Chemical contamination in southwest Puerto Rico: A survey of contaminants in the coral *Porites astreoides*

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ABSTRACT.—Coral (*Porites astreoides*) from eight sites in southwest Puerto Rico were analyzed for approximately 150 chemical contaminants, to provide a preliminary characterization of environmental contamination in the corals, and assess the relationships between chemical contamination in corals and adjacent sediments. Overall, the concentration of PAHs (polycyclic aromatic hydrocarbons) and PCBs (polychlorinated biphenyls) detected in the limited number of coral samples collected were comparable to concentrations found in sediments. However, the concentration of a chemical contaminant (e.g., PAHs) in the corals at a site was often different from what was found in adjacent sediments. The level of PCBs and DDT (dichlorodiphenyltrichloroethane) in the corals appeared higher just outside of Guanica Bay, and there was some evidence of a downstream concentration gradient for these two contaminant classes. The trace elements copper and zinc were frequently detected in *Porites astreoides*, and the concentrations were usually comparable to those found in adjacent sediments. Chromium was an exception in that it was not detected in any of the coral samples analyzed, although it was detected in all of the sediment samples.

INTRODUCTION

Coral reefs are among the most biologically rich ecosystems on earth, providing humans with living resources and services valued at \$375 billion per year (Costanza et al. 1997). Bryant et al. (1998) estimate, however, that 58% of the world's coral reefs are at medium to high risk from overexploitation, coastal development, and pollution from inland and marine based sources. The US Coral Reef Task Force (USCRTF) has identified pollution as a key threat to coral reef resources in Puerto Rico, the US Virgin Islands, and southeast Florida (FDEP 2004). Although pollution is frequently cited as a major factor in the decline of coral reefs (Burke and Maidens 2004; Fabricius 2005; Edinger et al. 1998), the concentration of chemical contaminants present in corals and coral reefs is for the most part, unknown. Quantifying the types and concentrations of chemical contaminants present is an important step towards understanding impacts on corals and coral reefs. For example, significant losses of hard cover coral have been seen in the Caribbean, in part due to disease

(Weil 2004), and understanding linkages between chemical contamination and coral disease could prove useful. Characterizing chemical contaminants present in coral reefs can also provide important baseline information needed to assess subsequent changes in environmental quality, as might result from the implementation of management actions (e.g., best management practices) to preserve or restore affected reef areas. This paper contains a preliminary characterization of chemical contaminants in corals from southwest Puerto Rico, and was part of a larger project to characterize environmental contamination in southwest Puerto Rico, and begin to assess linkages that may exist between contamination and coral condition. This paper is a companion to published results on organic and inorganic chemical contaminants in sediments (Pait et al. 2008a, 2008b). The goals of this work were to quantify chemical contaminants in coral samples, assess how the concentration in the corals compared to adjacent sediments, and determine if there was a relationship (correlation) between

contaminants in corals and sediments at a site.

MATERIALS AND METHODS

Study area

The study area in southwest Puerto Rico included the nearshore waters adjacent to the town of La Parguera and east to Guanica Bay (Figure 1). The study area is within a NOAA-funded Coral Reef Ecosystem Study (CRES) site, and has also been designated as a Natural Reserve by the Puerto Rico Department of Natural and Environmental Resources (DNER). Information on chemical contaminants in corals and sediments can be used to further characterize the area, and help identify issues which could impact the management of the coral reefs.

In this region, the shelf area extends approximately 10 km from shore, and then drops off at approximately 20 m. The shelf has both emergent and submerged reefs and contains a variety of hard and soft corals, along with extensive seagrass beds, coastal fringing mangroves and a series of mangrove islands (Kendall et al. 2001; Christensen et al. 2003). The predominant longshore current flow in the study area is from east to west (CFMC 1998). The town of La Parguera has a population of approximately 26,000 and is a popular weekend and vacation destination. Guanica Bay, in the eastern portion of the study area is bordered by the town of Guanica, and over the years several industrial operations including sugar processing, fertilizer mixing, and textile manufacture have operated there. In addition, the Lajas Valley (Figure 1) has a significant amount of agricultural production, and drains to Guanica Bay through a series of manmade canals.

For this project, a stratified random sampling design based on habitat characteristics was used to select the sampling points. Determining the location of corals and sediments in the study area was made possible by the extensive benthic habitat mapping completed by NOAA in the area (Kendall et al. 2001). Using ArcGIS[®], sampling points where both sediments and corals could be collected were randomly selected from an array of candidate locations.

Coral sample collection and processing

Samples of *Porites astreoides* were collected and analyzed from the eight sites (Coral 1 – Coral 9) shown in Figure 1. Due to logistical reasons, no samples were collected at Coral 7. *Porites astreoides* is a common species in Florida, the Bahamas and the Caribbean (Humann and DeLoach 2002), and occurs



FIG. 1. Coral sites sampled in south west Puerto Rico.

throughout the study area in southwest Puerto Rico. Samples were collected from the vessel Aquanauta using a GPS programmed with the station coordinates. The coral samples were taken by NOAA SCUBA divers in August 2005 using a hammer and an acetone-rinsed punch. The punch produced a coral core with a diameter of 1.2 cm and a similar core length. Downs (personal communication) has found that the living tissue of Porites astreoides extends about 1.2 cm into the coral matrix, and that taking a core of this depth will include the extent of living tissues. A core of this length also results in some of the coral skeleton being included in the sample analyzed. Approximately 20 cores were taken from multiple colonies at a site, placed in a 50 ml Teflon[®] centrifuge tube, drained of water and then placed in a dewar charged with liquid nitrogen. The samples were then stored in a -80° C freezer prior to processing. In the laboratory, corals were ground in an acid washed, solvent-rinsed (acetone) mortar and pestle, using the protocols found in Downs et al. (2005). Liquid nitrogen was added before the grinding commenced to cool the mortar, and during the grinding process to prevent the tissues from thawing and to keep the coral matrix brittle to facilitate the grinding process. The ground coral was placed into certified (IChem®) precleaned jars, and then frozen at -80° C, prior to analysis.

Chemical contaminant analysis

TDI-Brooks International, and the Trace Element Research Laboratory (TERL) at Texas A&M University, conducted the organic and inorganic (trace and major element) analyses, respectively. All coral cores from a site were composited in order to have enough material to detect the contaminants of interest. Each reported coral contaminant value represents the analysis of one composite sample from a site.

Sediments were also analyzed for chemical contaminants at the eight sites as part of the larger project. The top 3 cm of sediment were collected at a site using an acetonerinsed Van Veen sediment grab. Sediment samples were placed into certified precleaned jars, and the chemical analysis was performed on an aliquot of the whole sediment. Additional information on the sediment collections and analysis can be found in Pait et al. (2007). The results of the chemical contaminant analysis in the sediment and the coral samples are reported on a dry weight basis.

Approximately 150 chemical contaminants were analyzed in the samples collected. The 58 polycyclic aromatic hydrocarbons or PAHs analyzed for this project are referred to as total PAHs (Table 1), and were analyzed using gas chromatography/mass spectrometry in the selected ion monitoring mode. Thirty-eight polychlorinated biphenyl (PCB) congeners were quantified using gas chromatography/electron capture detection; the sum of these congeners is referred to as total PCBs. Thirty organochlorine pesticides were analyzed in the coral tissue and sediment samples using gas chromatography/electron capture detection. Butyltins were quantified using gas chromatography/flame photometry. Fifteen trace and major elements (mostly metals, Table 1) were analyzed in the samples. Silver, cadmium, copper, lead, and tin were analyzed using inductively coupled plasma mass spectrometry. Aluminum, arsenic, chromium, iron, manganese, nickel, silicon and zinc were analyzed using inductively coupled plasma - optical emission spectrometry. Mercury was analyzed using cold vapor atomic absorption spectrometry. Selenium was analyzed using atomic fluorescence spectrometry. All sample analyses were carried out using NOAA's National Status and Trends (NS&T) QA/QC-assured protocols. Additional information on these protocols can be found in Kimbrough et al. (2006), and Kimbrough and Lauenstein (2006).

Statistical analysis

All contaminant data were analyzed using JMP[®] statistical software. None of the coral data were normally distributed, and transformations (log10) were not effective. As a result, nonparametric tests including Wilcoxon rank-sum, Spearman's correlation, and Wilcoxon matched-pairs signed rank tests were run to examine differences, for example, in total PAH concentration between

	PAHs - High MW	Organochlorine		Major and Trace
PAHs - Low MW Weight	Weight	Pesticides	PCBs	Elements
Naphthalene	Fluoranthene	Aldrin	PCB8/5	Aluminum (Al)
1-Methylnaphthalene	Pyrene	Dieldrin	PCB18	Arsenic (As)
2-Methylnaphthalene	C1-Fluoranthenes/ Pyrenes	Endrin	PCB28	Cadmium (Cd)
2,6-Dimethylnaphthalene	C2-Fluoranthenes/ Pyrenes	Heptachlor	PCB29	Chromium (Cr)
1,6,7-Trimethy- Inaphthalene	C3-Fluoranthenes/	Heptachlor-Epoxide	PCB31	Copper (Cu)
C1-Naphthalenes	Naphthobenzo- thiophene	Oxychlordane	PCB44	Iron (Fe)
C2-Naphthalenes	C1-Naphthobenzo- thiophenes	Alpha-Chlordane	PCB45	Lead (Pb)
C3-Naphthalenes	C2-Naphthobenzo- thiophenes	Gamma-Chlordane	PCB49	Manganese (Mn)
C4-Naphthalenes	C3-Naphthobenzo- thiophenes	Trans-Nonachlor	PCB52	Mercury (Hg)
Benzothiophene	Benz[a]anthracene	Cis-Nonachlor	PCB56/60	Nickel (Ni)
C1-Benzothiophenes	Chrysene	Alpha-HCH	PCB66	Selenium (Se)
C2-Benzothiophenes	C1-Chrysenes	Beta-HCH	PCB70	Silicon (Si)
C3-Benzothiophenes	C2-Chrysenes	Delta-HCH	PCB74/61	Silver (Ag)
Biphenvl	C3-Chrysenes	Gamma-HCH	PCB87/115	Tin (Sn)
Acenaphthylene	C4-Chrysenes	2.4'-DDD	PCB95	Zinc (Zn)
Acenaphthene	Benzolblfluoranthene	4.4'-DDD	PCB99	
Dibenzofuran	Benzo[k]fluoranthene	2.4'-DDE	PCB101/90	
Fluorene	Benzo[e]nvrene	4 4'-DDE	PCB105	
C1-Fluorenes	Benzo[a]pyrene	2 4'-DDT	PCB110/77	
C2-Eluorenes	Porvlono	4 4'-DDT	PCB118	
C3-Eluorenes	Indeno[1 2 3-c d]	1234-Tetrachlo-	PCB128	
Co-Hubrenes	nucropo	robonzono	I CD120	
Anthracene	Dibenzo[a,h] anthracene	1,2,4,5-Tetrachlo- robenzene	PCB138/160	
Phenanthrene	C1-Dibenzo[a,h] anthracenes	Hexachlorobenzene	PCB146	
1-Methylphenanthrene	C2-Dibenzo[a,h] anthracenes	Pentachloroanisole	PCB149/123	
C1-Phenanthrene/ Anthracenes	C3-Dibenzo[a,h] anthracenes	Pentachlorobenzene	PCB151	
C2-Phenanthrene/ Anthracenes	Benzo[g,h,i]perylene	Endosulfan II	PCB153/132	
C3-Phenanthrene/ Anthracenes		Endosulfan I	PCB156/171/202	
C4-Phenanthrene/ Anthracenes	Butyltins	Endosulfan Sulfate	PCB158	
Dibenzothiophene	Monobutyltin	Mirex	PCB170/190	
C1-Dibenzothiophenes	Dibutyltin	Chlorpyrifos	PCB174	
C2-Dibenzothiophenes	Tributyltin	1 5	PCB180	
C3-Dibenzothiophenes	Tetrabutyltin		PCB183	
1	5		PCB187	
			PCB194	
			PCB195/208	
			PCB201/157/173	
			PCB206 PCB209	

TABLE 1. Chemical contaminants analyzed in *Porites astreoides* from southwest Puerto Rico.

Abbreviations: MW, molecular weight; PAH, polycyclic aromatic hydrocarbons; HCH, hexachlorocyclohexane; DDT, dichlorodiphenyltrichloroethane; DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; PCB, polychlorinated biphenyl.

coral and sediment, and concentration differences between coral and sediment at a site. Because the coral cores sampled at a site were composited for one analysis, between site comparisons for chemical contaminants in corals were not possible. Results are presented at the 0.05 level of significance.

Results and Discussion

Field data

Data collected in the field in August 2005 are shown in Table 2. The water depth ranged from 4 to nearly 19 m. *Porites astreoides* was abundant at the sites sampled, and occurred mainly as the encrusting form. The largest colony diameter measured approximately 40 cm. Dissolved oxygen near the water surface (<1 m) ranged between 4 and 5 mg/L. Secchi depth was used as a crude indicator of water clarity, and was lowest (3.7 m) at the Coral 1 and Coral 9 sites (Table 2). Coral 1 is at the mouth of Guanica Bay, and may be influenced by the outflow from this waterbody.

Organic contaminants

Total PAHs quantified in *Porites astreoides* and in adjacent sediments are shown in Figure 2a. Polycyclic aromatic hydrocarbons are typically associated with the use and combustion of fossil fuels such as oil and gasoline. A number of PAHs can bioaccumulate, are toxic, and are likely carcinogens. The sites on the figure are oriented in a west to east direction to be comparable with Figure 1. The range of concentrations for total PAHs found in the coral was similar to the sediments. More detailed summaries of the contaminant analysis can be found in Pait et al. (2009). Although there was substantial variation in total PAHs in corals and sediments across the study area, a nonparametric (Wilcoxon) analysis indicated the concentration of total PAHs in the corals was not significantly different (P > 0.05, ChiSquare = 0.5404) from the concentration in the sediments. The concentration of total PAHs in the sediment at a particular site, however, did not covary with the concentration in the coral (P > 0.05, Spearman Rho = -0.1429), and the Wilcoxon matched-pairs test indicated no significant correlation (P = 0.4609) between the paired measurements over the study area. Because a limited number of coral samples were taken, additional work is needed to better assess the relationship between PAHs in Porites astreoides and in sediments.

Total PAHs in the corals appeared somewhat elevated at Coral 3 and Coral 4, near the town of La Parguera. There is a significant amount of recreational boat traffic in and out of La Parguera, and this along with stormwater runoff and local atmospheric deposition, are some of the likely sources for the PAHs detected. The highest concentration of total PAHs in the coral was found at Coral 9 in the western portion of the study area, away from the town of La Parguera. The reef area at Coral 9 is somewhat offshore, but could be subjected to boat traffic, or

TABLE 2. Field data from the August 2005 collection of Porites astreoides.

Dissolved									
	Collection	Latitude	Longitude	Water	Oxygen	Temperature	Salinity	Conductivity	Secchi
Site	Date	(DD)	(DD)	Depth (m)	(mg/L)	(°C)	(ppt)	(mS)	Depth (m)
Coral 1	8/27/05	17.94219	-66.91481	9.1	4.63	30.0	33.9	56.8	3.7
Coral 2	8/27/05	17.93012	-66.93719	7.0	4.61	29.6	33.8	56.1	6.7
Coral 3	8/27/05	17.96335	-67.02396	10.7	5.32	30.1	34.4	57.5	5.8
Coral 4	8/28/05	17.93594	-67.04942	18.9	5.04	29.6	34.3	57.0	7.9
Coral 5	8/27/05	17.96351	-67.01735	9.1	5.31	30.1	34.5	52.5	bottom
Coral 6	8/27/05	17.96334	-67.04679	13.7	4.81	29.6	34.5	57.3	7.3
Coral 8	8/28/05	17.93339	-67.10513	4.3	4.89	30.1	34.5	57.7	bottom
Coral 9	8/28/05	17.9362	-67.11609	4.6	4.62	30.1	34.6	57.9	3.7

Abbreviations: DD, decimal degrees; m, meters; mg/L, milligrams/liter; ppt, parts per thousand; mS, milli-Siemans. contaminant-related impacts in corals. Pait et al. (2007) quantified correlations between total PAHs in sediments and corals in the study area in southwest Puerto Rico. A strong negative correlation was found between total PAHs in sediments and coral species richness. In the future, it would be valuable to expand the current work to assess the relationships between chemical contaminants in corals and inputs from surface water runoff or sedimentation.

The ratio of nonalkylated or "parent" PAHs to alkylated forms has been used to distinguish petrogenic from pyrogenic sources (Neff et al. 2005; Columbo et al. 1989). In general, alkylated PAHs are more abundant in petroleum products relative to combustion byproducts (Neff et al. 2005). In the sediments adjacent to the coral sites, the nonalkylated / alkylated ratio was 2.78 ± 0.39. The ratio in *Porites astreoides*, however, was 1.06 ± 0.49 , and the difference in the ratios between corals and sediments was significant (P < 0.05). At Coral 9, the nonalkylated to alkylated PAH ratio indicated that 95 % of the PAHs detected in the corals were alkylated. It appears that the corals collected in this limited sampling accumulated greater amounts of those PAHs associated with petrogenic sources such as oil and gasoline. Additional work is needed to assess whether corals are exposed to or preferentially accumulate greater levels of alkylated PAHs, or if the elevated levels of alkylated PAHs represent more recent accumulation of PAHs, compared to sediments.

Organic compounds such as PAHs, PCBs and DDT accumulate in sediments with higher silt and clay fractions. Pait et al. (2007) normalized the sediment concentration of PAHs from southwest Puerto Rico to the percent fines (% silt plus the % clay fractions), an approach which has been used to help identify sources of contaminants including PAHs (Birch 2003; Burgess et al. 2001). In biological tissues, dividing the organic contaminant concentration by the percent lipid can be used to normalize contaminant concentrations, and can help identify possible sources (Elskus et al. 2005). The results of normalizing PAHs by coral lipid content and sediment by the percent fines is shown in Figure 3a.

FIG. 2. Total PAHs(a), total PCBs(b) and total DDTs(c) in *Porites astreoides* and sediments from southwest Pu erto Rico. One analysis (composite sample) at each site.

perhaps localized circulation patterns. In Figure 2a, it can also be seen that the concentration of PAHs in the sediments at Coral 9 was substantially lower than in the coral. It is unclear why there was a difference in the concentrations of PAHs in coral versus sediments at certain sites. In general, corals appear to readily accumulate PAHs. Kennedy et al. (1992) showed that benzo[a] pyrene is rapidly taken up by the boulder coral *Montastrea annularis;* Knap et al. (1982) showed that the brain coral *Diploria strigosa* concentrated the PAH phenanthrene.

Larsen and Webb (2009), Flood et al. (2005), Fabricius (2005) and others have noted



180

160

140

120

100

80

60

Total PAHs (ng/g)



FIG. 3. Lipid and percent fines (% silt + % clay) normalized total PAHs(a), total PCBs(b) an total DDts(c) con centration in *porites astreoides* and sediment. Normalizations of this type can sometimes help identify sources of the contaminats

The results for the corals and sediments were similar to what was seen in Figure 2a.

Thomas and Li (2000) analyzed samples of Porites compressa from Kaneohe Bay in Oahu, Hawaii for a number of PAHs including fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[e] pyrene, and benz[a]pyrene. The total concentration of these PAHs in the coral was 220 ng/g. When the same PAHs are summed for *Porites astreoides* in the samples from southwest Puerto Rico, the mean total was substantially lower, 2.2 ± 0.48 ng/g. Readman et al. (1996) analyzed for PAHs phenanthrene, fluoranthene, (including and pyrene) in the coral Porites lutea from Kuwait. In sections of the coral corresponding to the 1988/1989 timeframe (prior to the Gulf War), the concentration of these PAHs was approximately 0.3 ng/g. It should be noted, however, that Readman et al. (1996) sectioned and analyzed coral skeleton.

The results of total PCB analysis in *Porites astreoides* and in adjacent sediments is shown in Figure 2b. Polychlorinated biphenyls were used in the past for numerous applications including electrical transformers and capacitors, and PCBs have been linked to reproductive and developmental toxicity. Total PCBs were significantly higher in the sediments compared to the corals (P < 0.05). Overall, the concentration of total PCBs in the corals did not covary (P > 0.05, Spearman Rho = -0.3095) with total PCBs in the sediments, however, the Wilcoxon matched-pairs test indicated a significant correlation (P < 0.05) between paired measurements.

At the two sites just outside of Guanica Bay (Coral 1 and Coral 2), the concentrations of total PCBs were similar in both corals and sediments at each site. At these sites, there was also some evidence of a concentration gradient in the corals collected moving downstream from the mouth of Guanica Bay. As part of the overall project, two sites within Guanica Bay were sampled for sediments (Pait et al. 2008a). The analysis of the sediment samples from inside Guanica Bay revealed substantially elevated (> 1,000 ng/g) and toxicologically relevant levels of PCBs. To compare, the Effects Range Median (ERM), which is the contaminant concentration above which toxic effects are more likely to occur in benthic test organisms, is 180 ng/g.

In Figure 3b, the concentration of total PCBs is normalized to percent lipid (coral) and % fines (sediment). Figure 3b shows a decreasing normalized total PCB concentration in sediments and perhaps a similar trend in corals moving downstream from Guanica Bay. Additional coral sample collection and analyses would be needed to better assess this trend.

El Nemr et al. (2004) analyzed *Acropora sp.* tissues from a number of sites along the Egyptian Red Sea Coast. The average concentration of seven congeners in the coral tissues was 18 ng/g (El Nemr et al. 2004). The highest concentration at the sites sampled in southwest Puerto Rico for these same congeners in Porites astreoides was only 0.64 ng/g. Miao et al. (2000) analyzed coral (Porites lobata) and sediment samples for a number of PCB congeners from four sites in the French Frigate Shoals in the Pacific Ocean. Seventeen of the congeners analyzed by Miao et al. (2000) were also analyzed in the coral samples from southwest Puerto Rico. The approximate mean concentration for these congeners in Porites lobata was 110 ng/g. In Porites astreoides from southwest Puerto Rico, the mean for the same 17 congeners was less than 1 ng/g. Miao et al. (2000) noted that over the years, both the military (1942-1946) and the US Coast Guard (1952-1979) have had airfields and refueling stations on the adjacent Tern Island. In the sediments, the approximate mean concentration for the 17 congeners was 100 ng/g; at the coral sites in southwest Puerto Rico, the mean concentration for these same PCB congeners in the sediments was lower, 5.70 ± 1.67 ng/g.

Total DDTs detected in Porites astreoides and in the sediments is shown in Figure 2c. A number of organochlorine pesticides, including DDT and chlordane, were used extensively as insecticides in the past. Organochlorine pesticides are typically neurotoxins, environmentally persistent, and readily accumulate in biota. Total DDTs refers to the sum of the two parent compounds, 2,4'-DDT and 4,4'-DDT, along with the metabolites DDD and DDE. Total DDTs were only detected in Porites astreoides at the two sites adjacent to Guanica Bay. Total DDTs concentration at Coral 1 was 0.62 ng/g and at Coral 2, the concentration was 0.11 ng/g. At both sites, the concentration of total DDTs in *Porites astreoides* was higher than in sediments. As with the PCBs, there was some evidence of a concentration gradient, indicating that DDT transported out of Guanica Bay could be a source in the corals. Additional sampling is needed to assess the possibility of a concentration gradient for DDT in corals, and assess why this was not also reflected in sediments at the site. Within Guanica Bay, total DDTs were found to be elevated in the two sediment samples taken as part of this project (Pait et al. 2008a). At one of the two sites within the Bay, total DDTs in the sediment (46.9 ng/g)

was slightly higher than the ERM concentration (46.1 ng/g), indicating a greater likelihood of biological effects on benthic organisms inhabiting this area.

The Lajas Valley is situated inland of a series of coastal hills known as the Sierra Bermeja (Figure 1), which separates the narrow coastal plain containing the town of La Parguera from the valley. Historically, the Lajas Valley was used for extensive sugarcane production, but now has significant pastureland along with the production of selected vegetable and melon crops (USDA 2004). Although now banned in the US, the insecticide DDT was likely used in the Lajas Valley in the past to control insects on crops such as sugarcane and pineapple.

As with PCBs, a comparison can be made between total DDTs found in *Porites* astreoides and in sediments, normalized to percent lipids and percent fines, respectively. Figure 3c shows higher normalized total DDTs in the corals, and a similar pattern in the sediments, in the area adjacent to Guanica Bay, indicating that DDT transported out of the Bay could be a source in corals and adjacent sediments. A number of studies have quantified DDT and its metabolites in coral tissues. Glynn et al. (1995) collected and analyzed sediment and Porites *astreoides* for residues of total DDTs from the Florida Keys National Marine Sanctuary, in the area near Key Largo. The highest concentration detected was 0.01 ng/g. Glynn et al. (1989) also looked at total DDTs in *Porites astreoides* further north, in Biscayne National Park, in an area known as Alina's Reef, and detected concentrations ranging from 3.41 - 43.56 ng/g. El Nemr et al. (2004) detected a mean total DDTs concentration of 5.7 \pm 0.8 ng/g in coral tissues from the Egyptian Red Sea Coast. None of the other pesticides analyzed (Table 1) were detected in the samples of *Porites astreoides* from southwest Puerto Rico.

Tributyltin (TBT), the compound formerly used in antifoulant paints for boat hulls, and associated with endocrine disruption in gastropods, was not found in any of the coral samples analyzed, or in any of the adjacent sediments. The concentration of the degradation products of TBT, namely dibutyltin and monobutyltin was $\leq 2 \text{ ng/g}$ in *Porites astreoides*.

Trace and major elements

Unlike a number of the organic compounds analyzed, all of the trace and major elements are found naturally to some extent in the environment. The mean and standard errors for the trace and major elements analyzed in *Porites astreoides* and in the sediments are shown in Table 3. Surprisingly, chromium was not detected in any of the coral samples analyzed, although this metal was detected in all of the sediment samples. At Coral 1, just outside of Guanica Bay, the chromium concentration in the sediment was 11.3 μ g/g. As part of the overall project, two sediment samples were taken within Guanica Bay. The sediment concentrations of chromium at the two sites within the Bay were 394 and 440 μ g/g (Pait et al. 2008b). Both of these values are above the ERM of $370 \,\mu g/g$, indicating that chromium may be having an adverse effect on the benthic organisms living near those sites. It is not clear why chromium was not found in any of the coral samples analyzed, particularly just outside of Guanica Bay. It may be related to the small number of samples taken as part of this project. Alternatively, it could be related to the uptake characteristics of Porites astreoides. Esslemont (2000)

found differences in the uptake of certain metals between coral species, and concluded that some species (*Goniastrea aspera* and *Pocillopora damicornis*) showed evidence of being able to regulate metals in more contaminated areas.

Esslemont (2000), in the Great Barrier Reef, detected chromium at concentrations ranging from 15 - 65 µg/g in Goniastrea aspera, Acropora formosa and Pocillopora damicornis, and noted that total chromium in sediments was actually lower than in corals; the highest sediment concentration was around 18 μ g/g, similar to the 11.3 μ g/g found in the sediments just outside of Guanica Bay. Scott and Davies (1997) detected chromium in coral skeleton from the genus Porites (species not identified) in Indonesia, at concentrations up to $1.5 \,\mu g/g$. Additional work is needed to assess the transport of chromium out of Guanica Bay and availability to corals.

The results of the copper analysis in *Porites astreoides* is shown in Figure 4a. The average copper concentration in the coral was $2.06 \pm 0.30 \ \mu\text{g/g}$. A nonparametric (Wilcoxon) analysis indicated that copper in corals was not significantly different (P > 0.05, ChiSquare = 0.6744) from the concentration in adjacent sediments, and the Spearman's test indicated that the concentration of copper in the sediment covaried with the concentration in the coral (P < 0.05).

Element	Coral Mean (µg/g)	Coral SE	Sediment Mean (µg/g)	Sediment SE	
Silver (Ag)	< 0.01	< 0.01	0.00	_	
Aluminum (Al)	37.8	7.31	2,600	653	
Arsenic (As)	0.00	-	2.59	1.38	
Cadmium (Cd)	0.00	-	0.00	-	
Chromium (Cr)	0.00	_	9.66	1.31	
Copper (Cu)	2.06	0.30	2.04	0.42	
Iron (Fe)	90.8	37.7	2,364	515	
Mercury (Hg)	0.00	_	0.00	-	
Manganese (Mn)	3.01	0.58	85.7	17.3	
Nickel (Ni)	1.32	0.30	4.78	0.94	
Lead (Pb)	< 0.01	< 0.01	1.23	0.21	
Selenium (Se)	0.05	0.05	0.16	0.02	
Silicon (Si)	62.8	8.27	9,375	1,890	
Tin (Sn)	0.02	0.02	0.00	-	
Zinc (Zn)	6.09	1.82	3.56	0.83	

TABLE 3. Mean concentrations of trace and major elements in *P. astreoides* and adjacent sediments.

SE, standard error.

Reef was 90 μ g/g.

Porites astreoides and in adjacent sediments is shown in Figure 4b. The mean concentration of nickel in the corals was $1.32 \pm$ $0.30 \,\mu g/g$, and $4.78 \pm 0.94 \,\mu g/g$ in the sediments. A Wilcoxon test indicated that the nickel concentration in the corals was different from that in the sediments (P < 0.05). In addition, the concentration of nickel in the sediment at a particular site did not covary with the concentration in the coral (P > 0.05, Spearman Rho = 0.4048), and a Wilcoxon matched-pairs test indicated a significant difference (P< 0.05) between paired measurements.

although copper in one sample from Alina's

The concentration of nickel detected in

At Coral 1, just outside of Guanica Bay, nickel was not detected in Porites astre*oides*. At the two sediment sites sampled in Guanica Bay as part of the overall project, the concentration of nickel in the sediment was elevated, 434 and 442 μ g/g (Pait et al. 2008b), which is substantially above the ERM value of 52 μ g/g. As with chromium, additional work is needed to better assess the presence and availability of nickel in corals in the area adjacent to Guanica Bay. Esslemont (2000) characterized trace elements in sediments and corals in the Townsville section of the Great Barrier Reef Marine Park. As part of that work, the bioavailability of trace elements including nickel were assessed by extracting the sediments with a series of solvents to determine the readily bioavailable versus less bioavailable fractions. Esslemont (2000) found that trace elements such as lead, copper and zinc in the sediments were more biologically available, while chromium, nickel and cadmium were less bioavailable to the corals from sediments. Additional work is needed to assess the transport of metals such as nickel and chromium (either dissolved or bound to sediment particles), and the bioavailability to Porites astreoides in southwest Puerto Rico.

Reichelt-Brushett and McOrist (2003) analyzed both living and nonliving components of the coral Acropora tenuis on the Great Barrier Reef. Skeletal concentrations of nickel ranged from 0.3 to 0.7 μ g/g, while tissue concentrations ranged from 0.7 to $3.8 \,\mu g/g$, similar to the concentrations found

FIG. 4. Copper(a), nickel(b), and zin c(c) in porites astreoides ans sediments frome southwest Puerto Rico. One sample an alysis (composite sample) at each site.

The Wilcoxon matched-pairs test, however, indicated no significant correlation (P = 0.7422) between paired measurements.

The highest concentration of copper detected in the corals sampled was $3.54 \,\mu g/g$ at Coral 4. David (2003) analyzed cores of Porites lobata from the western coast of Marinduque Island in the Philippines. The mean copper concentration in the coral cores was $3.1 \,\mu g/g$, similar to the mean in Porites astreoides. Glynn et al. (1989) investigated the presence of a series of trace elements in coral tissues within Biscayne Bay National Park. Several coral species including Porites astreoides were collected. Both living tissue and associated coral skeleton were analyzed. The copper concentrations typically ranged from 5 to 12 μ g/g,



5

4

2

1

0

Copper (µg/g) З in *Porites astreoides* in southwest Puerto Rico. Esslemont (2000) analyzed tissue and skeleton in *Goniastrea aspera*, and found concentrations ranging from 10 to 20 μ g/g, higher than what was found in *Porites astreoides*. Scott and Davies (1997) detected nickel in coral skeleton from *Porites spp.*, ranging from 0.25 to 5 μ g/g.

Zinc (Figure 4c) was detected in all of the coral samples analyzed. The average concentration of zinc in *Porites astreoides* was $6.09 \pm$ 1.82 µg/g. A nonparametric (Wilcoxon) analysis indicated that the concentration of zinc in corals was not significantly different (P > 0.05, ChiSquare = 2.8235) from the concentration in the adjacent sediments. The concentration of zinc in the sediment at a particular site, however, did not covary with the concentration of zinc in the coral (P > 0.05, Spearman Rho = -0.1905). This can also be seen in Figure 4c. At Coral 9 for example, the concentration of zinc in Porites *astreoides* (18.3 μ g/g) was nearly an order of magnitude higher than what was found in the sediments $(1.88 \, \mu g/g)$.

Zinc has been quantified in coral tissues from a number of areas. Miao et al. (2001) analyzed whole samples of *Porites evermanni* from the French Frigate Shoals. The highest zinc concentration detected in the coral was $4.3 \,\mu g/g$, similar to the mean found in *Porites astreoides*. At Disappearing Island in the French Frigate Shoals, zinc was measured in both the coral and sediment. The concentration of zinc in the coral was $2.3 \,\mu g/g$; the concentration of zinc detected in the sediment was 7 $\,\mu g/g$. David (2003) detected zinc at between 1 and $2 \,\mu g/g$ in cores taken from *Porites lobata* in the Philippines.

Conclusions

The results of the chemical contaminant analysis in the samples of *Porites astreoides* indicated that the corals accumulated organic contaminants such as PAHs and PCBs, and trace elements such as copper and zinc. Similar concentrations of these contaminants were frequently found in both corals and sediments.

An interesting pattern was seen for the PAHs. At some sites, the sediments contained higher levels of PAHs, while at others Porites astreoides was higher. The reason for this difference is unknown, although the number of coral samples analyzed for this project could be responsible. In addition, the corals appeared to contain higher levels of PAHs associated with petrogenic (alkylated), or uncombusted hydrocarbon sources compared to the sediments. This was particularly evident in the western portion of the study area, and could be an indicator of boat traffic through the area or some other unidentified source. The higher levels of petrogenic PAHs in the living coral tissues could also be an indicator of more recent deposition, or perhaps differences in bioavailability of certain PAHs to Porites *astreoides*. Additional sampling and analysis of corals is needed to better understand the distribution of this contaminant class.

There was also some, although limited, evidence that a contaminant concentration gradient in the corals moving away from Guanica Bay may exist. When normalized for percent lipids, levels of total PCBs and total DDTs in *Porites astreoides* appeared higher at the sampling site just outside of Guanica Bay, and lower at the site further away and downstream of the outflow. Additional analyses are needed to further investigate this possibility.

Copper and zinc were detected in *Porites* astreoides at levels similar to what was found in the adjacent sediments. Chromium, however, was not detected in any of the coral samples analyzed for this project. This included the site just outside of Guanica Bay (Coral 1). Pait et al. (2008b) found substantially elevated levels of chromium in the sediments at the two sites sampled within the Bay. Additional work is needed to better assess the presence, transport and perhaps the bioavailability of chromium to *Porites astreoides.* This is also true for nickel which appears elevated within Guanica Bay sediments, but was not detected in the coral sample taken just outside the Bay.

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