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Potential Effects of Chemical Contamination on South Florida Bonefish Albula vulpes

Christine P. Beck
Florida International University, cbeck006@fiu.edu

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Miami, Florida

POTENTIAL EFFECTS OF CHEMICAL CONTAMINATION ON SOUTH FLORIDA

BONEFISH *ALBULA VULPES*

A thesis submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

in

ENVIRONMENTAL STUDIES

by

Christine P. Beck

2016

To: Dean Michael R. Heithaus
        College of Arts, Sciences, and Education

This thesis, written by Christine P. Beck, and entitled Potential Effects of Chemical Contamination on South Florida Bonefish *Albula vulpes,* having been approved in respect to style and intellectual content, is referred to you for judgement.

We have read this thesis and recommend that it be approved.

_____
Henry Briceño

_____
Piero Gardinali

_____
Jennifer Rehage, Major Professor

Date of Defense: October 31, 2016

The thesis of Christine P. Beck is approved.

_____
Dean Michael R. Heithaus
College of Arts, Sciences, and Education

_____
Andrés G. Gil
Vice President for Research and Economic Development
and Dean of the University Graduate School

Florida International University, 2016

ABSTRACT OF THE THESIS

POTENTIAL EFFECTS OF CHEMICAL CONTAMINATION ON SOUTH FLORIDA

BONEFISH *ALBULA VULPES*

by

Christine P. Beck

Florida International University, 2016

Miami, Florida

Professor Jennifer Rehage, Major Professor

An ecological risk assessment was conducted on the risk to fish of chemical

contaminants detected in the habitat of *Albula vulpes* in South Florida, to evaluate

whether contaminants may be a driver of declines in the recreational bonefish fishery.

All available contaminant detection data from Biscayne Bay, Florida Bay, and the Florida

Keys were compared to federal and state guidelines for aquatic health to identify

Contaminants of Potential Ecological Concern (COPECS). For these COPECs, species

sensitivity distributions were constructed and compared with recent detections at the 90th

centile of exposure. Copper in Biscayne Bay was identified as the highest risk of acute

and chronic effects to fish, followed by a risk of chronic effects from both the recently

phased-out pesticide endosulfan in Florida Bay, and the pharmaceutical hormone estrone

in the Florida Keys.

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ABBREVIATIONS AND ACRONYMS

COPEC	Chemical of potential ecological concern
DDT	Dichlorodiphenyltrichloroethane
DDD	Dichlorodiphenyldichloroethane
EPA	United States Environmental Protection Agency
HQ	Hazard Quotient
K_d	Sediment-Water Partition Coefficient
K_{oc}	Organic Carbon-Water Partition Coefficient
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyl
RQ	Risk Quotient

INTRODUCTION

Contaminants in Coastal Environments

Coastal environments worldwide continue to be impacted by contaminants and pollution along with newer threats such as climate change and species invasions. Coastal development, urbanization, tourism, and agricultural and industrial activities can act as major sources of contaminants to socioeconomically-valuable marine and coastal ecosystems (Fleeger et al. 2003, Islam & Tanaka 2004, Mearns et al. 2009). In recent decades, global oceanic contaminant levels have declined only slowly and remain high (Bonito et al. 2016). In South Florida, coastal development and associated freshwater discharge, particularly from urban sources (Mitsova et al. 2011) and agricultural land use, makes pollution a concern to coastal waters. For example, a recent risk assessment by Carriger and Rand (2008) suggests that the concentrations of agricultural insecticides found in South Florida could be a potential hazard to fish, especially through trophic pathways (i.e., reduction of prey or consumption of contaminated prey).

Contaminants of concern include heavy metals, persistent organic pollutants, oils, radionuclides, pathogens, pharmaceuticals, nutrients, and sediments. These contaminants can cause major changes to the structure and function of phytoplankton, zooplankton, benthic and fish communities, as well as impact public health (Islam & Tanaka 2004). Contaminant effects may result from direct 1) lethal (mortality), and 2) sublethal effects on vulnerable species, as well as 3) indirect effects (Fleeger et al. 2003). Sublethal effects of interest include behavioral impairment or physiological stress associated with reproductive inhibition/failure, immune system suppression, disruption of endocrine system and metabolic processes (Fleeger et al. 2003, Islam & Tanaka 2004). Indirect effects refer to

complex ecological interactions involving multiple species, particularly those linked via trophic relationships (consumer-resource; Wootton 1994). With indirect effects, the influence of contaminants on other trophic levels (predators or prey), through either lethal or sublethal pathways, can lead to cascading or indirect effects on focal organisms that may be resistant to the contaminant. For example, indirect toxicant effects may lead to increased (e.g. via lower competition) or decreased abundance (e.g. via lower prey availability) of a focal species that is not susceptible to a particular contaminant.

For fishes and the fisheries they support, the direct or indirect loading of contaminants can degrade coastal fisheries, with important economic costs. Key concerns are the effect of contaminants on critical demographic parameters (e.g., recruitment, spawning biomass, and the dynamics of natural vs. fishing mortality). The decline of important fisheries such as the American Shad (*Alosa sapidissima*) in Chesapeake Bay has been associated with pollution (Islam & Tanaka 2004). These declines are likely to result from nonlethal pathways that affect the physiology, behavior, and ecology of susceptible life stages, although causal contaminant-effect linkages are often difficult to establish (Van der Oost et al. 2003, Islam & Tanaka 2004). For instance, lipid storage necessary for successful reproductive migration in the European Eel, *Anguilla anguilla,* is negatively impacted by DDT and PCBs (Geeraerts & Belpaire 2010, Van Ginneken et al. 2009). Weis et al. (2011) show that when comparing fish, crab, and shrimp from contaminated estuaries to those from reference sites, individuals from contaminated areas showed altered diets, growth rates, behaviors, and population sizes, with important implications for the fisheries these taxa support.

South Florida Pollution and Bonefish

In South Florida coastal waters, heavy metals (Lewis 2000), pesticides (Long et al. 2002), and nutrient pollutants (MacCauley et al. 2002, Carey et al. 2011) have been detected, and there appears to be a spatial gradient of contamination from the most heavily polluted metropolitan northern Biscayne Bay (Carnahan et al. 2008) to the least polluted area offshore the Florida Keys (Strom et al. 1992). Some pollutants reach the coast from canal discharge, the contents of which depend on surrounding land use (Carey et al. 2011), whereas others such as the insecticide endosulfan (Hapeman et al. 2013) are deposited atmospherically. Biscayne Bay resident dolphins that were frequently sighted in Northern Biscayne Bay had five times higher concentrations of a persistent organic pollutant than those frequently sighted in the southern, more rural areas of the bay (Litz et al. 2007).

Contaminants in fishes have high ecological relevance, since fish play a major role in food webs and energetic transfer across ecosystem boundaries, as well as support socioeconomically-valuable commercial and recreational fisheries (Van der Oost et al. 2003, Mearns et al. 2009). In South Florida, recreational fishing is major driver of the tourism industry and the regional economy. In 2012, the total economic impact of saltwater fishing was estimated at $ 5.3 billion, making Florida number 1 in the economic value of angling in the US (USFWS 2012, Fedler 2013). About 9% of the economic impact ($ 466 million) resulted from the Florida Keys Flats recreational fishery, a regionally important catch and release fishery.

One of the key species in the Flats Fishery is bonefish (*Albula vulpes*). However, the sustainability of this catch-and-release fishery has been called into question by multiple lines of evidence that point to a decrease in bonefish numbers and bonefishing quality

occurring at least since the late 1990s, with no evidence of a recovery (Larkin et al. 2010, Frezza & Clem 2015, Santos et al. in prep, Rehage et al. unpublished key informant and angler survey data). The mechanism and drivers of the bonefish decline are unknown, and the potential of coastal contamination as a driver of bonefish decline is investigated in the present study. Other suspected drivers include changes in seagrass cover (Fourqurean & Robblee 1999, Santos et al. 2015), prey availability (Liston 2013), catch-and-release recreational fishing pressure (Danylchuk et al. 2007), and alterations to the local hydrology (Marshall et al. 2014, Frezza & Clem 2015).

There is some evidence in support of the hypothesis that contaminants in South Florida may be negatively affecting fish. In Biscayne Bay, developmental abnormalities have been observed in 17 fish species, which may have been caused by embryonic exposure to chemicals (Browder et al. 1993), and with multiple species affected, alternative genetic causes are unlikely. Scale disorientation syndrome in pinfish has been documented in Biscayne Bay with prevalence varying by location (Corrales et al. 2000). Some deformities in Biscayne Bay fish have been correlated with total hydrocarbons and aromatic hydrocarbons in the sediment (Gassman et al. 1994). However, in each case the causative contaminant of the deformities remains unidentified.

Bonefish have several biological and ecological traits which may perhaps increase their susceptibility to toxins in the environment. However, adult bonefish had similar frequency of disease as other fish in a 1976 survey of Biscayne Bay (Udey et al. 2002), which did not suggest an exceptional susceptibility to disease-causing agents. During their early life stage as leptocephalus larvae with translucent ribbon-like bodies, they have high surface area-volume ratios (Pfeiler 2008), which may enhance uptake of some

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contaminants (Knight 1995). Their maximum lifespan in Florida is at least 20 years (Larkin et al. 2007), making long term accumulation of toxins a concern. They use their downturned mouths to prey upon benthic species including mollusks, crabs, shrimps, other invertebrates, and small fish (Ault et al. 2007), which exposes them to contaminants both in the sediment and accumulated through the food chain.

Research Questions

In this study, the following questions are investigated:

(1) What contaminants have been detected in South Florida coastal waters, and which ones are of concern?

(2) What effects do these South Florida contaminants of concern have, particularly on fishes?

(3) What risk do South Florida contaminants pose to bonefish?

Risk Assessment Approach and Review

To address these questions, an ecological risk assessment was conducted. An ecological risk assessment characterizes the likelihood of a particular stressor or set of stressors having harmful effects on an ecosystem or species (EPA 1998). The goal of this risk assessment is to examine existing data on contaminants in South Florida for evidence of both acute and chronic risk to bonefish *Albula vulpes*.

The risk assessment for bonefish follows on previous risk assessments that have focused on risks from contaminated sediment and particularly from pesticide and metal exposure to aquatic biota throughout South Florida. Risk assessments of pesticides in South Florida have consistently identified the organochlorine insecticide endosulfan as posing the greatest risk of effects, both acute and chronic, to aquatic organisms at fresh and

saltwater sites (Scott et al. 2002, Harman-Fetcho et al. 2005, Carriger and Rand 2008a and b, Rand et al. 2010, Carriger et al. 2006, Quinete et al. 2013). The pesticide chlorpyrifos has also been identified as posing a potential elevated risk to aquatic organisms (Harman-Fetcho et al. 2005), whereas other pesticides were determined to have low risk. It should be noted that endosulfan is being phased-out of use by the Environmental Protection Agency in 2016, so the exposure of organisms to endosulfan is expected to be greatly reduced.

Bioassays have found elevated levels of toxicity in the Miami River (Long et al. 2002) and canal mouths entering Biscayne Bay and Manatee Bay (Cantillo & Lauenstein 2004), which have been associated with elevated levels of metals, PBDEs, PCBs, and other contaminants, although the specific contaminants causing toxicity remain uncertain. Among these contaminants, the Miami River has been found to have a high degree of contamination from metals (Long et al. 2002, Julian 2015) and PCBs (Julian 2015), but open areas of Biscayne Bay were found to have low levels of contamination and toxicity (Cantillo & Lauenstein 2004, Long et al. 2002, Julian 2015). For the metals studied, copper in Biscayne Bay (Castro et al. 2013) and Miami Dade County fresh and saltwater areas (Schuler et al. 2008) has been identified as posing a risk of chronic and acute effects to aquatic invertebrates and fish. In Everglades National Park, lead and chromium are of potential concern to aquatic organisms (Castro et al. 2013). A risk assessment of mercury in Everglades National Park found a high probability of risk of chronic effects in piscivorous birds, mammals, and reptiles that ate large fish (Duvall & Baron 2000).

The EPA's Ecological Risk Assessment Framework (EPA 1998) provides guidance and identifies a series of stages to systematically evaluate and organize data along with

assumptions and uncertainties to better understand and predict the relationship between stressors (contaminants) and ecological effects in a manner that is useful for decision making (Figure 1, EPA 1998). Recent examples of this approach applied to fishes include risk assessments of contaminant effects on the Rio Grande Silvery Minnow (Marcus et al. 2010), effects of coal fly ash on a Tennessee fish community (Rigg et al. 2015), and effects of mining on Virginia native fishes (Diamond & Serveiss 2001). We focused on the core 3 stages of the ecological risk assessment process (main box in Figure 1). First, the Problem Formulation stage clarifies the goals and depth of the risk assessment. Next, the Analysis stage allows for the characterization of exposure and ecological effects. Then, the Risk Characterization stage determines how likely the exposures are to have ecological effects, and makes a statement of sources of uncertainty and limitations in the analysis.
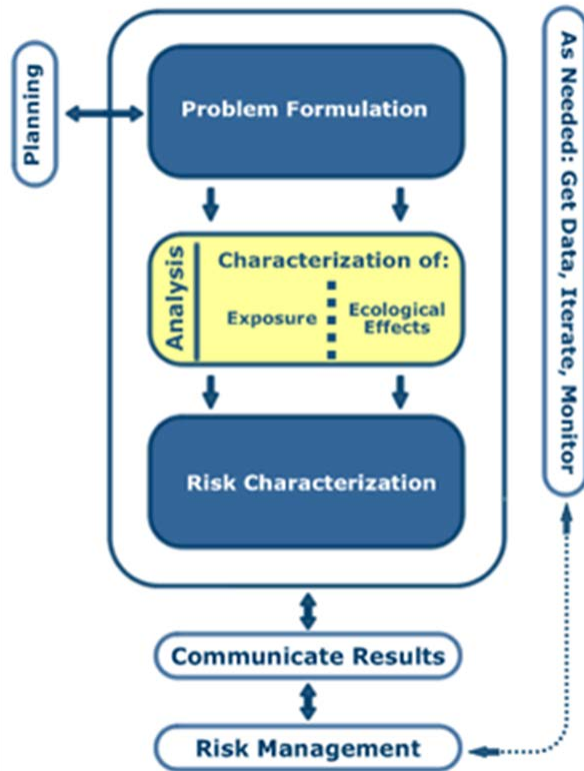
Figure 1. Stages of EPA's ecological risk assessment framework. The stages of risk formulation, analysis, and risk characterization are communicated in this study (EPA 1998).

METHODS

Literature Search

To conduct the risk assessment, we used existing data to evaluate the current risk of chronic and acute effects of exposure to contaminants for bonefish in their main South Florida habitat – the Florida Keys, Florida Bay, and Biscayne Bay. For this study, Barnes Sound (US 1) was used as the southern boundary of Biscayne Bay, Florida Bay included the area from Long Sound to Long Key, and the bay side of the Upper Keys, and the Florida Keys included the ocean side of the Upper Keys and all of the Middle and Lower Keys. We used *Web of Science, ProQuest,* and *Google Scholar* databases to search for published studies and grey literature, and examined publications within any study found, as well as recent citations of these studies. Search terms included combinations of "Pollutant" OR "Contaminant" OR "Toxin" OR "Toxicity" AND "Florida Bay" OR "Florida Keys" OR "Biscayne" OR "South Florida" Or "Everglades". Additional reports were found by consultation with contaminant experts in South Florida.

This search yielded 31 were contaminant studies with relevant data from 1973 to 2015. Relevant studies provided data on contaminants tested and concentrations detected on any medium (water, sediment, and/or tissue) in Biscayne Bay, Florida Bay, or the Florida Keys. Information was extracted from these 31 focal studies including: location detected, matrix (sediment, water, tissue), concentration mean, minimum, and maximum.

Identifying Contaminants of Potential Ecological Concern (COPECS)

From the 31 studies, the maximum concentration of each contaminant was found for each matrix type (sediment and water) at each location (Biscayne Bay, Florida Bay,

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Florida Keys). A hazard quotient (HQ) was calculated for each reported chemical following the same method as Hull et al. (2015):

$$Hazard\ Quotient =\ HQ_i = \frac{Maximum\ concentration\ of\ contaminant_i}{Guideline\ for\ contaminant_i}$$

where HQ_i is the ratio of the maximum concentration (across multiple studies) to the appropriate guideline concentration for that particular chemical and media (sediment or water).

Relevant state or federal concentration guidelines used for calculating *HQ_i* included: 1. For sediment, the Florida Department of Environmental Protection Sediment Quality Assessment Guidelines for Marine Sediment Toxic Effect Levels (DEP SQAG 1994). 2. For water, the State of Florida Surface Class III Water Quality Standards for Predominantly Marine Waters (DEPIII WQS 2010). When state guidelines were unavailable for a contaminant, US EPA Aquatic life criteria for continuous chronic saltwater exposure (EPA ALC SWCCC 2016) was used. Additionally, the freshwater Canadian Environmental Quality Guidelines for Aquatic Life was used for the pesticide Atrazine, since there is no US guideline (CCME 1999). These water and sediment guidelines are based on aquatic organism exposures, including fishes, and are meant to provide the minimum level expected to have adverse biological effects to multiple aquatic taxa. For contaminants without guidelines, such as pharmaceuticals, the source literature was used as a reference for whether there was a concern for fish health at the concentrations found. There were not guidelines for the protection of aquatic life based on fish tissue concentrations, so these were excluded.

These calculated HQ_i served as the basis to identify contaminants of potential ecological concern (COPECs) in bonefish habitat, with $HQ_i > 1$ indicating that the contaminant has been found in the habitat at levels exceeding concentrations from guidelines to protect aquatic life or the environment. We also identified as COPECs contaminants without HQ_i (due to a lack of guidelines) based on concern for fish health raised by the source literature. COPECs are contaminants identified as potentially harmful, and are subsequently included in further risk assessment.

Risk Assessment: Exposure Data

For the COPECS identified, an additional search of published studies and government databases (NOAA Status and Trends, EPA National Coastal Condition Assessment, South Florida Water Management District DBHydro) was conducted for actual measured concentrations of each COPEC in the region (Biscayne Bay, Florida Bay, or the Florida Keys) in which it had been found exceeding guidelines. In order to best evaluate current risk while having sufficient data, only data taken between 1998 to 2015 was considered, although this still resulted in only a small amount of data (TABLE 1). For PCBs, the sum of 18 reported PCB congeners was taken for the NOAA status and trends site, and multiplied by 2 (Deshpande et al. 2000) to approximate total PCBs from the 18 NOAA reports.

For each COPEC the available 1998-2015 concentration data (TABLE 1) were ranked from highest to lowest, and the 90th centile concentrations were selected as the exposure threshold (e.g. Schuler et al. 2008). The 90th centile is the value for which 90% of the data points are smaller. A 90th centile assumes that any sample taken has only a 10% chance of exceeded the estimated 90th centile concentration if exposure data are unbiased

and representative for the region where collected (Schuler et al. 2008). The 90th centile is a commonly used exposure benchmark (Solomon et al. 1996), which reduces the effect of outliers, and represents the likely exposure of most individuals in the environment. Zero values were included in the calculation only from data sources that had at least 1 detection of that contaminant in that region. For estrone, a reported 85th centile (Singh et al. 2010) was used, and for chlorpyrifos and endosulfan, reported 90th centiles (Carriger and Rand 2008b) were used because individual data points were not available.

TABLE 1. Source and Date of Exposure Data for 12 COPECS. For each chemical the number of samples (N), data source, and years of collection of exposure data are shown.

Region	Chemical	N	Source	Years
Biscayne Bay	Arsenic	63	Castro et al. 2013	2006-2007
			NOAA National Status and Trends	1999
			NOAA Mussel Watch	2007
			EPA Coastal Condition Assessment	2000 2001 2005 2006 2010
	Copper	61	Castro et al. 2013	2006-2007
			NOAA National Status and Trends	1999
			NOAA Mussel Watch	2007
			EPA Coastal Condition Assessment	2000 2001 2005 2006 2010
	Benz(a)anthracene	30	NOAA National Status and Trends	1999
	Chrysene	30	NOAA National Status and Trends	1999
	Fluoranthene	30	NOAA National Status and Trends	1999
	Pyrene	30	NOAA National Status and Trends	1999
	PCBs	34	NOAA National Status and Trends	1999
	DDT	15	NOAA National Status and Trends	1999
Florida Bay	Chlorpyrifos	24	Carriger & Rand 2008, Fulton et al. 2004	1998-2000
	Endosulfan	24	Carriger & Rand 2008b, Fulton et al. 2004	1999-2000
	Lindane	37	EPA Coastal Condition Assessment	1999 2006 2010
			NOAA Mussel Watch	2007
	DDT & metabolites	31	EPA Coastal Condition Assessment	1999, 2006
Florida Keys	Estrone	68	Singh et al. 2010	2004, 2006

As done by previous studies (Schuler et al. 2008), sediment contaminant concentrations were converted to estimated pore water concentrations to allow for comparison with effects data from toxicity experiments since those are typically based on water concentrations. The published partitioning coefficients (K_d and K_{oc}) used for these concentrations conversions are listed in Table 2. Nonionic organic contaminants were expected to largely be in the organic carbon portion of the sediment (Di Toro 1991), so we used organic carbon measurements from the original samples and K_{oc}s (Table 2) to estimated porewater concentration on an organic carbon basis. For example, for copper, the 90th centile sediment concentration was 19.48 mg/kg out of the 61 values used for the risk assessment, and using the equation and partitioning coefficient ($\log K_d = 3.5$, Table 2), the 90th centile sediment concentration was converted to a pore water concentration of 6.16 ug/L:

$$\text{Estimated porewater copper concentation} = \text{water concentration} \div 10^{logKd}$$

$$= 19.48 \frac{mg}{kg} \div \frac{10^{3.5} L}{kg} \times 1000 \left(conversion \frac{ug}{mg} \right) = 6.16 \frac{ug}{L}$$

Table 2. Partitioning coefficients used to convert the 90th centile sediment concentrations to estimated 90th centile pore water concentrations for all contaminants.

Contaminant	Partitioning Coefficient	Source
Arsenic	$\log K_d = 2.4$	USEPA 2005
Copper	$\log K_d = 3.5$	USEPA 2005
PCB total (Aroclor 1254)	$\log K_{oc} = 6.1$	Sklarew & Girvin 1987
Chrysene	$\log K_{oc} = 5.9$	Lu et al. 2006
Fluoranthene	$\log K_{oc} = 4.6$	EPA BC Guidelines organic carbon basis
Pyrene	$\log K_{oc} = 5.4$	Lu et al. 2006
Benz(a)anthracene	$\log K_{oc} = 5.3$	EPA BC Guidelines organic basis
DDT	$\log K_{oc} = 5.2$	Swann et al. 1981
Lindane	$\log K_{oc} = 3.7$	DiToro et al. 1991

Risk Assessment: Toxicological Effects Data

Effects data were based on 3 toxicity endpoints, concentrations lethal to half of test subjects or LC50s, the lowest concentrations with effects on test subjects or LOECs, and concentrations having effects on half of test subjects or EC50s (Shaw-Allen & Sutter 2012). These were used to construct Species Sensitivity Distribution (SSD) curves for both acute (LC50s) and chronic (EC50s, LOECs) effects. Acute effects describe adverse effects from a limited number of exposures over a short period of time, while chronic effects describe effects as a result of long term exposure.

No toxicological studies have been conducted on bonefish nor on closely-related species, so to use what is known about overall risk to fish and aquatic organisms, Species Sensitivity Distribution (SSD) curves were constructed using the EPA SSD Generator (SSD Generator V1, downloaded from http://www.epa.gov/caddis/da_software_ ssdmacro.html) with toxicological data from available saltwater and freshwater fish species. A SSD curve shows toxicity endpoints (or concentrations at which an effect was detected for a given species species) for a number of species, ranking species from most to least sensitive. These SSD curves allow estimation of what concentration is likely to be hazardous to 5% or 10% of species, the HC5 and HC10. An HC10 was used in this risk assessment, as has been previously used by other South Florida Risk Assessments (Schuler et al 2008, Rand et al. 2010, Carriger and Rand 2008b). The HC10 is a commonly used threshold for risk that is expected to protect of 90% of the species. There are very limited data on bonefish in South Florida A 1976 survey of fish health in Biscayne Bay did not find bonefish to be among the most diseased of species in the Bay except for damage to the caudal fin, likely from fishing captures (Udy et al. 2002). This survey lends limited

support to the assumption made in using the HC10 that bonefish are not among the most sensitive 10% of species to contaminants.

Data from saltwater fish were used preferentially and prioritized for the estimation of the SSD curves. However, if there were less than 5 saltwater fish species, freshwater fish were included, and if less than 5 freshwater fish species were available, other aquatic taxa were included (e.g., amphibians, crustaceans, insects, mollusks, aquatic plants). For PCBs, toxicity data were taken for Arochlor1254 because it is one of the common and most toxic mixtures, and is commonly used for this purpose (Schwacke et al. 2002). There were not enough data to construct SSD curves for the PAHs Chrysene and Benz(a)anthracene, so values for Pyrene, a similar 4-ring PAH with more relevant data available, were substituted. For DDT and metabolites effects data for DDT were used. The hazardous concentration HC10 of each of these distributions was identified. The value is used as benchmark below which is estimated to protect 90 percent of fish (or aquatic) species.

Risk Assessment: Risk Characterization

To compare exposure data to effect data, an acute risk quotient (RQ_{acute}) and a chronic risk quotient ($RQ_{chronic}$) was calculated for each contaminant. The RQs were calculated by dividing the 90th centile for the exposure data by the 10th centile of the toxicity data:

$$\frac{90th\ \%\ exposure\ concentration}{10th\ \%\ effect\ concentration} = RQi$$

The RQ_{acute} evaluates short term or immediate risk of mortality, whereas the $RQ_{chronic}$ evaluates risk of sublethal effects that have long-term influence on population

dynamics and performance. RQ greater than 1 identify an exposure where more than 1% of organisms are expected to suffer effects. High risk of acute effects was identified when RQ_{acute} was greater than 0.5 (EPA 1998, EPA 2008). $RQ_{acute} < 0.5$ were considered of low acute risk. In contrast, for $RQ_{chronic}$ values > 1 were considered high risk, whereas values $<$ 1 were considered of low chronic risk.

To further characterize risk, joint probability curves (or exceedance profiles) were constructed for contaminants with high RQ, using the program EX2.1 (RIVM 2014), when enough exposure data was available. These curves describe the relationship between the magnitude of the effect and the probability of occurrence for that effect. A point on the curve describes the probability of a concentration exceeding the endpoint for a given percentage of species in a SSD. The area below the curve signifies the percent of organisms at risk determined by the exposure and effect data provided. To make the risk assessment relevant to life history stages of interest (postlarval/early juveniles vs. subadults/adults), when feasible additional joint probability curves were constructed using nearshore concentrations (<1 km from land) and open bay concentrations (> 1 km from land).

RESULTS

Identification of COPECS

In Biscayne Bay 4 categories of contaminants with guidelines (metals, PCBs, PAHs, and banned pesticides) showed $HQ_i > 1$ in sediment samples (Figure 2), whereas no water samples in Biscayne Bay had exceedances. In Biscayne Bay, the following COPECs were identified: arsenic, copper, PCBs, benz(a)anthracene, chrysene, fluoranthene, pyrene, and DDT & its metabolites. The highest concentrations were detected at coastal locations or inflow points to Biscayne Bay (i.e., Miami River, Goulds Canal, Sunset Harbor, the C111 canal mouth at Manatee Bay, and Maule Lake-a heavily urbanized part of northern Biscayne Bay, APPENDIX A).

In Florida Bay, the COPECS identified included current-use pesticides chlorpyrifos and endosulfan in water samples, and banned pesticides lindane and DDT (and its metabolite DDD) in sediment samples (FIGURE 3). For both pesticide types, studies reported higher concentrations in South Florida canals than within FLBAY itself (APPENDIX A). In the Florida Keys region, no guideline contaminants were detected with $HQ_i > 1$. Estrone was considered to be a COPEC, despite not having a guideline, based on Key Largo Harbor exceeded levels known to effect fish reproductive hormones in the laboratory (Singh et al. 2010).
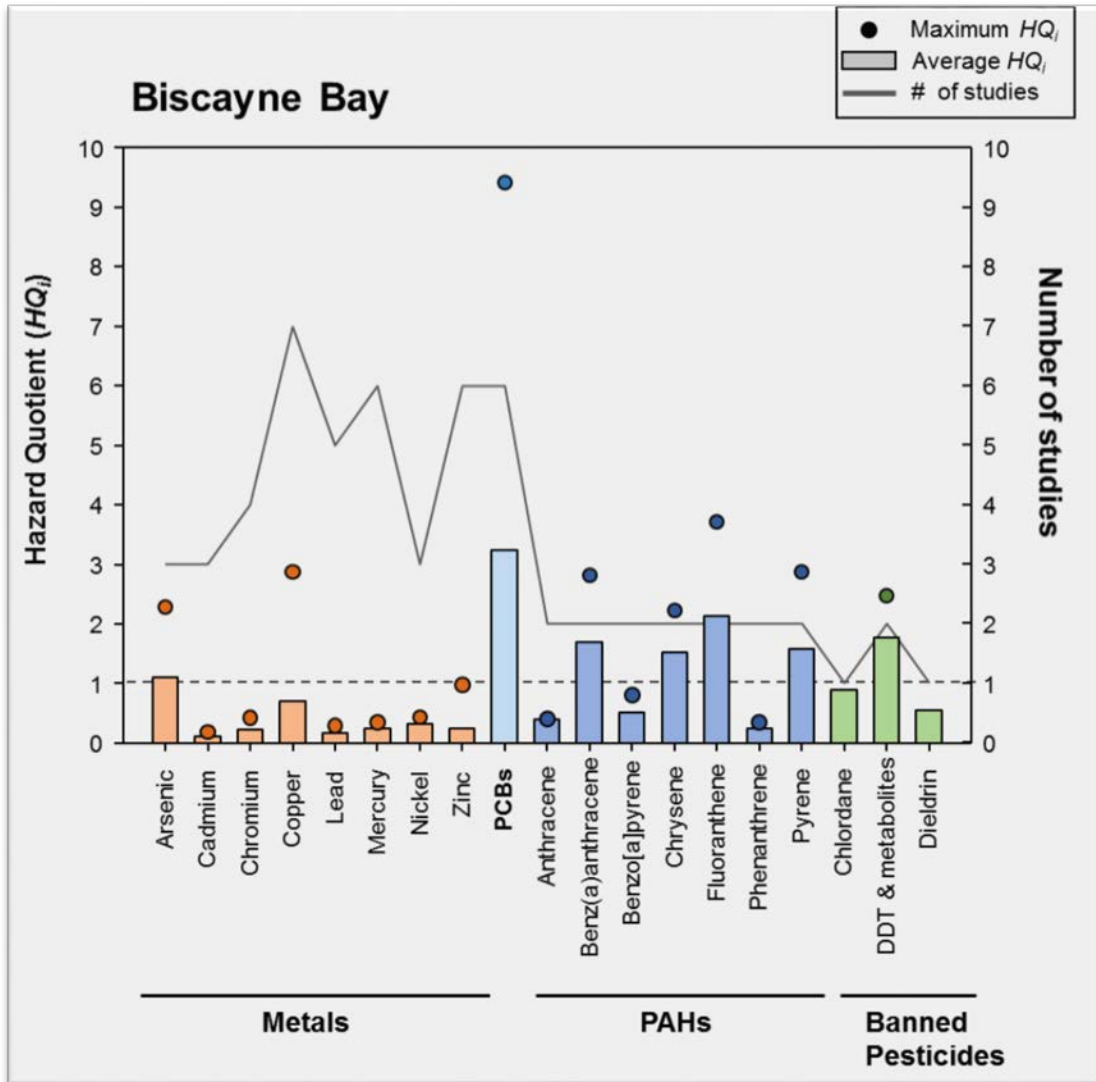
Figure 2. Hazard quotients (HQ) in Biscayne Bay for 4 categories of chemicals: Metals, PCBs, PAHs, and banned pesticides. Shown are the average and maximum HQ (if > 1 study) for each chemical, along with the number of studies. All values are from sediment. Dotted line indicates a HQ or ratio of 1, such that values >1 are above guidelines and thus of concern. Biscayne Bay included samples as far south as Card Sound, and samples from canal mouths and the Miami River.
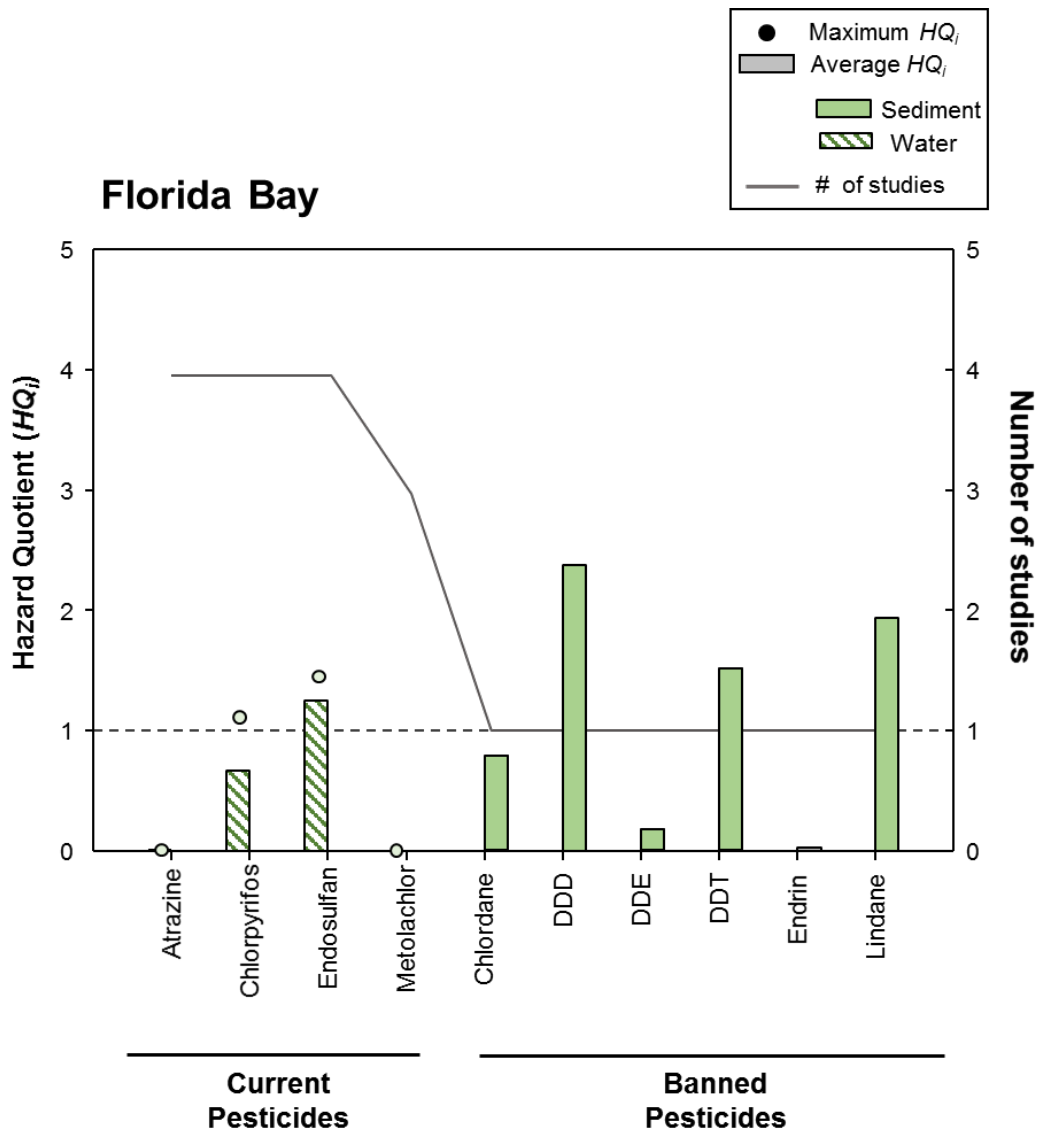
Figure 3. Hazard quotients (HQ) in Florida Bay for Current and Banned Pesticides. Shown are the average and maximum HQ (if > 1 study) for each chemical, along with the number of studies. Current Pesticides values are from water, while Banned Pesticides values are from sediment. Dotted line indicates a HQ or ratio of 1, such that values >1 are above guidelines and thus of concern.

Exposure Data Results

Recent data availability for exposure were limited, with each contaminant only having between 15 and 68 data points or samples for the time period 1998-2015 (Table 3). All 12 chemicals have detectable concentrations, except for the banned pesticide Lindane (banned in 2007), which was not detected in 30 samples tested in Florida Bay. Long term data from the Goulds Canal in Biscayne Bay (from NOAA Mussel Watch) shows that sediment concentrations of the banned toxins Lindane, DDT, and PCBs have been decreasing since the 1990s (Figure 4). For copper, exposure data was highest in the nearshore environment (< 1 km from land) than at greater distances (Table 3) and does not seem to be declining, at least for the Goulds Canal (Figure 4).

TABLE 3. Summary of Exposure Concentration Data. Shown are the 90th centile concentrations (or concentration for which 90% of the data points are smaller) for each COPEC, along with the # of samples in each dataset and sources. Concentrations are water or estimated pore water concentrations (ug/L). For copper, a 90th centile concentration was calculated for the nearshore (within 1 km of land), open bay, and for all points.

Region	Chemical	90th Centile Concentrations (ug/L)	N	Source
Biscayne Bay	Copper (all data)	5.8	61	(1) (2) (3)
	Copper (nearshore)	54.5	23	(1) (2) (3)
	Arsenic	37.7	63	(1) (2) (3)
	Benz(a)anthracene	0.0049	30	(1)
	Chrysene	0.0014	30	(1)
	Fluoranthene	0.061	30	(1)
	Pyrene	0.006	30	(1)
	PCB Total	0.00073	34	(1) (2)
	DDT Total	0.001	15	(1)
Florida Bay	Lindane	None detected	37	(1) (2)
	DDT Total	0.00009	31	(2)
	Chlorpyrifos	0.00319*	24	(4)
	Endosulfan	0.0101*	24	(4)
Florida Keys	Estrone (85th centile reported, in Key Largo Harbor)	0.0022*	16	(5)

1. NOAA National Status and Trends Database. 2. EPA Coastal Condition Assessment
3. Castro et al. 2013 4. Carriger & Rand 2008b. 5. Singh 2010. * Values are from published studies and not calculated.
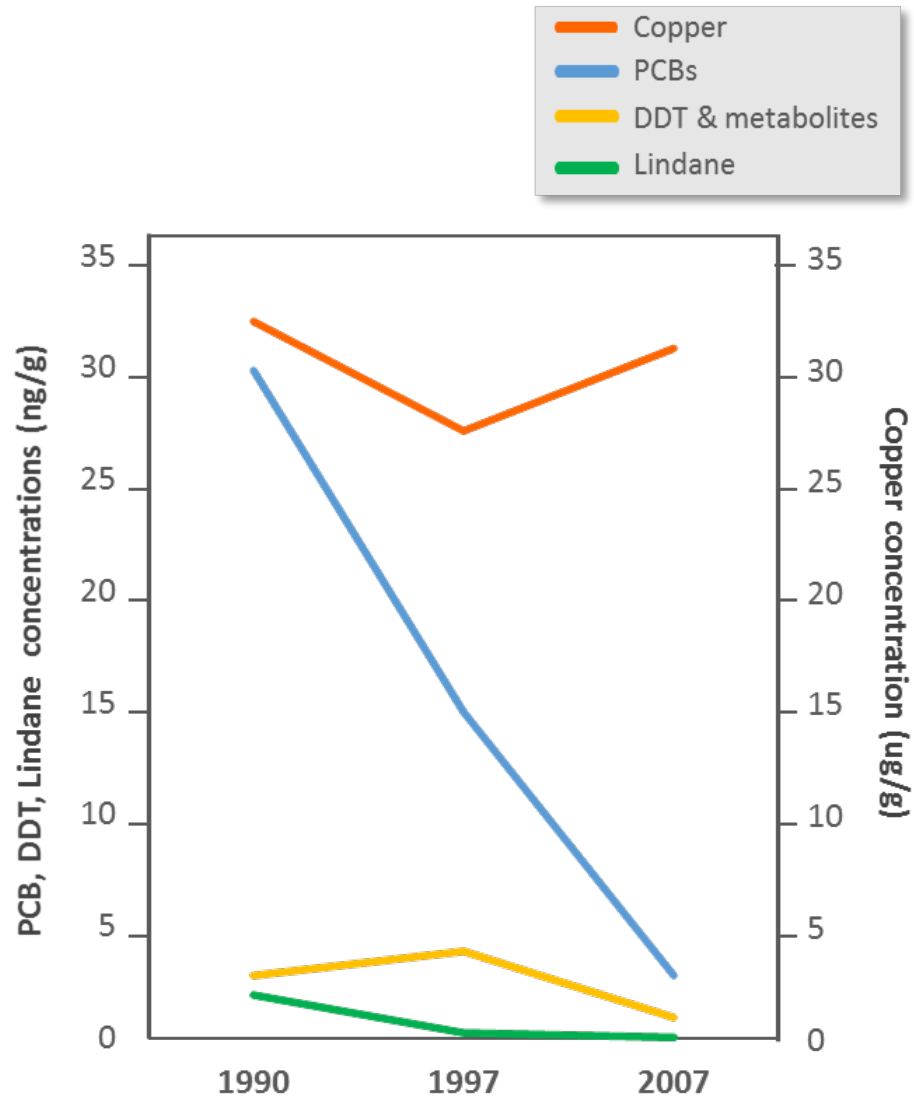
Figure 4. Mussel Watch sediment contaminant concentrations from Gould's Canal in southern Biscayne Bay. There is a major decline in the banned contaminants PCBs, DDTs, and Lindane since 1990, but no notable decline in copper.

Effects Data Results

Data from between 6 and 45 species were used for building acute and chronic SSD curves for each contaminant (Table 4). SSD curves are shown for copper (Figure 5), endosulfan (Figure 6), and estrone (Figure 7), all found to be a potential risk to fish and bonefish in South Florida (see *Risk characterization results* below). The 10th centile acute

concentration for copper was 25.2 ug/L, while chronic concentration was 2.2 (Figure 5, Table 4). For endosulfan, the 10th centile acute concentration was 0.12 ug/L, and the chronic concentration was 0.0017 ug/L (Figure 6, Table 4).

For estrone, the 10th centile chronic concentration was 0.0022 ug/L (Figure 7, Table 4). For acute effects of estrone, there is not enough acute toxicity data to construct a species sensitivity curve, and as a hormone its effects would likely be sublethal (chronic). Pharmaceutical hormones, such as estrone, are not expected to have acute toxicity to fish at environmentally relevant levels (Ternes and Joss 2006).

TABLE 4. Details of the effects data for both acute and chronic effects for the COPECS. Shown are the # of species (N_{spp}) used in SSD curves, the endpoint (LC50, LOEC or EC50), the type of taxa used (SW=Saltwater, FW=freshwater), and the resulting 10th centile effect concentrations for focal contaminants.

Contaminant	N_{spp}	Endpoint	Taxa	10 Centile Effect ug/L
Arsenic acute	36	LC50s	All fish	2160.0
Arsenic *chronic*	6	LOECs	All fish	856.31
Copper acute	45	LC50s	SW fish	25.18
Copper *chronic*	30	LOECs	SW & FW fish	2.22
Chlorpyrifos acute	11	LC50s	SW fish	0.60
Chlorpyrifos *chronic*	18	LOECs	All fish	0.11
DDT acute	20	LC50s	All fish	0.25
DDT *chronic*	6	LOECs EC50s	All fish	0.16
Endosulfan acute	11	LC50s	SW fish	0.12
Endosulfan *chronic*	10	LOECs	All fish	0.0017
Estrone acute	NA	NA	Insufficient data	NA
Estrone *chronic*	6	LOECs	All fish	0.0022
PCBs (Aroclor 1254) acute	12	LC50s	All fish	0.31
PCBs *chronic*	8	LOECs	Fish & other taxa	0.1806
Benz(a)anthracene			see Pyrene	
Chrysene			see Pyrene	
Fluoranthene acute	7	LC50s	Fish & other taxa	0.25
Fluoranthene *chronic*	16	LOEs	Fish & other taxa	1.58
Pyrene acute	17	LC50s	Fish & other taxa	1.44
Pyrene *chronic*	8	LOECs EC50s	Fish & other taxa	0.85
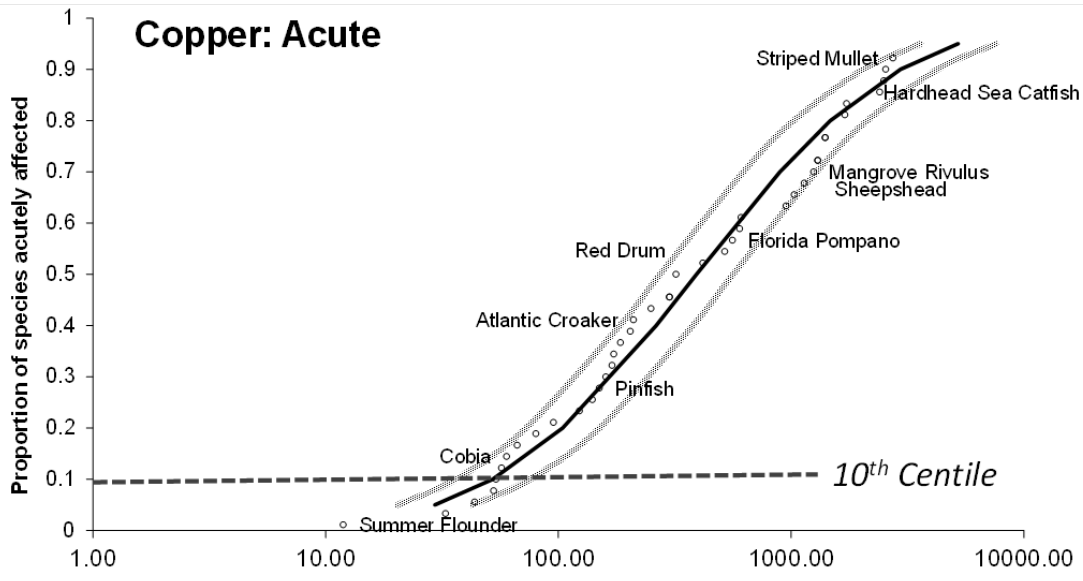
Figure 5. Species Sensitivity Distributions for Acute and Chronic Effects of Copper. Acute effects used LC50s for saltwater fish species, while chronic effects used LOECs for fresh and saltwater fish species. Each point represents a fish species, with some species of interest shown. 95% confidence intervals are shown, and the 10th centile of species affeted is shown by the dashed line.

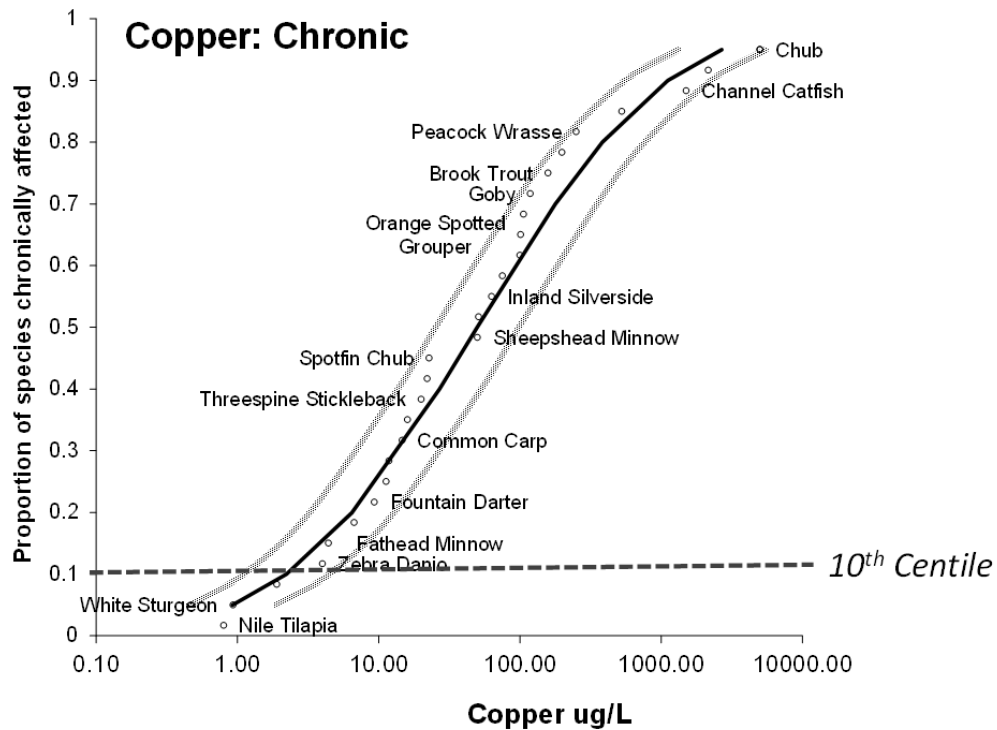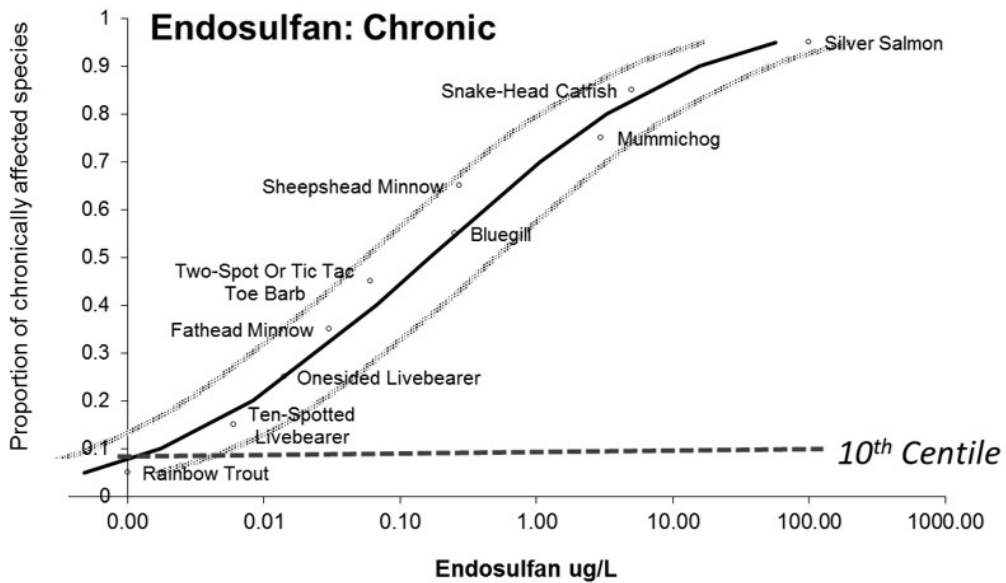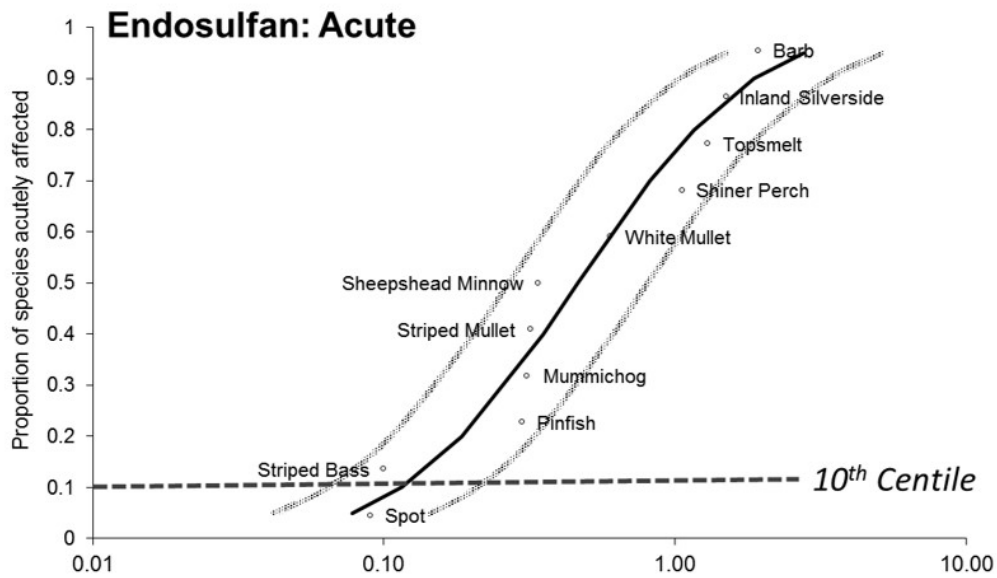**Figure 6**. Species Sensitivity Distribution for Acute and Chronic Effects of Endosulfan. Acute effects used LC50s for saltwater fish species, while chronic effects used LOECs for fresh and saltwater fish species. Each point represents a fish species, with some species of interest shown. 95% confidence intervals are shown, and the 10th centile of species affects is shown by the dashed line.
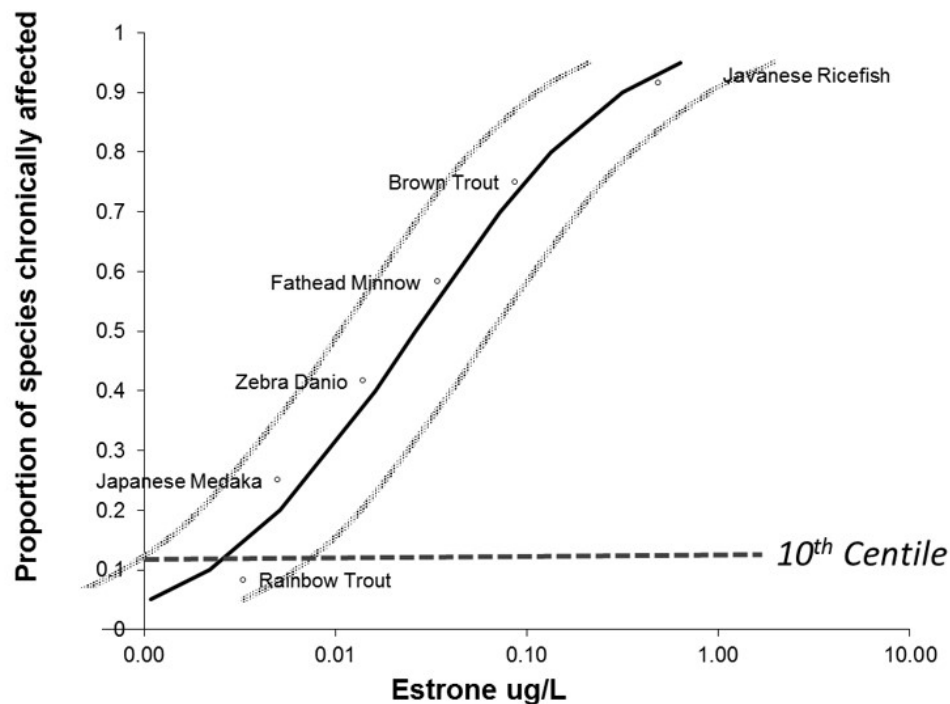
Figure 7. Species Sensitivity Distribution for Chronic Effects of Estrone. Effects used are LOECs for 6 fish species. 95% confidence intervals, and the 10th centile of species affected (dashed line) are shown.

Risk Characterization Results

The calculated risk quotients (RQ$_i$s) show that out of the 12 contaminants examined, copper in Biscayne Bay, endosulfan in Florida Bay, and estrone in the Florida Keys pose a chronic risk to at least 10% of species at the 90th centile of exposure, with copper posing the highest risk (Table 5). All other contaminants are expected to pose a low risk based on RQ$_{acute}$ < 0.5 and RQ$_{chronic}$ < 1.

Further assessment of risk was possible for copper but not endosulfan or estrone, because of the use of summary data presented in publications rather than actual environmental concentrations. For copper, the exposure data were sorted into 3 categories of interest, all samples, nearshore (within 1 km), and open bay (>1 km from shoreline),

with RQs (Table 6). Copper may pose an acute risk to bonefish in nearshore but not in areas away from shore, and may pose an chronic risk in both nearshore and open bay habitats.

TABLE 5. Risk quotients (RQs) calculated for acute and chronic risk for the 12 COPECS in each of the 3 focal regions. Light blue shading indicates RQ < 0.5 or low risk, while RQs > 1 indicate high risk and are bolded and highlighted in orange. *Lindane was not detected in recent studies of Florida Bay, thus an RQ of zero is reported. For estrone**, not enough acute toxicity data are available to calculate an RQ_{Acute}. Estrone samples came from an inshore canal sample in Key Largo.

Chemical	Biscayne Bay		Florida Bay		Florida Keys	
	RQ_{Acute}	$RQ_{Chronic}$	RQ_{Acute}	$RQ_{Chronic}$	RQ_{Acute}	$RQ_{Chronic}$
Arsenic	0.017	.044				
Copper	0.37	**8.8**				
PCBs	0.003	0.09				
Lindane			0*	0*		
DDT & metabolites	0.00036	0.00057	0.0041	0.0064		
Endosulfan			0.09	**5.8**		
Chlorpyrifos			0.028	0.029		
Estrone**					No data	**1.0**
Chrysene	0.00095	0.0016				
Fluoranthene	0.25	0.039				
Pyrene	0.0041	0.007				
Benz(a)anthracene	0.0034	0.0057				

The area beneath the joint probability curve (Figure 8) is the Expected Ecological Risk (EER), which represents the probability that a random species at a random exposure would be effected. The acute EER of copper in open bay is 0.01%, while nearshore it is 1.83%. The chronic EER of copper is much higher, 17.9% in the nearshore and 3.4% in

open bay areas. This means that bonefish have a 17.9% probability of being a species affected by chronic exposure in the nearshore environment and a 3.4% probability in areas further away from the shoreline.
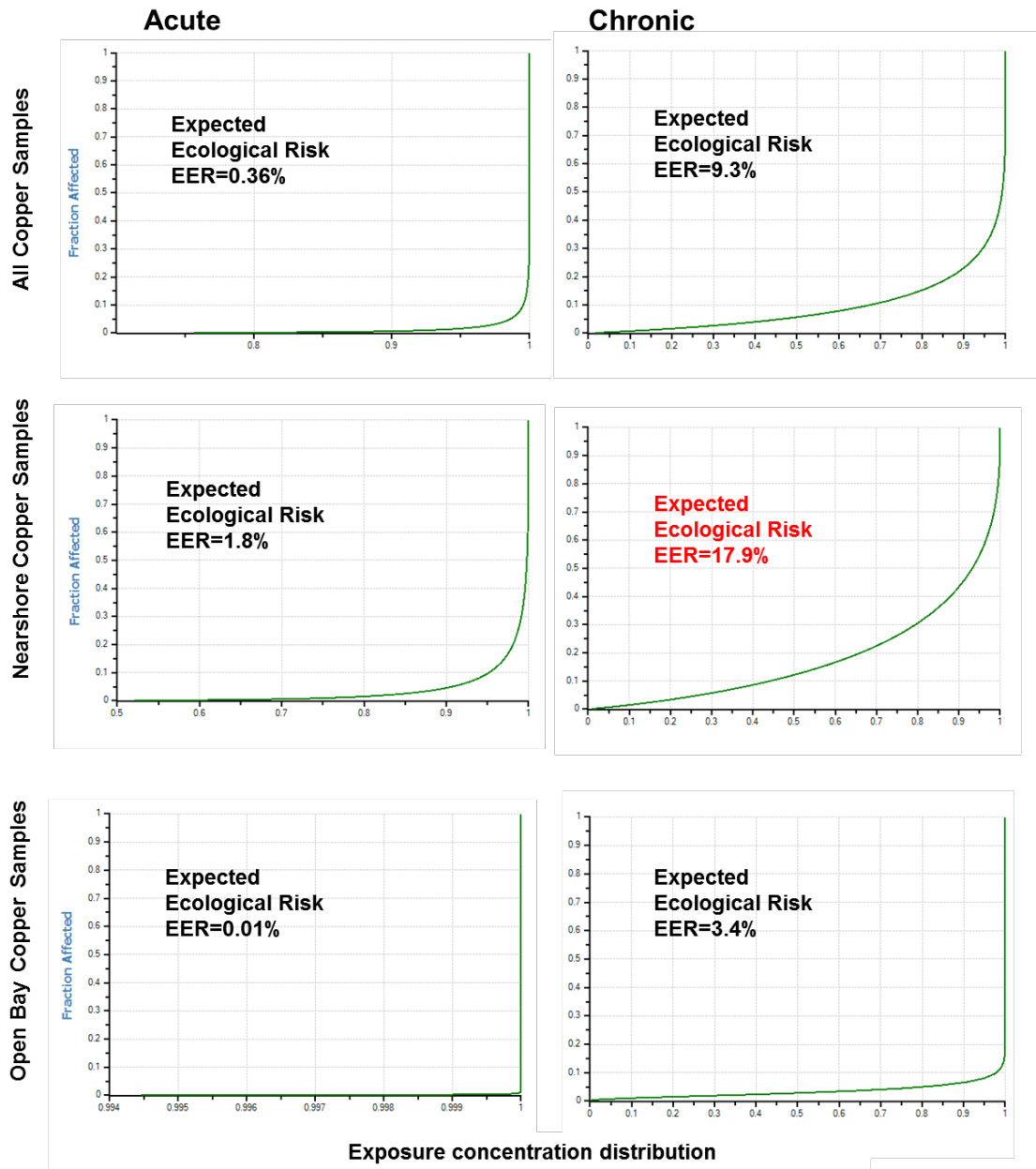
Figure 8. Joint probability curves for acute and chronic effecters of copper on fish in Biscayne Bay for all, nearshore (<1 km) and open bay (>1km) samples. The area under the curve represents the Expected Ecological Risk, or the risk that a randomly selected species will be affected at a randomly selected environmental concentration.

TABLE 6. Risk Quotients (RQs) for copper in the nearshore (< 1 km) and open bay (> 1 km) in Biscayne Bay. Light blue shading indicates RQ < 0.5 or low risk, while RQs > 1 indicate high risk and are bolded and highlighted in orange. In nearshore Biscayne Bay, RQ_{Acute}>1 indicates an acute risk to 10% of species 10% of the time. $RQ_{chronic}$>1 indicates a chronic risk to 10% of species at least 10% of the time, with the most risk nearshore and the least risk in open bay habitat.

Biscayne Bay	RQ_{acute}	$RQ_{chronic}$
Copper (all samples)	0.37	**8.8**
Nearshore (< 1 km from land)	**3.3**	**77.5**
Open Bay (> 1 km from land)	0.1	**2.3**

DISCUSSION

The risk assessment presented here evaluated the risk of 12 contaminants flagged as COPEC for exceeding water quality and sediment contaminant guidelines, and/or levels known to be deleterious to fishes. The risk assessment identified the metal copper, the pesticide endosulfan, and hormone estrone as the highest risk contaminants in Biscayne Bay, Florida Bay, and the Florida Keys respectively. For copper, risk was associated with both acute and chronic effects, while for endosulfan and estrone, risk to bonefish was associated with chronic effects. For the 3 contaminants, risk was present, or increased in the case of cooper, along the coastline (< 1 km from land) and thus pose a risk to early life stages in bonefish. In addition, the risk assessment predicted low risk of chronic and acute effects to bonefish in Biscayne Bay from arsenic, PCBs, DDT, benz(a)anthracene, fluoranthene, and pyrene, and low risk in Florida Bay from DDT and chlorpyrifos.

These results are largely in agreement with findings of past risk assessments. Copper has been previously identified as a risk to South Florida coastal environments (Schuler et al. 2008, Castro et al. 2013). The source of our endosulfan exposure data (Carriger and Rand 2008b) and other risk assessments (Carriger et al. 2006, Rand et al. 2010, Quinete et al. 2013) also identified endosulfan as a risk to South Florida aquatic environments. For estrone, no risk assessment has been conducted. The only disagreement found relative to previous assessments was that we did not find risk from the current pesticide chlorpyrifos unlike Harman-Fetcho et al. (2005), although their focal study area was mainly inland waters.

The highest risk found in our risk assessment came for copper in Biscayne Bay. Copper enters the estuarine environment in South Florida as runoff from agricultural and industrial use, and is applied directly to surface water as an algaecide (Schuler et al. 2008). The acute and chronic risk from copper were greater in nearshore habitats than in open Biscayne Bay. For nearshore habitats located less than 1 km from land, the acute risk of copper was above the threshold expected to affect 10% of species 10% of the time, as shown by an RQ>1. The nearshore acute EER (expected ecological risk) of 1.8% represents the probability of acute effects for a randomly selected fish species at a random Biscayne Bay coastal exposure. Although this EER represents a relatively small risk, bonefish have a 1.8% probability of being a species affected by acute copper contamination, and thus mortality along BBAY shorelines.

The acute effect of copper presents a particular concern to late-stage larval bonefish, which are expected to recruit to nearshore habitats, although the precise characteristics and location of these habitats in South Florida remain unknown (Adams et al. 2008, Dahlgren et al. 2008, Haak et al. unpub. data). *Albula vulpes* larvae are rarely seen in South Florida (Harnden et al. 1999, Adams et al. 2008, Dahlgren et al. 2008), despite subadults and adults of the species inhabiting seagrass flats throughout the region and constituting the recreational fishery. Whether this rarity of larval and postlarval life stages is natural, an artifact of a lack of sampling in the appropriate habitats, or potentially a result by human activity is unclear. Regardless, our risk assessment suggests that coastal contamination by copper in BBAY could be a potential contributing factor. Because adult fish are not expected to spend the majority of their time in these highly contaminated nearshore sites, their risk of acute mortality from copper exposure is expected to be lower.

Chronic effects from copper posed the highest risk in our assessment, particularly in the nearshore environment. The EER of the copper chronic effects were higher than the EER of the acute effects by approximately an order of magnitude. For BBAY, the 90th centile concentration is expected to cause chronic effects in about 23% of fish species, based on the joint probability curve. Bonefish have a 23% probability of being a species affected by chronic copper contamination along Biscayne Bay shorelines. Copper chronic effects to saltwater and freshwater fish from laboratory studies include behavioral changes in activity, aggregation, aggression, freezing behavior, swimming, surfacing, and foraging (Petrauskiene & Vosylienë 1995, Petrauskiene 1999, Tilton et al. 2011, Zizza et al. 2014). Declines in biomass, body condition, length, and growth have also been noted in laboratory settings (Reader et al. 1989, Karytug et al. 2007, Roussel et al. 2007, Zhao et al. 2011). Reproductive declines in egg size, sperm count, and sperm mobility have been caused by chronic exposure to copper (Shakila et al. 1985, Lahnsteiner et al. 2004). These types of effects could reduce overall survival of late-stage larval bonefish, and thus settlement success, with negative consequences for bonefish populations. The estimated porewater 90th centile exposure for copper in BBAY (5.8 ug/L, TABLE 2) was higher than the LOEC (Lowest Ecological Effect Concentration) for Nile tilapia (0.8 ug/L, and one of the better studied and most sensitive species to copper), shown to decrease food consumption and growth, increase liver weight and metabolic rate, as well as change cells, enzymes, and biochemistry (Abdel-Tawwab et al. 2007).

Chronic exposure to endosulfan in Florida Bay presented the second highest risk in the analysis. Endosulfan is an organochlorine pesticide used in South Florida agriculture that is being phased out of use in 2016. The source of endosulfan to Florida Bay has been

runoff from canals and atmospheric deposition as a result of spraying (Hapeman et al. 2013). Endosulfan detections used in our risk analysis were collected in nearshore environments in FLBAY (i.e., Joe Bay), thus we expect endosulfan to also represent a risk to late state larval bonefish that may use these habitats. Juvenile *Albula vulpes* have been collected in coastal embayments in this region of northeastern FLBAY (Little Blackwater Sound, Haak et al. unpubl data).

Exposure to endosulfan can be expected to decline as it is phase out of use in Agriculture. Long-term Mussel Watch data from the Goulds Canal in southern Biscayne Bay (FIGURE 4) shows this type of a decline for earlier banned chemicals, including the pesticides Lindane and DDT, and PCBs. However, endosulfan stored in organism tissue and sediment may still persist in the environment for years. Effects of endosulfan observed in the laboratory include changes to the biochemistry, physiology, growth, behavior, and reproduction of aquatic organisms (Matthiessen & Logan 1984, Bhusari et al. 1985, Shafiei & Costa 1990, Pandey 2006, Holdway & Smith 2008, Sarma et al. 2009). The 90th centile water exposure for endosulfan in our analysis (0.0101 ug/L) was higher than LOECs for cellular changes in Rainbow Trout (0.001 ug/L, Arnold et al. 1996) and changes in predatory behavior in Ten-Spotted Livebearer (0.006 ug/L, Gutierrez et al. 2013), but less information is available for low concentration effects on saltwater fishes.

Estrone, a female sex hormone with multiple pharmaceutical uses including birth control, was found in canals in Key Largo Harbor in association with wastewater (Singh et al. 2010). We calculated an $RQ_{chronic} = 1.0$ for estrone, (due to a chance occurrence of a 10th centile of effects and 85th centile of exposure that were the same). This indicates that estrone is only expected to affect the most sensitive 10% of species in the top 15% of

exposures. The effects of estrone in toxicological studies in fish are all related to reproduction (Hutchinson et al. 1999, Andersen et al. 2001, Pounds et al. 2002, Roepke et al. 2005, Vethaak et al. 2005, Imai et al. 2007). Freshwater rainbow trout were affected by estrone with an increase in vitellogenin, a yolk producing protein (at a concentration of 0.0033 ug/L, Thorpe et al. 2003). The lowest known concentration to affect saltwater fish caused an increase in liver vitellogenin in Java Medaka, (at 0.484 ug/L, Imai et al. 2007), which is about 10 times greater than the highest detection in Key Largo (APPENDIX A). Bonefish are not likely to be present in the canals of Key Largo Harbor, and estrone outside of this area is expected to be greatly diluted.

This risk assessment has made a number of important assumptions and has several potential sources of error. Toxicological data on bonefish are unavailable, nor are there data on a suitable surrogate species, as is sometimes used to evaluate an endangered or species of conservation concern (e.g., Marcus et al. 2010). The use of SSD curves and selected the HC10 value assumes that bonefish are not among the 10% most sensitive species to the examined contaminants. Further, the use of toxicological effects data assumes that species in toxicology studies are representative of all species (including bonefish), and that organisms in the laboratory have similar effect thresholds to organisms in the wild.

Another important limitation in this study is the small volume of environmental exposure data, such that over the past 18 years of studies there was found only between 15 and 68 data points per contaminant collected in the focal coastal embayments with which to evaluate potential exposure to bonefish. This sample size is in the lower end of the range of sample sizes used in previous South Florida risk assessments, ranging from 11 samples

(Julian et al. 2015) to 3522 samples (Schuler et al. 2008). This is a small number of samples and using them in risk assessment assumes that they representative of both the spatial and temporal variation in concentrations in habitats that could expose bonefish to contaminants. Additionally, construction of SSD and joint probability curves assumes a random sample and a lognormal distribution. However, data used could be biased towards locations with higher contamination (e.g., canal entry points to the bays), which would lead to risk over-estimation. Last, error may have been introduced with the estimation of pore water concentrations from sediment samples.

In sum, highest potential contaminant risk to bonefish found by this risk assessment was from chronic effects of copper, followed by acute effects of copper nearshore which could negatively affect recruitment of bonefish to coastal habitats. Chronic effects from endosulfan in Florida Bay and estrone in Key Largo Harbor to also were found to pose a potential risk to fish, although this was less likely. Risk posed by endosulfan is expected to decline in the near future, while there is no indication that copper may be declining in South Florida coastal waters. Increased ecological information for bonefish in South Florida, particularly delineation of critical habitat for early life stages, as well as additional information on bonefish recruitment dynamics would help identify areas on which to focus future contaminant studies. Toxicity studies specifically conducted on bonefish are also needed to ensure that bonefish are not more sensitive than expected to these particular and other potentially risky contaminants. Increased sampling of contaminants in habitat bonefish use most, such as on flats and nearshore environments known to be used by juveniles, should permit a more thorough probabilistic risk assessment. Our findings

suggested that contaminants could be a source of risk to early life history bonefish using

shorelines and could be part of the overall picture of bonefish decline.

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APPENDIX

APPENDIX A. Details of the 30 chemicals detected over guidelines (Hazard quotients, HQ$_i$ > 1) across regions, locations and matrices (sediment, water and animal tissue).

Category	Chemical	Region	Matrix [a]	Location [b]	Hazard Quotient
Metals	Arsenic	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay (G)	1.4
				Manatee Bay (Y)	2.3
				Miami River (I)	1.5
				Miami River & Adjoining Biscayne Bay (K)	90/226 samples exceeding guidelines
	Cadmium	Biscayne Bay	Sediment[2]	Miami River (I)	2.1
				Miami River & Adjoining Biscayne Bay (K)	27/226 samples exceeding guidelines
	Chromium	Biscayne Bay	Sediment[2]	Miami River & Adjoining Biscayne Bay (K)	8/226 samples exceeding guidelines
	Copper	Biscayne Bay	Sediment[2]	Goulds Canal (C)	1.6
				Maule Lake (C)	2.9
				Miami River (I)	122.2
				Miami River & Adjoining Biscayne Bay (K)	75/226 samples exceeding guidelines
	Lead	Biscayne Bay	Sediment[2]	Miami River (I)	6.6
				Miami River & Adjoining Biscayne Bay (K)	52/226 samples exceeding guidelines
	Mercury	Biscayne Bay	Sediment[2]	Miami River (I)	11.0
				Miami River & Adjoining Biscayne Bay (K)	71/226 samples exceeding guidelines
		Inland Canals	Sediment[2]	Canal C-111 (G)	1.5

Category	Chemical	Region	Matrix [a]	Location [b]	Hazard Quotient
	Nickel	Biscayne Bay	Sediment[2]	Miami River & Adjoining Biscayne Bay (K)	4/226 samples exceeding guidelines
	Silver	Biscayne Bay	Sediment[2]	Miami River & Adjoining Biscayne Bay (K)	30/226 samples exceeding guidelines
	Zinc	Biscayne Bay	Sediment[2]	Miami River (I)	7.9
				Miami River & Adjoining Biscayne Bay (K)	29/226 samples exceeding guidelines
PAHs	Benz(a)anthracene	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay (G)	2.8
		Inland Canals	Sediment[2]	Canal C-111 (G)	3.1
PAHs	Benzo[a]pyrene	Inland Canals	Sediment[2]	Canal C-111 (G)	1.6
	Chrysene	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay (G)	2.2
	Chrysene	Inland Canals	Sediment[2]	Canal C-111 (G)	1.9
	Dibenz[a,h]anthracene	Inland Canals	Sediment[2]	Canal C-111 (G)	1.9
	Fluoranthene	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay (G)	3.7
		Inland Canals	Sediment[2]	Canal C-111 (G)	4.4
	PAH high weight	Biscayne Bay	Sediment[2]	Miami River & Adjoining Biscayne Bay (K)	51/226 samples exceeding guidelines
	PAH low weight	Biscayne Bay	Sediment[2]	Miami River & Adjoining Biscayne Bay (K)	25/226 samples exceeding guidelines
	PAHs	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay (G)	1.0
				Miami River & Adjoining Biscayne Bay (K)	33/226 samples exceeding guidelines

Category	Chemical	Region	Matrix [a]	Location [b]	Hazard Quotient
		Inland Canals	Sediment[2]	Canal C-111 (G)	1.3
	Pyrene	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay (G)	2.9
		Inland Canals	Sediment[2]	Canal C-111 (G)	2.6
PCBs	PCBs	Biscayne Bay	Sediment[2]	Biscayne Bay (F)	9.4
				Goulds Canal (C)	1.6
				Maule Lake (C)	5.7
				Miami River & Adjoining Biscayne Bay (K)	106/226 samples exceeding guidelines
Pesticides Currently Used	Chlorpyrifos	Florida Bay	Water[5]	Joe Bay (D)	1.1
		Inland Canals	Water[5]	Canals South Florida (H)	10.4
				Canal C-111 (E)	1.5
	Diazinon	Inland Canals	Water[5]	Canals South Florida (L)	22.5
	Endosulfan I	Inland Canals	Water[3]	Canals South Florida (L)	25.3
	Endosulfan II	Inland Canals	Water[3]	Canals South Florida (L)	9.0
	Endosulfan	Florida Bay	Water[3]	Everglades (E)	1.5
				Florida Bay (O)	1.0
				Highway Creek (D)	1.0
				Joe Bay (D)	1.3
		Inland Canals	Water[3]	Canal C-111 (O)	14.3
				Canal C-111 (E)	35.0
				Canal C-111 (O)	54.8
Pesticides Banned or Severely Restricted	Chlordane	Biscayne Bay	Sediment[2]	Miami River & adjoining Biscayne Bay (K)	7/226 samples exceeding guidelines
	Chlordane	Inland Canals	Sediment[2]	Canals near Big Cypress	68.6

Category	Chemical	Region	Matrix [a]	Location [b]	Hazard Quotient
				and Everglades [(M)]	
				Canals South Florida [(L)]	24.3
			Water[3]	Canals South Florida [(L)]	83.7
	DDD	Florida Bay	Sediment[2]	Shell Creek [(G)]	2.4
		Inland Canals	Sediment[2]	Canals Near Big Cypress and Everglades [(M)]	12.3
				Canals South Florida [(L)]	114.8
	DDE	Inland Canals	Sediment[2]	Canals Near Big Cypress and Everglades [(M)]	43.0
				Canals South Florida [(L)]	101.5
	DDT	Biscayne Bay	Sediment[2]	Canal C-111 mouth at Manatee Bay [(G)]	1.2
		Florida Bay	Sediment[2]	Shell Creek [(G)]	1.5
		Inland Canals	Sediment[2]	Canals Near Big Cypress and Everglades [(M)]	9.8
				Canals South Florida [(L)]	65.6
			Water[3]	Canals South Florida [(H)]	17.9
	DDT & metabolites	Biscayne Bay	Sediment[2]	Canal C-111 Mouth at Manatee Bay [(G)]	1.1
				Goulds Canal [(C)]	2.5
				Maule Lake [(C)]	2.0
				Miami River & Adjoining Biscayne Bay [(K)]	68/226 samples exceeding guidelines
	Dieldrin	Biscayne Bay	Sediment[2]	Miami River & Adjoining Biscayne Bay [(K)]	19/226 samples exceeding guidelines
		Inland Canals	Water[3]	Canals South Florida [(H)]	28.6
	Lindane	Florida Bay	Sediment[2]	Shell Creek [(G)]	1.9

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Category	Chemical	Region	Matrix [a]	Location [b]	Hazard Quotient
		Inland Canals	Sediment[2]	Canals Near Big Cypress and Everglades [(M)]	106.9
	Heptachlor	Inland Canals	Water[3]	Canals South Florida [(H)]	33.3
	Heptachlor epoxide	Inland Canals	Sediment[6]	Canals Near Big Cypress and Everglades [(M)]	12.8
	Mirex	Inland Canals	Water[3]	Canals South Florida [(H)]	1.9

[a]Guidelines used for hazard quotient calculations: **2.** Florida Department of Environmental Protection Coastal Waters Sediment Quality Assessment Guidelines Saltwater Threshold Effect Levels, **3.** Florida Department of Environmental Protection Class III Marine Chronic Surface Water Quality Standards 2010, **5.** USEPA Saltwater Continuous Chronic Exposure Aquatic Life Criteria, and **6.** Canadian Environmental Quality Guidelines Aquatic Life Criteria.

[b]Sources: **A:** Adams & Onorato (2005), **B:** Adams et al. (2005), **C:** Cantillo et al. (1997), **D:** Carriger & Rand (2008), **E:** Fulton et al. (2004), **F:** Gassman et al. (1994), **G:** Goodman et al. (1999), **H:** Harman-Fetcho et al. (2005), **I:** Julian (2015) **K:** Long (2002), **L:** Miles & Pfeuffer (1997), **M:** Miller et al. (2004) **N:** Ogden et al. (1973), **O:** Scott et al. (2002), **P:** Strom & Graves (2001), **Y:** Cantillo & Lauenstein (2004)