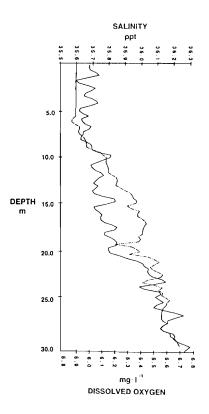


Fig. 11. Dissolved oxygen (mg l⁻¹) and salinity (parts per thousand) depth profile at the offshore blue water station on July 24, 1992.

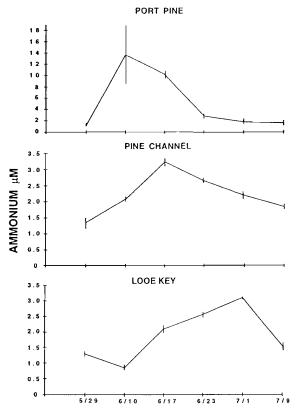


Fig. 12. Ammonium concentrations (μ M) at three stations (Port Pine, Pine Channel, Looe Key) between May 29 and July 9, 1992. Values represent means ± 1 standard error (n = 3).

occurred at PC on June 17 and at LK on July 1 (Fig. 12); the maximum NH₄+ concentrations occurred at the BW station on July 24. Over the entire study, NH₄+ concentrations at PP correlated significantly with rainfall (r = 0.37, p = 0.023). NH₄+ averaged 5.48 \pm 5.1 μ M at PP, 2.25 \pm 0.69 μ M at PC, 1.86 \pm 0.97 μ M at PR, 2.02 \pm 0.88 μ M at LK, and 1.1 \pm 0.61 μ M at BW. Nitrate plus nitrite averaged 1.09 \pm 0.77 μ M at PP, 1.38 \pm 0.50 μ M at PC, 0.70 \pm 0.31 μ M at PR, 0.84 \pm 0.51 μ M at LK, and 0.26 \pm 0.09 μ M at BW.

In contrast to $\mathrm{NH_4}^+$, TDP concentrations increased at all stations immediately following the initial rainfall and then decreased over the remainder of the study. TDP concentrations at PP during May were <0.3 μ M and increased to >0.9 μ M concurrent with rainfall in early August; over the entire study, TDP concentrations at PP correlated significantly with rainfall (r = 0.37, p < 0.001). The increase in TDP following the rainfall was observed at PC, LK, and BW; following this increase, TDP decreased over the remainder of the study at these stations (Fig. 13).

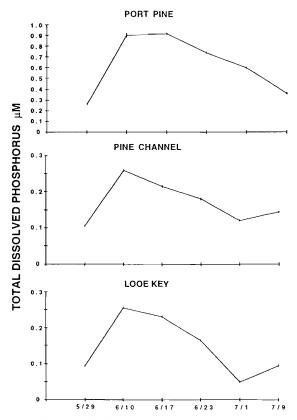
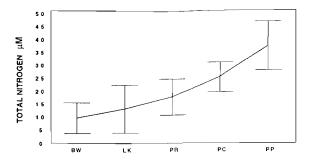


Fig. 13. Total dissolved phosphorus concentrations (μ M, n = 22) at three stations (Port Pine, Pine Channel, Looe Key) between May 29 and July 9, 1992. Values represent means ± 1 standard error (n = 3).

As a result of temporal changes in dissolved inorganic nitrogen (DIN = NH_4^+ plus NO_3^- plus NO₂⁻) and SRP concentrations, the DIN:SRP ratios increased from low values in the dry season to maximum values immediately following the initial rainfall event. For example, the DIN:SRP ratio at PP increased from 7:1 on May 22 to 70:1 on June 10, which was 4 d after the first major rainfall event; following this increase, the ratio decreased to 12:1 by July 24. A longer period was observed for the rise in the DIN:SRP ratio in nearshore waters, where values increased from 11:1 to 27:1 at PC and 11:1 to 17:1 at PR 11 d following the initial rain event. At the most offshore sites, a 3-wk period passed following the June 6 rain event before the DIN:SRP ratios increased from 9:1 to 26:1 at LK and from 5:1 to 9:1 at BW.

Over the entire study, the average TN concentrations along the offshore gradient were highest and most variable at PP and decreased with increasing distance from shore, with the lowest values at BW. TN averaged $36.6 \pm 9.5 \,\mu\text{M}$ at PP, $24.7 \,\mu$



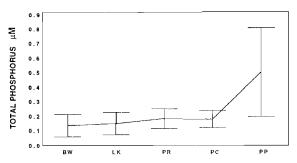


Fig. 14. Mean total nitrogen (upper) and total phosphorus (lower) concentrations (μ M) at five monitoring stations (Port Pine, PP; Pine Channel, PC; Patch Reef, PR; Looc Key, LK; blue water, BW) during the study period. Values represent means ± 1 standard deviation (n=22).

 \pm 5.8 μM at PC, 17.2 \pm 6.9 μM at PR, 12.7 \pm 9.3 μM at LK, and 9.1 \pm 6.9 μM at BW (Fig. 14). TP concentrations showed a similar pattern, averaging 0.49 \pm 0.30 μM at PP, 0.17 \pm 0.06 μM at PC, 0.17 \pm 0.07 μM at PR, 0.14 \pm 0.08 μM at LK, and 0.13 \pm 0.08 μM at BW (Fig. 14).

Concentrations of chl a increased at all stations along the eutrophication gradient from the dry period into the rainy period. Chl a concentrations at PP during May were <2.0 μ g l⁻¹ and increased markedly to >20 μ g l⁻¹ within days following the first major rainfall on June 6 (Fig. 15); over the entire study, chl a concentrations at PP correlated significantly with rainfall (r = 0.57, p = 0.001). Chl a also increased after June 6 at both PC and PR, where it remained elevated for the remainder of the study; maximum chl a values occurred at LK in late June (Fig. 15). Over the entire study, chl a averaged 2.94 \pm 0.49 μ g l⁻¹ at PP, 0.26 \pm 0.10 μ g l⁻¹ at PC, 0.37 \pm 0.13 μ g l⁻¹ at PR, 0.26 \pm 0.11 μ g l⁻¹ at LK, and 0.18 \pm 0.09 μ g l⁻¹ at BW.

Discussion

DECREASED SALINITY AND NUTRIENT ENRICHMENT

This study demonstrates the ecological effects of episodic stormwater nutrient discharges on coastal

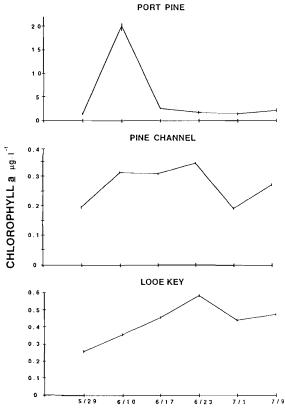


Fig. 15. Chlorophyll *a* concentrations (μg l⁻¹) at three stations (Port Pine, Pine Channel, Looe Key) between May 29 and July 9, 1992.

waters of the Florida Keys. Decreased salinity followed the rainfall at all stations in June, including LK which is located ~9 km from shore and where salinity dropped from 37‰ to 31‰ over the 3 wk following the onset of rainfall. The 16.6 inches of rain that fell in June during this study was greater than the long-term average of 9.5 inches for June in south Florida; however, total rainfall over the entire period of study was below average due to scant rainfall in April, May, and July (MacVicar 1983). Similar observations of decreased salinity at several offshore bank reef sites in the Florida Keys were made during July 1993 and were speculated to have been caused by flood waters from the Mississippi River impinging on the Florida Keys region (Ogden et al. 1994); however, no proof of that phenomenon was provided. As shown in our study, such decreases in salinity can occur throughout nearshore waters and bank reefs of the Keys from local stormwater discharges, particularly when rainfall is near or above average during the wet season.

Dramatic salinity reductions from freshwater discharges similar to those in the present study can be detrimental to the health of sensitive coral reef communities irrespective of nutrients or other pollutants carried by the fresh water. Jokiel et al. (1993) described how storm floods in late December 1987 reduced salinity in the surface waters of Kaneohe Bay, resulting in a massive freshwater "reef kill"; corals, echinoderms, and crustaceans all had extremely high mortality rates and virtually all coral was killed to a depth of 1-2 m. Similarly, Sakai and Nishihira (1991) reported reduced salinity from terrestrial runoff near a river mouth in Okinawa, Japan, caused severe mortality of corals following an extended dry season. Even relatively minor salinity reductions can have negative effects on reef coral recruitment. Richmond (1993) conducted experiments with coral gametes and showed that a 20% decrease in salinity from 35% to 28% resulted in an 86% drop in fertilization rate; success of larval development following fertilization was also inhibited by freshwater runoff, by as much as 50% (Richmond 1993).

The salinity issue is of particular concern to the Florida Keys National Marine Sanctuary Program as some scientists have speculated that high salinities were a primary factor causing stress and die-off of seagrasses over baywide scales in the late 1980s (e.g., see M. Durako cited in McIvor et al. 1994). To date, no scientific evidence is available to support this hypothesis (Boesch et al. 1993). The "hypersalinity hypothesis" was recently extrapolated to the offshore bank reefs of the Florida Keys as a mechanism to explain recent coral reef stress and die-off (Porter et al. 1994). Our data from Looe Key showed the highest salinities were <38‰ and averaged 36.4‰, close to that of oceanic seawater, which is the optimal salinity for growth of most corals. Despite a lack of supporting evidence for the hypersalinity hypothesis, the Water Quality Protection Program for the Florida Keys National Marine Sanctuary (United States Environmental Protection Agency 1993) developed strategies aimed at restoring freshwater flows (i.e., quantity, not quality) through the Everglades. Water managers in South Florida began increasing freshwater deliveries in 1991 through Shark River Slough (Everglades) and into the Florida Bay-Florida Keys region, an action that has continued to the present. The freshwater inputs to Shark River Slough come from agricultural areas north of the Everglades and contain high concentrations of nitrogen (~120 µM, data on file with South Florida Water Management District); most nitrogen taken up by the wetlands vegetation and microbes of the Everglades is re-released as NH₄' and little net uptake or denitrification occurs (Gordon et al. 1986; Urban et al. 1993). Accordingly, the recent 300% increase in large-scale water flows has considerably increased N loads to N-limited waters

of western Florida Bay (Boesch et al. 1993), resulting in significant regionwide nitrogen enrichment.

In addition to the regional background sources of nutrients and chl a advected into coastal waters of the Florida Keys, local rainfall and potable water supplies (5.5 billion gallons per year) pumped into the Florida Keys result in additional wastewater nutrient burdens via submarine groundwater discharge. These inputs result in local increases in phytoplankton biomass as observed in the present study. Rainfall itself contains significant concentrations of NH₄⁺ and NO₃⁻, which enhance primary production in coastal waters adjacent to urbanized areas (Paerl 1985). Rainfall in the Florida Keys during our study had an average DIN concentration of 15 μ M, including \sim 6.2 μ M of ammonium. Menzel and Spaeth (1962) reported similar ammonia concentrations (4.97 µM) for rainfall at Bermuda. Low to undetectable concentrations of TP and SRP were present in the rainfall, pointing to the importance of wastewater sources of phosphorus. Potable water deliveries to the Florida Keys have resulted in high human population densities and nutrient-enriched groundwaters from the widespread use of septic tanks, cesspits, and injection wells. Episodic rainfall events are important meteorological forcing mechanisms that increase submarine groundwater discharge and nutrient loads to coastal waters.

STORMWATER DISCHARGES AND DECREASED DO

Our study showed that rainfall events are followed by periods of critically low DO in sensitive seagrass and coral reef communities in the Florida Keys. Predawn DO at all stations dropped to hypoxic levels ($\leq 2.5 \text{ mg l}^{-1}$) within days after the initial stormwater discharges in June. The impacts of reduced DO were most dramatic at the inshore PP station, where anoxia developed immediately following the first heavy rain event and persisted for several days. The anoxia at PP was caused by enhanced submarine discharge of groundwater contaminated by septic tank effluent. Untreated or partially treated domestic wastewaters, including septic tank effluent, have high BOD concentrations that can reduce DO in surface receiving waters (Mitchell 1974; Bicki et al. 1984). Lapointe et al. (1990), using heat-pulsing groundwater flow meters, showed that rainfall events greatly enhance lateral groundwater flow and submarine groundwater discharge into canals and nearshore waters of the Florida Keys. Hence, heavy rainfall events would transport unusually high BOD and nutrient burdens into surface waters, resulting in severe oxygen depletion as observed in this study. Additional factors contributing to anoxia and hypoxia include cascading effects of organism die-offs that add to the BOD and exacerbate environmental impacts. Nutrient enrichment increases water-column light attenuation due to increased phytoplankton biomass, suspended materials, and dissolved organic matter, resulting in light limitation of phytoplankton growth (Marsh 1977; Laws and Redalje 1979) and reduced oxygen concentrations. Over time, increased sediment oxygen demand (SOD) resulting from the bacterial mineralization of accumulated organic matter leads to cumulative reduction of DO (Mee 1988) and hypereutrophication in wastewater-impacted waters (Lapointe et al. 1994).

The DO record from LK following the stormwater discharges in early June shows that peak midday DO levels can increase following such events but the minimal predawn DO levels actually decrease. These results support our previous conclusions that predawn DO measurements are a necessity for monitoring programs because they represent critical periods affecting organism die-offs in coastal waters; daytime values can be misleading as they are higher than pre-dawn values and highly dependent on many factors, including time of measurement, weather conditions, etc. (Lapointe and Clark 1992). The diel variability in DO at LK illustrates a classic eutrophication response, whereby nutrient enrichment from stormwater discharges enhances phytoplankton biomass and leads to high DO concentrations during midday hours when maximum photosynthesis is occurring. However, the increased phytoplankton biomass also increases community respiration, leading to decreased DO at predawn periods. In addition, light attenuation by the increased phytoplankton biomass (as well as suspended solids and dissolved organic matter from the stormwater discharges) would reduce downwelling irradiance, leading to decreased oxygen production by corals, seagrasses, and benthic macroalgae.

The ecological effects of chronic stress due to low DO in nearshore waters of the Florida Keys have been apparent for many years. Anoxic and hypoxic DO levels have long been known to be associated with sewage nutrient inputs to coral reef (Johannes 1975) and seagrass ecosystems (Odum and Wilson 1962). Low DO levels not only stress marine organisms but can also become lethal through bacterial contamination, toxicity, and respiratory dysfunction (Pastorok and Bilyard 1985). Residents of the Florida Keys have witnessed die-offs of marine organisms in canal systems following heavy stormwater events, which have led to dramatic ecological change in these communities over time. For example, cumulative wastewater impacts have resulted in the long-term loss of turtle grass (Thalassia testudinum) and replacement by phytoplankton, macroalgae, Cuban shoalweed (Halodule wrightii) and the jellyfish Cassiopeia in wastewater-impacted canals and nearshore waters (Tomasko and Lapointe 1991; Lapointe et al. 1994). The 44% loss of coral cover at LK between 1984 and 1989 (Porter and Meier 1992) may also be related to DO stress as illustrated in our study; reef corals are sensitive to water-column DO concentrations as they are oxygen conformers (J. Porter personal communication).

DYNAMICS OF NUTRIENT ENHANCED PHYTOPLANKTON BLOOMS

The different patterns we observed for the development of phytoplankton biomass (chl a) along the eutrophication gradient following stormwater inputs reflect the predominant physical transport mechanisms and the varying spatial scales of phytoplankton growth following nutrient enrichment. Elevated nutrient concentrations associated with stormwater discharges at the inshore PP station were followed by increased phytoplankton biomass. The magnitude of the time delay at the more offshore stations was directly related to the distance from shore. For example, a 1-wk delay was observed at the nearshore PC station compared to a 3-wk delay at the more offshore LK station. This finding is consistent with physical transport studies in nearshore surface waters that show net cumulative flows in the lower Keys from the Gulf of Mexico and Florida Bay toward the offshore bank reefs and Atlantic Ocean (Smith 1994). This large-scale pattern of phytoplankton growth is also related to biological and chemical factors. The doubling time of phytoplankton biomass from inshore to offshore waters would require greater time delays, on a scale of days to weeks. That phenomenon, combined with cumulative nutrient inputs via submarine groundwater discharge and offshore spatial dispersion by tidal currents, would result in additional time delays of weeks to months for larger scale nutrient enrichment and development of phytoplankton biomass. Our July 24 observation of reduced salinity and DO in surface water overlying oceanic water of higher salinity and DO at the most offshore station (BW) illustrates the time delay needed for widespread spatial spreading to offshore waters.

Changes in the concentrations of NH₄⁺ and TDP and in the DIN:SRP ratio over time following the initial rainfall event reflect increased P limitation of phytoplankton biomass. In contrast to TDP concentrations that were at maximum levels immediately following the initial rain event at all stations, chl a and NH₄⁺ concentrations at PC, PR, and LK reached maximum values 1–3 wk following the initial rainfall. This pattern results from watershed nutrient inputs from enriched groundwaters in the Florida Keys that have high N:P ratios (~100:1, Lapointe et al. 1990) so that phytoplankton biomass following stormwater discharges becomes increasingly limited by phosphorus compared to nitrogen.

Over time this results in the accumulation of NH₄+ and chl a as DOP, the major dissolved phosphorus pool, becomes depleted. This conclusion is supported by parallel changes in the DIN:SRP ratios over time, from relatively low values before the onset of rainfall to higher ratios 1-3 wk later, depending on distance from shore. Net flows from the Gulf of Mexico to the Atlantic Ocean facilitate spatial spreading and transport of lower salinity and NH₄+-enriched nearshore water offshore, a phenomenon that extended to 12 km offshore during the present study (see Fig. 11). This "ammonium wake" downstream of the Florida Keys is similar to the NH₄+-enriched surface waters observed downstream from island masses in the castern Caribbean (Corredor et al. 1984).

NUTRIENT THRESHOLDS FOR EUTROPHICATION

Our results showed that nutrient concentrations over broad areas of the Florida Keys were above nutrient threshold concentrations noted for the demise of coral reefs from eutrophication. The detailed studies of Tomascik and Sander (1985) showed decreased coral growth rates and die-off of reef corals occurred on fringing reefs impacted by tourist development in Barbados when annual mean chl a levels averaged $0.4 \mu g l^{-1}$ or less; the corresponding annual mean DIN and SRP concentrations were $\sim 1.0 \mu M$ and $0.1 \mu M$, respectively. In Kaneohe Bay, Hawaii, Smith et al. (1981) reported annual mean chl a of $0.68 \mu g l^{-1}$, DIN concentration of 1.1 μ M, and SRP concentration of \sim 0.1 μ M for the least polluted area of the bay that was considered eutrophic by Laws and Redalje (1979). The chl a and nutrient concentrations for onset of eutrophication on these two polluted reefs indicate that mean values of chl a of $\sim 0.4 \mu g \, l^{-1}$, DIN of 1.0 µM, and SRP of 0.1 µM represent thresholds above which coral reefs decline (Bell 1992). Recent studies of natural eutrophication from seabird guano enrichment on the Belize Barrier Reef have shown similar nutrient threshold concentrations for macroalgal overgrowth of seagrass and reef coral communities (Lapointe et al. 1994).

Comparison of nutrient and chl a concentrations in our study with the threshold values above indicate that levels were relatively high at all the stations in our study. All four Hydrolab stations had NH₄+ concentrations averaging well over the DIN threshold of 1.0 μ M; over the course of the study, NH₄+ averaged 5.48 μ M, 2.25 μ M, 1.86 μ M, and 2.03 μ M at PP, PC, PR, and LK, respectively. TDP concentrations were also elevated, averaging 0.49 μ M, 0.17 μ M, 0.17 μ M, and 0.14 μ M at PP, PC, PR, and LK, respectively. The average TDP concentration on nearby coral reefs in the western Caribbean was \sim 0.07 μ M in 1990, about half the average

concentration we measured at LK in this study. Levels of chl *a* were also 200% higher on bank reefs of the Florida Keys National Marine Sanctuary compared to more oligotrophic reefs in the western Caribbean (Lapointe et al. 1993).

Comparison of our NH₄⁺ data for LK to data collected at the same site in 1985 and 1989 indicates that NH₄⁺ concentrations have increased significantly at this offshore location over the past decade. The NH₄⁺ concentration measured at weekly intervals between April and August 1985 averaged $0.26 \pm 0.12 \,\mu\text{M}$; NO₃⁻ and NO₂⁻ during the same period averaged 0.19 ± 0.11 µM (Lapointe and Smith 1987). Accordingly, DIN concentrations averaged $\sim 0.45 \mu M$, below the threshold of $\sim 1.0 \mu M$ for eutrophication and the demise of coral reefs (Bell 1992). The NH_4^+ and NO_3^- plus NO_2^- data of Lapointe and Clark (1992) measured in August 1989 also indicated DIN concentrations at LK of ~0.50 µM, below the threshold nutrient concentrations noted for decline of coral reefs. In the present study, LK had a mean DIN concentration of 2.9 \pm 1.1 μ M, well above the threshold values. This apparent increase in DIN concentrations over the past decade correlated with a 44% loss of coral cover and decreased water clarity, as well as increased macroalgal dominance, coral bleaching, and black-band disease (Porter and Meier 1992). These symptoms are consistent with our evidence of anthropogenic nutrient enrichment and nitrogen build-up fueling the eutrophication process.

Several important conclusions can be drawn from this study to help guide future monitoring and water quality restoration efforts. First, the importance of diel variability in DO must be recognized and water quality standards and monitoring protocols should be developed to address this and the impact of low DO on primary and secondary production in these sensitive coral reef communities. Second, high frequency sampling with diel studies are needed to resolve episodic stormwater nutrient inputs and their ecological effects. Sampling at monthly intervals, or longer, will miss the important episodic events observed in the present study. Third, our results show that concentrations of nutrients and chl a in our study area are now above critical threshold levels known to mark the decline of coral reefs; DO concentrations also fell below the State of Florida's minimum standards for marine water quality (4.0 mg l-1) at all stations. The high concentrations of nutrients and chl a and low concentrations of DO in coastal waters of the Florida Keys demonstrate that special precautions should be exercised in the treatment and discharge of wastewaters and landbased runoff. Advanced wastewater treatment (nutrient removal) is necessary to protect sensitive coral reef communities from deterioration via nutrient

overenrichment. Nutrient reduction strategies must be implemented at local, regional, national, and international levels if nutrient and chl *a* concentrations are to be maintained below threshold levels for coral reefs. Until these recommendations are implemented, the future of coral reefs in the Florida Keys, and similar coral reef systems worldwide, is threatened.

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