EPA Grant #2 - Narrative

Project Title: Monitoring anthropogenic sources of pollution and chemicals of emerging concern (CECs) around Key West, Florida: A partnership between the City of Key West and the College of the Florida Keys.

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1. Applications Introduction:

a. Situation, Need, and Previous Efforts:

Key West Water Quality

The City of Key West has a long history of being proactive on water quality issues. Key West was the first local government in the Keys and most of South Florida to convert from septic to sewers in 1989, eliminating outfalls. The Wastewater Treatment Plant is award winning and state of the art, treating to Advanced Wastewater Treatment standards before deep well injection at 3,280 feet. Regarding stormwater and runoff, Key West was the first local government in the Keys to create a Stormwater Master Plan (2001) and has made great strides to reduce non-point pollution throughout the island. Recently, the City's 2020 Strategic Plan called for more, with ~5,000 citizens prioritizing further efforts to "improve water quality and the cleanliness of nearshore waters". To this end, the City became more involved in the Florida Keys National Marine Sanctuary's Water Quality Protection Program and now has a seat on the Steering Committee. The City now wishes to partner with the College of the Florida Keys (CFK) to continue important

monitoring of the Key West harbor and ship channel, but also to expand the project to other areas of concern (AOC) to determine potential sources of anthropogenic pollution (i.e. sewage waste discharge) and chemicals of emerging concern (CECs) such as endocrine disrupting oxybenzone. The City of Key West wishes to work with the College to create a Water Quality Improvement Plan, which will both prioritize increased monitoring and actions that the City can take to improve water quality.

Issue 1: Chemicals of Emerging Concern (CECs)

Chemicals of emerging concern in the Florida marine environment are represented by a host of pollutants from a variety of sources. They include but are not limited to endocrine disrupting compounds (EDCs) often reported in personal care products like sunscreen. Recently, the organic ultraviolet (UV) filter oxybenzone (Benzophenone-3 or BP-3), a component of many sunscreen products and known EDC has been implicated in a variety of harmful effects on humans, corals, and other wildlife (Danovaro et al., 2008: Downs et al., 2015; Tsui et al., 2017; Siller et al,, 2018; Wijerde et al., 2019). Recognizing the potential impacts to coral reef ecosystems, in February 2019 the City of Key West banned sunscreen products containing oxybenzone. However, the local legislation was subsequently preempted by the state allowing tourists to continue using sunscreen products with oxybenzone. Therefore, the City is now interested in determining if the harmful chemicals are present in local waters around the island community.

There is a knowledge gap in the scientific literature regarding oxybenzone and the vector for transmission into corals. Oxybenzone has been found in coral tissue (Tsui et al., 2017; Mitchelmore et al., 2019) but Mitchelmore et al., (2021) concluded that UV filter concentrations, including BP-3, in the waters immediately surrounding the coral reefs studied were below toxicity threshold levels and their presence is not causing significant harm to coral reefs. However, BP-3

is an oil with low solubility in water (Mitchelmore et al., 2021) and it is highly lipophilic (i.e. lipid soluble) (Kin and Choi, 2014; Tsui et al., 2017; Mitchelmore et al., 2021), which means it is easily absorbed by phytoplankton. BP-3 floats at or near the surface where the largest concentration of phytoplankton exist. Therefore, if BP-3 is getting into the food chain through phytoplankton, then the concentrations in the water near the corals is irrelevant, because corals are facultative heterotrophs that eat zooplankton, which are primary consumers that eat phytoplankton. The recent study by Tsui et al. (2017) suggests that > 65% of the coral tissues studied had BP-3 and >20% of coral samples from the study sites contained BP-3 concentrations exceeding the threshold values for causing larval deformities and mortality in the worst-case scenario. Adding to the alarm, is the fact that BP-3 is also an endocrine disruptor and photo-toxicant – meaning it is more poisonous in sunlight. Moreover, Danovaro et al., (2008) estimated 4K-6K tons of sunscreen wash off during activities in reef areas annually. Recent sampling from the waters of Higgs Beach in Key West during March of 2021 indicated BP-3 concentrations of 6.5 μg/L (Downs 2021; unpublished data), which is near the toxicity threshold for staghorn coral, *Acropora cervicornis*, at 9 μ/L reported by Downs et al., (2016). Regardless, even if beachgoers with BP-3 sunscreens do not enter the ocean, they may eventually wash-off in beach showers, hotel, or even at home, washing sunscreen products down the drain. However, treatment plants do not effectively remove BP-3 (DiNardo and Downs, 2018) creating another potential source of the pollutant (Downs et al., 2022), especially in areas where sewage can infiltrate ground water through septic tanks or cesspools, or shallow well injections. Therefore, it is critical to sample both the water and the food chain in areas where these sunscreen products are used including the beaches and other AOC around the islands of Key West.

Issue 2: Water Quality in the Key West Harbor and Ship Channel

During 2020, the COVID-19 pandemic resulted in a near global shut down of non-essential human activity termed the "anthropause". Later that year during the Fall of 2020 as things began to reopen, CFK began monitoring water quality in the Key West harbor and shipping channel as during the fall semester Marine Data Collection (MDC) course to capture baseline data and any perceived improvements in water quality due to the COVID-19 pandemic anthropause. The monitoring focused on basic water quality parameters including: (1) dissolved oxygen (DO) concentrations using a DO meter (YSI Pro Solo, Xylem, Inc.) with an optical DO (ODO) sensor on a 10 m cable, (2) temperature and conductivity (also reported by the YSI Pro Solo), (3) titration for ammonia (API Saltwater Master Test Kit), (4) secchi depth (a proxy for turbidity), (5) salinity with a refractometer, and (6) low range hydrogen sulfide (H_2S) (Industrial Test Systems, Inc., part #481297-20). Water quality monitoring continued in the spring 2021 in the MDC class and then evolved into a more robust research project as reports indicated that the cruise ship industry was planning to resume activity in Key West. The primary concern associated with the return of the cruise ship industry or any other external influence (e.g. hurricanes) centered around the potential disturbance of the seafloor. The unique COVID-19 situation allowed particles suspended in the water column to settle for months. Working with the Florida Keys National Marine Sanctuary (FKNMS) and the National Parks Service (NPS), additional water quality monitoring equipment (YSI 6600 data sondes) with sensors for turbidity, temperature, and salinity, were deployed at four locations including: (1) the entrance to the Key West Harbor, (2) the entrance to the Key West ship channel, (3) near Eastern Dry Rocks (EDR) – Sanctuary Preservation Area, and (4) Western Dry Rocks (a control area presumably . Western Dry Rocks was chosen as a location assumed to be far enough from the Key West harbor and ship channel to not be affected by disturbances and to act

as a control site for the project. The other locations (1-3) were chosen to create a triangular water quality monitoring array that could track any disturbances between the harbor, ship channel, and EDR (Figure 1 – blue callout). Subsequently, CFK applied for funding and was awarded a grant starting in January 2022 to expand the project creating a more comprehensive array (Figure 1 – green callouts) with better water quality monitoring technology.

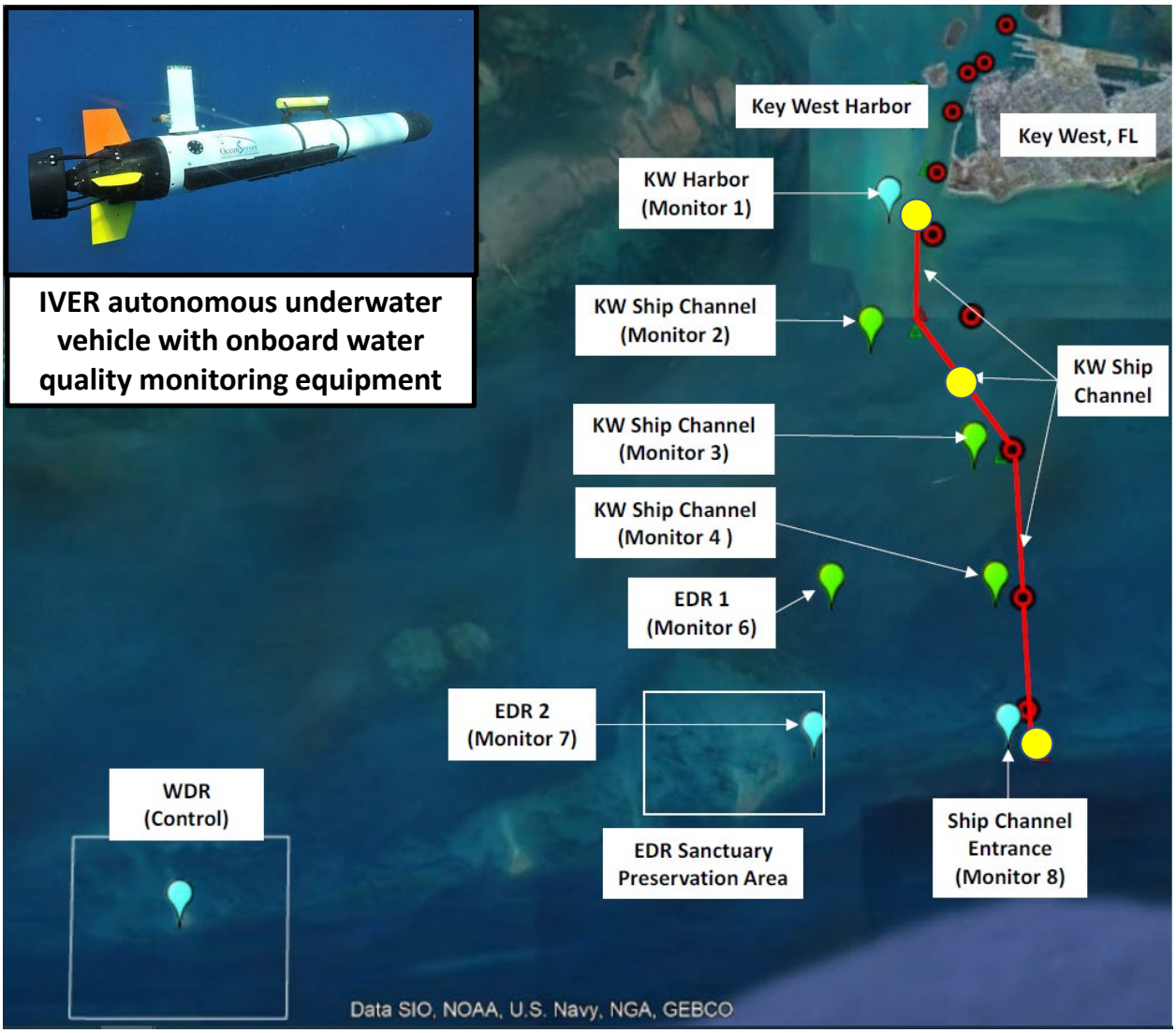

Figure 1. An aerial view of the water quality monitoring project for the Key West harbor and ship channel.

Unfortunately, a medical emergency during October 2021 forced the first cruise ship to return to Key West before the array was completely funded and deployed. However, aerial footage of the event highlights the current need for the KWWQ and its continuation into the future (Figure 2).

Figure 2. An aerial view of an environmental disturbance caused by the first cruise ship to arrive in the Key West harbor after being closed during the COVID-19 pandemic (photo courtesy of Arlo Haskell).

Recognizing the need to continue water quality monitoring in the Key West Harbor and Ship Channel and to expand water quality monitoring to other AOC beyond the EPA funded KWWQ project, the City of Key West reached out to CFK to develop a partnership to expand the water quality monitoring project around the entire island. The partnership intends to use college students, interns, and research assistants from the College marine science programs including the Bachelor of Science in Marine Resource Management (BRM).

Issue 3: Local Water Quality Areas of Concern (AOC)

Other water quality AOC identified by the community include mooring fields in and around Key West and the Stock Island Landfill just outside of Key West.

Ammonia ($NH3/NH4^+$) in the marine environment can be indicator of sewage discharge. Preliminary water samples taken during the spring and summer showed elevated ammonia concentrations (0.25 ppm $NH3/NH4^+$) in the Key West harbor near Fleming Key mooring field (Figure 3 – Area 7).

Water quality monitoring efforts in surrounding waters and offshore from Key West consistently showed no indications of ammonia (i.e. 0.0 ppm $NH3/NH4^+$). Therefore, there is

concern for untreated sewage discharge from mooring fields in in and around the islands of Key West.

Figure 3. Aerial view of Key West showing the proposed areas of concern for water quality monitoring: (1) Ft. Zachary Taylor State Park, (2) Southernmost Point, (3) Smather's Beach and Higgs Beach, (4) Stock Island Mooring Field, (5) Stock Island Landfill (red dot) and College of the Florida Keys lagoon, (6) Garison Bight Mooring Field, (7) Fleming Key Mooring Field, and (8) Wisteria Island Mooring Field.

Although ammonia is a good indicator of nitrogenous waste from sewage discharge, there are many sources of nitrogenous waste in marine waters including marine animals, agricultural run-off, etc. Therefore it does not directly implicate anthropogenic sources. However, sucralose, a chemical found in artificial sweetener and persistent in the marine environment, has been reported

as an effective indicator of anthropogenic sources of sewage (Brorström-Lundén et al., 2008; Currens et al., 2019; Firth et al., 2022). Therefore the proposed project will supplement monitoring in the Key West mooring fields by including sample analysis for sucralose as an indicator of human waste discharge.

~~The~~ Stock Island Landfill opened in 1930 and was originally a dump site resides immediately adjacent (i.e. < 20 m) to the shallow marine waters of Jewfish Basin and approximately 150 m from the lagoon at the College of the Florida Keys (Figure 3 – red dot at #5). The landfill was believed to have been started by dumping garbage into shallow grass beds and building up from there. The landfill was closed in 1990 and was constructed without a liner or leachate collection system (Bruner, 2016), which is currently required for all Florida landfills (Florida Administrative Code 62-701.400 Landfill Construction Requirements), so there is concern about contaminants leaching during King Tides into the waters of Jewfish Basin and the lagoon at CFK. Moreover, Chapter 62-701 of the Florida Administrative Code requires landfill water quality monitoring (F.A.C. 62-701.510.2 Water Quality Monitoring Requirements). Therefore, the proposed project will also focus and collect water samples for analysis from the marine waters adjacent to the Stock Island Landfill.

Therefore, the proposed project (hereto referred to as the KWWQ – AOC) will continue ongoing water quality monitoring in the Key West harbor and ship channel, expand monitoring for potential anthropogenic pollution including chemicals of emerging concern (i.e. oxybenzone) associated with sunscreen products, indicators of waste discharge (ammonia, sucralose, and phytoplankton) associated with mooring fields around the islands, and toxic chemicals from the Stock Island Landfill.

b. Objectives

- Continue water quality monitoring in the Key West harbor and ship channel using existing technology and infrastructure.
- Expand water quality monitoring to seven AOC around the islands of Key West using an Autonomous Underwater Vehicle equipped with sensors for dissolved oxygen, temperature, salinity, turbidity, and total algae.
- Expand water quality monitoring to beach AOC around the southern section of Key West for oxybenzone in the marine food chain.
- Expand water quality monitoring to seven AOC around the islands of Key West for sewage discharge indicators (i.e. ammonia and sucralose).
- Expand water quality monitoring to marine environment near Stock Island Landfill for toxic pollutants (i.e. hydrogen sulfide).
- Provide data and input for the City of Key West's Water Quality Improvement Plan.

c. Applications, Benefits, and Importance

1. Linkage to EPA Strategic Plan: Goal 5. Ensure Clean and Safe Water for all Communities
    - Objective 5.2 Protect and Restore Waterbodies and Watersheds
2. Expected Outputs
    a. Development of a long-term water quality monitoring program.
    b. Characterization of sources and causes of water quality impairment around the islands of Key West that will inform marine resource management and allow management action plans.
    c. Develop semi-annual and final performance reports.
3. Expected Outcomes

a. Increase the knowledge of marine resource managers at the City of Key West, Florida Keys National Marine Sanctuary, Florida Department of Environmental Protection, and the U.S. EPA.

b. Development and planning for risk assessments, if necessary.

c. Development of the City of Key West Water Quality Improvement Plan.

The proposed project will provide the necessary data to inform marine resource management decisions regarding water quality AOC around the City of Key West, and the surrounding waters of the Florida Keys National Marine Sanctuary. In addition, the project will provide educational opportunities including internships and research assistantships for marine science and resource management students from the College of the Florida Keys.

2. Methods

a. Description of Major Tasks:

Task 1: Continue Key West Water Quality Monitoring – Harbor/Ship Channel (KWWQ-HSC):

The proposed project will sustain and build upon the current KWWQ-HSC project. The project relies heavily on technology to monitor water quality monitoring in the Key West harbor and ship channel including: (1) YSI EXO3 archival data sondes (YSI Inc.), with (2) optical sensors that measure (*i*) dissolved oxygen, (*ii*) turbidity, (*iii*) total microalgae, (*iv*) conductivity (a proxy for salinity), and (*v*) temperature, and (3) an EcoMapper Autonomous Underwater Vehicle (AUV) equipped with a EXO3 data sonde and sensors in the nose cone and side-scan sonar (Figure 4).

Figure 4. An image of the YSI EcoMapper Autonomous Underwater Vehicle (AUV) (Photo courtesy of YSI).

The equipment is only being used in the Key West harbor and ship channel (Figure 2) but will be deployed in other AOCfor the proposed project (Figure 3). Sampling missions will be programed for each AOC and stored in the memory of the EcoMapper reducing complexity and increasing efficiency for sampling deployments. The anticipated sampling frequency will target bi-weekly deployments for each AOC. Data will be downloaded, copied on CFK servers and a project external drive (i.e. backed-up twice).

Task 2. Monitoring Key West Beaches for Oxybenzone and Sucralose

Plankton tows will be conducted in AOC 1-3 (Figure 3) on the southern beaches in Key West. The plankton net will consist of two nets with differing mesh sizes nestled within each other. The inner net will have a 30.5 cm diameter with a 500 µm mesh and 38 cm length. The outer net will also have a 30.5 cm diameter but a 35 µm mesh and 76.2 cm length (Figure 5).

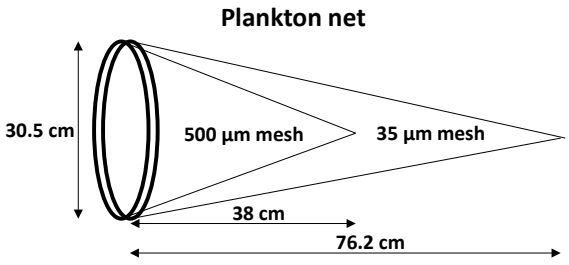

Figure 5. Plankton net design with a 500 µm mesh net embedded in a longer 35 µm mesh net.

The net design allows for collection of zooplankton and many phytoplankton, especially larger diatoms and several species of microalgae, without being rapidly clogged during plankton tows.

Five plankton tows will be collected in each beach AOC. The exact length of each tow will be between 10 m - 50 m, depending on plankton density and plankton net clogging. Each sample will be taken randomly in the specific study area. The total calculated volume of each plankton

sample will be 36.5 m^3. At the conclusion of each plankton tow, the nets will be separated, and both will be washed with filtered seawater (< 5 μm) into a cleaned and triple rinsed 20 L collection container. The container will be placed on ice and taken back to the CFK marine science laboratory where it will be filtered using a Millipore Vacuum Filtration (MilliporeSigma, Inc.) system with a 10 cm Lifegard™ Cartridge Filter with a 2 μm nominal pore size. Filtered samples (i.e. filter and filtrate) will be frozen and shipped to the Florida International University (FIU) – Environmental Analysis Research Laboratory (EARL) for analysis of oxybenzone and sucralose concentrations.

Parallel to plankton tows, water samples will be collected at the surface and at depth using a Van Dorn water collection tool. Five 140 ml water samples will be stored in new, pre-labeled, triple rinsed, 200 ml high-density polyethylene (HPDE) bottles allowing space for the sample to expand when freezing. Sample will be sent to the FIU Center for Aquatic Chemistry and Environment (CAChE) Nutrient Analysis Core Facility for analysis of filtered nutrients (FN): ammonia/ammonium as N (NH_3/NH_4-N), nitrite as N (NO_2-N), nitrate and nitrite as N (N+N), and soluble reactive phosphorus as P (SRP) all at the same time.

Task 3. Monitoring Key West Mooring Fields for Ammonia and Sucralose

Water samples will be collected at AOC mooring sites 4, and 5-8 (Figure 3). Water samples for ammonia and sucralose will be collected exactly as described above and sent to the respective FIU laboratory for analysis (ammonia at FIU – CAChE and sucralose at FIU – EARL).

online solid-phase extraction followed by liquid chromatography-high resolution mass spectrometry (SPE-LC-HRMS) method using a Q-Exactive system for the determination of the occurrence and distribution of selected wastewater tracers/indicators, recalcitrant PPCPs and steroid hormones in South Florida surface waters.

Task 4. Monitoring Hydrogen Sulfide at the Stock Island Landfill

A hydrogen sulfide (H_2S) data logger (SulfiLogger^{TM}; Sulfilogger, Inc.) will be placed on a mooring line in the lagoon at CFK approximately 150 m from Stock Island Landfill. The SulfiLogger^{TM} continually measure H_2S in the water at 0.0 – 0.5 mg/L (Note: H_2S is toxic to fish at 0.02 mg/L). The expected battery life for the SulfiLogger^{TM} is about 30 days. Therefore, the system will be checked, charged, and data downloaded at least once per month. Water quality data will be stored as described above.

Task 5 - Water Sampling Platform

The College has two research vessels available for the proposed project: (1) a 12.8 m Corinthian catamaran (Figure 6 - A) and (2) a 9.75 m ft renewable energy test vessel (RETV) (Figure 6 B-D).

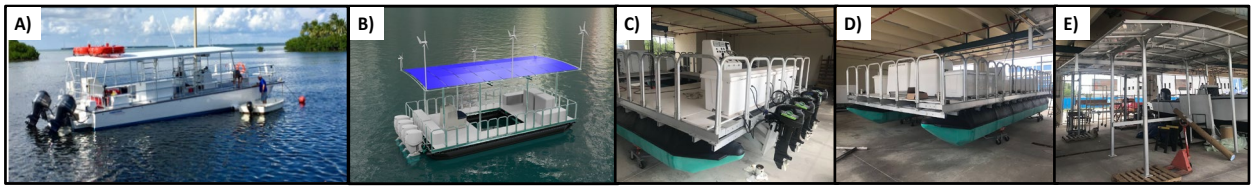

Figure 6. A) The CFK 12.8 m Corithian catamaran, B) a rendering of the CFK renewable energy test vessel (RETV) (Notice - central 3 m x 3 m opening), C) the RETV stern showing 4, 20 hp outboard electric engines, D) the RETV stern, and E) the RETV solar and wind turbine awning.

The RETV is the preferred research vessel for the proposed project. The RETV is designed to carry equipment and deploy instruments, divers, etc. through the central 3 m x 3m opening (i.e. moon pool) and has a wide 4.9 m berth with space to work. It functions on 100% wind and solar and requires no fossil fuel to provide power to the engines and other equipment.

b. Environmental Impact

No additional environmental impacts are anticipated beyond the small footprint 0.5 m^2 for each data sondes place on the seafloor for the ongoing KWWQ-HSC project.

3. Project Management:

CFK will be the lead institution on the KWWQ-AOC project and the primary contributor to the early phases of the project. CFK has partnered with the City of Key West, which will provide resources to sustain project beyond the life of the award, provide access to infrastructure to expand the project, and use the information it's Water Quality Improvement Plan. FIU will be a primary partner with a lead role in water sample analysis

a. Administration: The KWWQ-AOC project will be administered by CFK and follow all College policies and procedures. The Principal Investigator (PI) will be CFK Chief Science & Research Officer, Dr. Patrick H. Rice. The PI will be responsible for all aspects of the project. The PI will report directly to the EPA, the Vice President (VP) of Academic Affairs, and the Executive VP Business & Chief Financial Officer (CFO) as necessary. The PI will work directly with the Director of Sponsored Programs, who will in turn report to the VP Academic Affairs on issues relating to: (1) project budget, and (2) project progress reports. The PI will be the lead and work directly with Scientific Divers, Research Assistants, and interns.

b. Roles and Responsibilities: In addition to the PI (Rice) the KWWQ-AOC project team will consist of Marine Research Assistant, Interns, and CFK marine science students. The roles and responsibilities of each are as follows:

- Marine Research Assistant (MRA) will be involved with all aspects of the KWWQ-AOC project and work closely with the PI (Rice) to coordinate projects and interns, prepare, calibrate, and deploy equipment, collect samples, and other various duties as assigned.
- CFK interns will work closely with the MRA, and PI (Rice). There will be six internships during the duration of the project. Each intern will collect water samples and conduct water quality monitoring in the field with the MRA. Interns will work with the MRA to deploy the IVER AUV

to monitor water quality in AOC (Figure 3). The interns will prepare technical reports for college credit, which will be used by the PI (Rice) to prepare semi-annual and final reports.

4. Support Requirements and Conditions

a. ***Permits Required:*** Permits will be required to deploy the equipment on the seafloor within the study area of the FKNMS. The College currently has the necessary FKNMS permits (Permit # FKNMS-2022-032) for this activity. No additional permits are required.

b. ***Data or Facility Access:*** none. The College of the Florida Keys is a public institution of higher education and therefore all official College activities are public record.

Literature Cited:

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