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Contaminants in tropical island streams and their biota

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ABSTRACT

Environmental contamination is problematic for tropical islands due to their typically dense human populations and competing land and water uses. The Caribbean island of Puerto Rico (USA) has a long history of anthropogenic chemical use, and its human population density is among the highest globally, providing a model environment to study contaminant impacts on tropical island stream ecosystems. Polycyclic Aromatic Hydrocarbons, historic-use chlorinated pesticides, current-use pesticides, Polychlorinated Biphenyls (PCBs), and metals (mercury, cadmium, copper, lead, nickel, zinc, and selenium) were quantified in the habitat and biota of Puerto Rico streams and assessed in relation to land-use patterns and toxicological thresholds. Water, sediment, and native fish and shrimp species were sampled in 13 rivers spanning broad watershed land-use characteristics during 2009–2010. Contrary to expectations, freshwater stream ecosystems in Puerto Rico were not severely polluted, likely due to frequent flushing flows and reduced deposition associated with recurring flood events. Notable exceptions of contamination were nickel in sediment within three agricultural watersheds (range 123–336 ppm dry weight) and organic contaminants (PCBs, organochlorine pesticides) and mercury in urban landscapes. At an urban site, PCBs in several fish species (Mountain Mullet *Agonostomus monticola* [range 0.019–0.030 ppm wet weight] and American Eel *Anguilla rostrata* [0.019–0.031 ppm wet weight]) may pose human health hazards, with concentrations exceeding the U.S. Environmental Protection Agency (EPA) consumption limit for 1 meal/month. American Eel at the urban site also contained dieldrin (range < detection-0.024 ppm wet weight) that exceeded the EPA maximum allowable consumption limit. The Bigmouth Sleeper *Gobiomorous dormitor*, an important piscivorus sport fish, accumulated low levels of organic contaminants in edible muscle tissue (due to its low lipid content) and may be most suitable for human consumption island-wide; only mercury at one site (an urban location) exceeded EPA's consumption limit of 3 meals/month for this species. These results comprise the first comprehensive island-wide contaminant assessment of Puerto Rico streams and biota and provide natural resource and public health agencies here and in similar tropical islands elsewhere with information needed to guide ecosystem and fisheries conservation and management and human health risk assessment.

1. Introduction

Environmental pollution is a problem for many tropical islands, especially those with dense human populations and competing land uses (Hunter and Arbona, 1995). Few contaminant studies have been conducted in the tropical Caribbean islands (Rodríguez and Pérez de González, 1981; Neal et al., 2005), and there have been no studies to date on the occurrence and effects of contaminants in freshwater stream ecosystems in this region. More knowledge is needed on the occurrence and patterns of contaminants in Caribbean freshwater stream ecosystems to inform fisheries and natural resource conservation and management and human health risk.

The Caribbean island of Puerto Rico is densely populated, supporting nearly 440 people per square kilometer, which provides an appropriate model to study human-influenced aquatic contaminants (Martinuzzi et al., 2007; Neal et al., 2009; Kwak et al., 2016). During

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the past century, rapid industrialization and the subsequent human population growth have strained the limited natural resources of the island (Hunter and Arbona, 1995). Most of the rivers have been transformed by dam construction or other structures that are conducive for water collection (Cooney and Kwak, 2010, 2013; Kwak et al., 2016). However, the residents of Puerto Rico are becoming increasingly aware of the benefits associated with conserving stream ecosystems. González-Cabán and Loomis (1997) demonstrated that citizens would be willing to pay a total of $11.33 million to prevent dam construction on Río Mameyes, the last remaining free-flowing river in Puerto Rico.

The streams of Puerto Rico provide many services for local populations, including water for drinking, recreation, irrigation, and as a source of fish and crustaceans for consumption. Good water quality is necessary to protect human health as well as ecological integrity. However, Puerto Rico has experienced an era of rapid and fluctuating human population growth leading to deteriorated water quality (Hunter and Arbona, 1995; Fitzpatrick and Keegan, 2007). The streams have a history of die-offs of fish, shellfish, and shrimp, resulting from contamination by industrial, agricultural, and municipal wastes, and epidemiological evidence also suggests that water contamination has jeopardized human health (Hunter and Arbona, 1995; Colón et al., 2000). Additionally, some human populations in Puerto Rico have high marine fish consumption rates, potentially exposing them to high levels of contaminants such as metals (Mansilla-Rivera and Rodríguez-Sierra, 2011). Yet, there is a notable lack of research and available information on the degree and effects of water contamination in Puerto Rico and associated human risks from consumption of native freshwater fish, and no Commonwealth agency is mandated with developing fish and shellfish consumption advisories.

Rivers and streams are influenced by their surrounding landscapes (Vannote et al., 1980; Allen, 2004). Direct correlations have been clearly demonstrated between land use and water quality (Lenat and Crawford, 1994; Bolstad and Swank, 1997; Fisher et al., 2000; Tong and Chen, 2002). Surface runoff, especially after a drought, is a major contributor to non-point source pollution because it transports sediment and associated chemicals into aquatic ecosystems. Runoff from varying types of land use is enriched with different contaminants; for example, runoff from urban areas may be enriched with rubber fragments and heavy metals from vehicles, whereas runoff from agricultural lands may be enriched with fertilizers and pesticides (Lenat, 1984; Osborne and Wiley, 1988; Cooper, 1993; Johnson et al., 1997; Tong and Chen, 2002). Further, vegetation modifies land surface characteristics, water balance, and the hydrologic cycle through evapotranspiration, interception, infiltration, percolation, and absorption (Tong and Chen, 2002). Human-altered land use also transforms the hydrological system by changing runoff patterns and composition and quality of receiving water bodies (Changnon and Demissie, 1996; Mander et al., 1998; Warne et al., 2005).

Puerto Rico has undergone a number of anthropogenic alterations to its landscape as a result of agriculture, deforestation, stream channelization, industrial and municipal pollution, urbanization, and impoundment of rivers (Neal et al., 2009; Kwak et al., 2016). Historically, Puerto Rico's economy was predominantly agricultural, but in the early 1900s, global markets changed and the economy shifted toward industry and tourism (Hunter and Arbona, 1995). While rapid industrialization of Puerto Rico most likely led to an increased influx of a variety of contaminants into the environment, tourism relies upon clean waters, beaches, and other minimally disturbed areas, such as the El Yunque National Forest. Therefore, it is imperative that contaminants and water quality be assessed in Puerto Rico stream ecosystems to guide natural resource planning and economic development.

The aim of this study was to quantify contaminants in water, sediment, and biota in the stream ecosystems of Puerto Rico across a spectrum of watershed land-use patterns. This was accomplished in two phases; first by extensively sampling and analyzing habitat and biota island-wide for contaminants, and second by conducting focused, intensive studies in selected areas of management and human health importance.

2. Methods

This research began with an island-wide study of 13 of the 46 streams (hereafter, extensive study) encompassing a variety of land-use categories. Following the extensive sampling, more intensive sampling was conducted on one representative stream from each land-use classification (4 sites; hereafter, intensive study). Prior knowledge of target species distribution and abundance was provided by Kwak et al. (2007). Rivers were sampled during the summers of 2009 (extensive study) and 2010 (intensive study), and sites were categorized based on primary watershed land-use patterns or distinctive riparian features, including one reference site within a protected National Forest watershed [Río Mameyes (1R)], two industrial sites [Río Tallaboa (2I), Río Cañas (3I)], two urban sites [Río Piedras (4U), Río Bayamon (5U)], eight agricultural sites [Río Añasco (6A), Río Yauco (7A), Río La Plata (8A), Río Jacaguas (9A), Río Guanajibo (10A), Río Cartagena (11A), Río Arecibo (12A), and Río Fajardo (13A), a site with substantial recreational fishing activity] (Fig. 1). This study provided a 28% coverage of all river drainages in Puerto Rico, and because of its broad spatial coverage and sampling of its dominant land use types, it characterizes the potential pollution conditions from other riverine systems on the island.

Data from the initial extensive contaminant sampling (13 sites) were used to select sites and contaminants for additional intensive sampling, which included additional species and sample replicates. Four sites, among those sampled in the extensive contaminant survey, were selected for intensive contaminant investigation in 2010 to represent specific water quality or watershed land-use effects. These sites were 1R (reference), 7A (agricultural), 3I (industrial), and 4U (urban). Water, sediment, and biota were sampled at each site.

Physicochemical characteristics of water were measured at each site with a Yellow Springs Instrument (YSI) 556 multi-probe system and a Hach CEL/850 Portable Aquaculture Laboratory and included temperature, pH, alkalinity (mg/L $CaCO_3$), total hardness (mg/L $CaCO_3$), conductivity (µS/cm), nitrate concentration (µg/L NO_3^-), nitrite concentration (mg/L NO_2^-), and orthophosphorus concentration (mg/L PO_4) for both the extensive and intensive studies. Water was collected using a 1-L container, rinsed repeatedly with site water, and then was submersed 0.25–0.50 m beneath the water surface, filled, and stored on ice in a cooler.

2.1. Universal passive sampling devices (uPSDs)

Time-integrated contaminant concentrations in water were sampled using Universal Passive Sampling Devices (uPSDs) (Hirons, 2009). Passive sampling devices are an efficient method for sampling and measuring water contaminants (Heltsley et al., 2005). They estimate ecologically relevant contaminant exposure (Hirons, 2009) and bioconcentration for aquatic species (Heltsley et al., 2005). uPSDs offer advantages over traditional grab sampling because they represent exposure of the bioavailable portion and they collect transient contaminants at trace levels (Hirons, 2009).

Two types of uPSDs were deployed in this study; fiber passive sampling devices (fPSDs) and cartridge passive sampling devices (cPSDs). The fPSDs have a surface area of 5.8 cm^2, and cPSDs have an internal surface area of 6.2 cm^2 (Hirons, 2009). The fPSDs are hollow, polyethersulfone fibers filled with Waters Oasis HLB® sorbent, with a diameter of 1 mm and pore size of 0.2 µm. The cPSDs are incased in porous stainless steel and filled with the same polymeric sorbent, Oasis HLB®. Three fPSDs were deployed at each site during the extensive survey and six cPSDs were deployed at each site during the intensive study. They remained submersed in the water for 3–4 weeks. Each uPSD was wrapped in aluminum foil immediately upon retrieval and placed inside a plastic bag with a label, indicating the retrieval date and time, sampling location, and condition of the uPSD. The uPSDs were held on ice inside a cooler in the field and promptly transferred to a −20 °C freezer for storage.

2.2. Sediment

One composite sediment sample was collected from each site for the extensive study, and three per site for the intensive study, using a stainless steel scoop, rinsed with site water prior to use. Each sample consisted of 3–5 scoops from depositional areas within the site area, totaling approximately 0.75 L. Only sediment from the surface layer (top 5 cm) was collected and any rocks, debris, or biota were removed. Each sample was sealed in a food-grade sealable plastic bag, stored on ice in a cooler, and then promptly transferred to a −20 °C freezer for storage.

In addition to contaminant analysis, sediment samples were also analyzed for total organic carbon, particle-size, and iron concentration for post-contaminant analysis normalization purposes for both extensive and intensive studies. Aliquots from sediment samples were dried at 60 °C and submitted to the Environmental and Agricultural Testing Service Laboratory in the Department of Soil Science at North Carolina State University in Raleigh, North Carolina (USA), for analysis of total carbon content and to the Soil Physical Properties Laboratory in the Department of Soil Science at North Carolina State University for particle size analysis, using the hydrometer method (Gee and Or, 2002). For particle size analysis, samples were treated with hydrogen peroxide to remove organic matter if it exceeded 2%. Freeze-dried sediment aliquots were analyzed for iron concentration by Environmental Conservation Laboratories in Cary, North Carolina (USA), using U.S. Environmental Protection Agency (EPA) Method 6010C (www.epa.gov/sam).

2.3. Fish and shrimp

Few native fish species inhabit the streams of Puerto Rico and other islands in the Caribbean and Greater Antilles because these volcanic islands are relatively newly formed and are isolated from potential sources of colonizing species (Neal et al., 2009; Kwak, 2016). Only six freshwater native fish are commonly found in Puerto Rico and all share common specialized life history traits; specifically, they are diadromous (Kwak et al., 2007, 2016; Neal et al., 2009). Samples of all native freshwater fish species were analyzed for contaminants, with the exception of the Fat Sleeper (*Dormitator maculatus*), which was not collected at any site. Native species sampled included Bigmouth Sleeper (*Gobiomorous dormitor*), Smallscaled Spinycheek Sleeper (*Eleotris perniger*), American Eel (*Anguilla rostrata*), Mountain Mullet (*Agonostomus monticola*), Sirajo Goby (*Sicydium* spp.), River Goby (*Awaous banana*), and *Macrobrachium* shrimp. Exotic species, introduced by anglers, the aquaculture industry, and aquarium owners, are commonly found in Puerto Rico, but this study focused on the native species, especially those of recreational sport fish, human consumption, and natural heritage value. However, several exotic species were collected and analyzed during this study for informational purposes, including Mozambique Tilapia (*Oreochromis mossambicus*), Redbreast Sunfish (*Lepomis auritus*), and Channel Catfish (*Ictalurus punctatus*). Target species represented a range of taxa and feeding strategies and all are consumed by humans, except for the Smallscaled Spinycheek Sleeper. Fish and shrimp were collected using backpack electrofishing (Kwak et al., 2007). Specimens were sorted by species into labeled food-grade sealable plastic bags, kept on ice in the field, and then promptly transferred to a −20 °C freezer for storage.

Fish and shrimp were analyzed as composite samples using whole

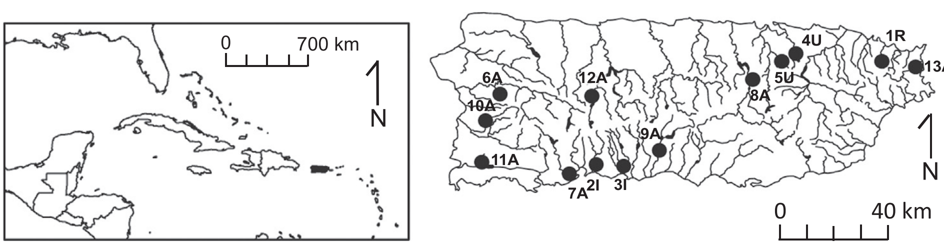

Fig. 1. Puerto Rico stream sampling site characteristics and location.

Site	Designated land Use	River name	Latitude	Longitude	Watershed land use: Agriculture (%)	Forest (%)	Shrub and Woodland (%)	Urban (%)
1R	Reference	Mameyes	N18°21'23.7"	W65°46'06.9"	2.7	95.6	1.0	0.1
2I	Industrial	Tallaboa	N18°00'17.3"	W66°43'53.0"	22.0	47.1	25.4	5.3
3I	Industrial	Cañas	N18°01'23.2"	W66°38'26.4"	30.0	27.4	32.3	9.8
4U	Urban	Piedras	N18°23'02.8"	W66°03'31.2"	24.8	26.3	8.8	39.4
5U	Urban	Bayamon	N18°19'51.7"	W66°06'04.2"	25.0	50.0	13.4	11.6
6A	Agricultural	Añasco	N18°14'14.9"	W67°02'42.6"	77.9	7.9	13.4	0.8
7A	Agricultural	Yauco	N17°59'12.9"	W66°50'25.7"	24.9	31.5	36.6	6.1
8A	Agricultural	La Plata	N18°13'28.4"	W65°12'58.9"	44.2	21.6	25.5	8.1
9A	Agricultural	Jacaguas	N18°04'11.1"	W66°30'33.5"	36.9	39.4	26.3	4.8
10A	Agricultural	Guanajibo	N18°09'29.8"	W67°05'06.7"	53.5	34.4	10.2	1.8
11A	Agricultural	Cartagena	N18°01'42.5"	W67°06'48.6"	40.4	41.8	13.6	4.2
12A	Agricultural	Arecibo	N18°15'34.9"	W66°43'20.4"	13.5	25.0	58.7	2.4
13A	Agricultural	Fajardo	N18°19'20.5"	W65°38'59.3"	34.5	53.8	7.4	2.8

body or muscle tissue. The whole body of Sirajo Gobies and River Gobies was analyzed because the local people consume the whole body of these fish, as do instream and avian predators. The whole body of Smallscaled Spinycheek Sleeper was analyzed for contaminants because of consumption by predators and associated food web implications. The edible muscle, excluding skin or scales, of American Eel, Mozambique Tilapia, Bigmouth Sleeper, Redbreast Sunfish, and Channel Catfish, was excised and analyzed. Abdominal muscle tissue (edible portion) was analyzed for *Macrobrachium* shrimp.

2.4. Laboratory analyses and quality control

The selected toxicants were analyzed in water, sediment, and biota to describe how they were compartmentalized within each component of the ecosystem. A detailed description of all analytical procedures and quality control protocols are presented in Buttermore (2011) and a brief supportive summary and overview are given herein. Only sediment and biota were analyzed for metals (mercury, selenium, copper, nickel, zinc, cadmium, and lead) because the passive sampling devices used in this study do not accumulate metals. Passive sampling devices, biota, and sediment samples were analyzed for 34 current-use pesticides, 26 chlorinated pesticides, 48 polycyclic aromatic hydrocarbons (PAHs), and 20 polychlorinated biphenyl congeners (PCBs), except current-use pesticides and PAHs were not analyzed in fish and shrimp muscle samples because of relatively rapid metabolism and reduced accumulation (Cope et al., 2011).

Analysis of organic contaminants in uPSDs, sediment, and biota was performed at the North Carolina State University Department of Environmental and Molecular Toxicology Chemical Exposure Assessment Laboratory in Raleigh, North Carolina (USA), using a gas chromatograph-mass spectrometer (Buttermore, 2011). Sediment and biota samples were freeze dried and submitted to Environmental Conservation Laboratories in Cary, North Carolina (USA), for inorganic toxicant analyses following approved U.S. EPA standard methods (www.epa.gov/sam).

A rigorous quality assurance protocol was followed during all analyses. For metal analyses, quality assurance included blanks, laboratory control samples (LCS), matrix spike, matrix spike duplicates, post spikes, and surrogate internal standards. The blanks were uncontaminated (i.e., no target analytes detected), with the exception of one detection of iron (3.6 ppm), one detection of copper (0.07 ppm), and 2 detections of lead (< 0.13 ppm), but all were below the method reporting limit (MRL). The relative percent difference (RPD) of duplicate samples averaged 15% and ranged 0.4–64%. Overall, percent recoveries averaged 95%. All LCS percent recoveries were within range (mean = 99%, range = 85–110%). Results were not corrected for recoveries, due to acceptable accuracy (precision and bias) revealed by this protocol. Only measured concentrations greater than the MRL for each of the analytes are reported.

Procedural blanks, uPSD blanks (for uPSD batches), matrix spikes, and surrogate internal standards (SIS) were used to assess organic contaminant data quality. Procedural blanks were uncontaminated with few exceptions. Five PAHs were detected during sediment analysis (< 8 ppb). PCB 138 was detected in a procedure blank during sediment analysis (2 ppb) and during fish analysis (< 2 ppb). Mean RPD values were 6% (range, 0–17%). Average surrogate recoveries were 80% for uPSDs, 61% for sediment, and 75% for fish. Results were not corrected for recoveries, due to acceptable accuracy. Detection limits are reported in Table S1. Only measured concentrations greater than the MRL for each of the analytes are reported. Parent DDT was not detected in any sample; thus, results for DDTs refer to the sum of DDT metabolites. Duplicate samples were also analyzed for quality assurance of lipid content of fish and shrimp and organic carbon content and particle size composition of sediment samples. The mean RPD value for lipid data was 9% (range, 0–18%). RPD values for sediment total organic carbon averaged 3% (range, 0–5%), and percent clay averaged 3% (range, 0–7%). Moisture content was similar among fish and shrimp taxa; within-taxon means ranged from 70.1% moisture for American Eel to 80.1% for Bigmouth Sleeper. *Macrobrachium* shrimp were moderate in moisture content with a mean of 74.6%. Sediment moisture content was much more variable among sites due to variation in substrate material and organic content; within-site means ranged from 23.9% moisture in Río Añasco (site 6A) to 63.3% in Río Cañas (site 3I).

2.5. Contaminant criteria and guidelines

Established criteria and guidelines provide perspective to assess the hazard of chemicals measured in water, sediment, and fish. EPA national recommended water quality criteria, EPA Office of Pesticide Program's aquatic life benchmarks, consensus based sediment guidelines, and EPA consumption limit tables were consulted (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table; https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk; MacDonald et al., 2000; U.S. Environmental Protection Agency, 2000). EPA aquatic life benchmarks are estimates of concentrations below which chemicals are not expected to harm aquatic life and are based on the most sensitive toxicity endpoint for taxa. The consensus-based Threshold Effect Concentration (TEC) reflects the sediment concentration below which harmful effects to benthic organisms are unlikely to be observed, and the consensus-based Probable Effect Concentration (PEC) represents a threshold that if exceeded, harmful effects are likely to be observed. The Severe Effect Level (SEL) represents a threshold where adverse effects of the majority of sediment-dwelling organisms are expected (MacDonald et al., 2000). Consumption limit tables (U.S. Environmental Protection Agency, 2000) are useful to infer human risk associated with consumption of fish and shrimp.

3. Results

3.1. Water quality

Water quality measurements varied widely among sampling sites. Value ranges for water quality variables were, temperature, 22.7–34.7 °C; total dissolved solids, 0.08–0.90 g/L; conductivity, 106–1451 μS/cm; salinity, 0.05–0.69 ppt; nitrate as NO_3^-, 0.3–10.0 mg/L; nitrite as NO_2^-, 0.006–0.670 mg/L; ammonia, 0.00–0.69 mg/L as NH_3; phosphorus as PO_4^-, 0.02–2.06 mg/L; alkalinity, 33–317 mg/L $CaCO_3$; hardness, 43–235 mg/L $CaCO_3$; turbidity, 1–22 FAU; pH, 7.18–8.90; dissolved oxygen, 4.34–12.36 mg/L. Stream water from the reference site, with a primarily forested watershed, was low in ionic and nutrient content. Measurements of total dissolved solids, conductivity, salinity, nitrogen, phosphorus, alkalinity, and hardness were generally low at the reference site, whereas the agricultural sites tended toward greater measured concentrations of total dissolved solids, conductivity, salinity, ammonia, phosphorus, alkalinity, and hardness.

3.2. Water contaminants

Low concentrations of contaminants were estimated in water by uPSDs at all sites. No PCBs were detected at any site. The only chlorinated pesticides detected were chlordane compounds. Current-use pesticides (CUP) detected in water included butylate, carbaryl, trifluralin, simazine, prometon, atrazine, metolachlor, and malathion. Prometon was detected at an urban site (4U), but was not detected at any other site. Trifluralin was the most frequently detected CUP and was found at all tested sites, with the exception of an industrial site (2I). An urban site (4U) generally had the greatest water contaminant concentrations, including chlordanes, total CUP, and total PAHs.

3.3. Sediment contaminants

Sediment total organic carbon was less than 4% at all sites, with the exception of an industrial site (3I) that had a mean total organic carbon content of approximately 8%. Clay composition and iron concentration was variable among sites. Clay composition ranged from 3% to 20%, and iron concentration ranged from 23.9 to 60.3 g/kg dry weight.

Organic contaminants were at low concentrations in sediment at all sites. Chlordanes (cis-chlordane, trans-chlordane, and transnonachlor), DDTs (4,4′-DDE and 4, 4′-DDD), and hexachlorobenzene were the only chlorinated pesticides detected in sediment. DDTs were detected at greatest concentrations at agricultural sites. Chlordanes had greatest concentrations at an industrial (3I) and an agricultural (4U) site. Tebuthiuron, carbaryl-1, carbofuran-1, cyhalothrin (lambda), and bifenthrin were the only CUPs found in sediment. Overall, PCBs in sediment were greatest at urban sites. The greatest concentrations of total PAHs were found at the industrial site (3I) (mean = 493.0 ppb dry weight). The reference site (1R) appeared to be the least contaminated site, with no detections of OCs or CUPs and the lowest level of PAHs. However, low levels PCBs were detected at site 1R.

Cadmium, lead, mercury, selenium, and zinc were found at low concentrations in sediment samples. Copper concentrations were at moderately high levels (38.3–103 ppm dry weight) in sediment and occurred predominately at agricultural sites. Nickel concentrations in sediment were variable among sites ranging from 4.63 to 336 ppm dry weight and were generally elevated at agricultural sites (7A, 9A, and 10A; Fig. 2).

3.4. Fish and shrimp

Relatively high concentrations of PCBs and low levels of chlorinated pesticides, with the exception of dieldrin, were detected in fish tissue

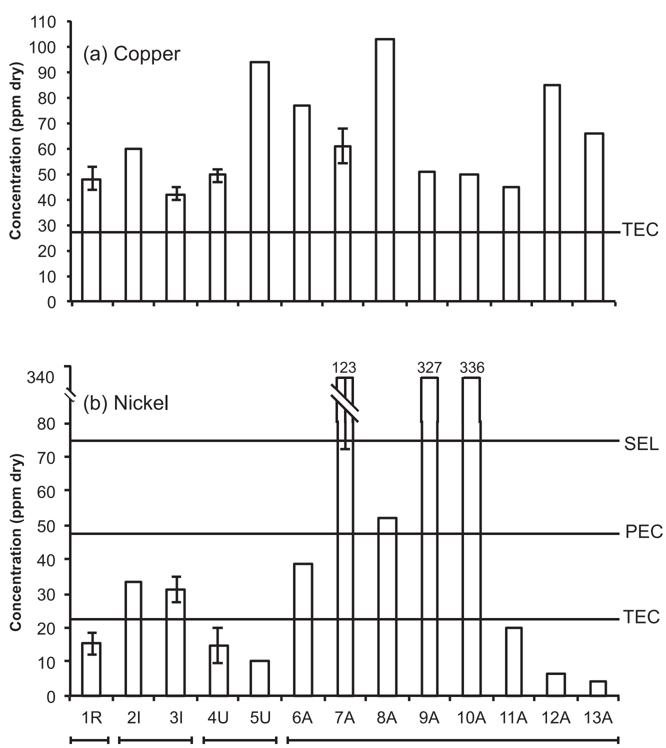

Fig. 2. Concentrations of (a) copper and (b) nickel (ppm dry weight) in sediment from Puerto Rico streams with guideline exceedances denoted by the horizontal lines, where TEC indicates the consensus-based threshold effect concentration, PEC indicates the consensus-based probable effect concentration, and SEL indicates the severe effect level (MacDonald et al., 2000).

(Table 1; Fig. 3). Mountain Mullet and American Eel were generally the most contaminated species, and an urban site (4U) had the most contaminated biota, in terms of organic pollution. Chlordane, DDTs, hexachlorobenzene, dieldrin, and lindane were the only chlorinated pesticides detected in fish tissue. High concentrations of dieldrin were found in American Eel at the urban site (4U). PCB concentrations were greatest in Mountain Mullet, American Eel, and River Goby from an urban site (4U). DDTs were greatest in River Goby and American Eel from an agricultural site (7A). Hexachlorobenzene was greatest in Mountain Mullet samples from an urban site (4U).

Fish tissue generally contained low concentrations of metals. Cadmium, nickel, mercury, and lead concentrations were below the method reporting limit (MRL) and method detection limit (MDL) for fish samples (Cd: < MDL = 59%, < MRL = 90%; Ni: < MDL = 57%, < MRL = 74%; Hg: < MDL = 75%, < MRL = 87%; Pb: < MDL = 77%, < MRL = 97%; N = 115). Copper and selenium concentrations of several samples were below the MRL and MDL (Cu: < MDL = 35%, < MRL = 48%; Se: < MDL = 33%, < MRL = 43%; N = 115), whereas zinc was above the MRL for most samples (< MDL = 0%, < MRL = 6%; N = 115) and varied among species and sites. Selenium concentrations were similar among all biota, and observed concentrations were low, ranging from 0.298 to 0.934 ppm wet weight. Cadmium and copper concentrations were greatest in *Macrobrachium* spp. Mercury was greatest in nonnative Channel Catfish from site 8A, but Bigmouth Sleeper from site 4U had the greatest concentrations of mercury among native fish species (Fig. 3).

Mountain Mullet and American Eel had the greatest concentrations of organic contaminants, associated with their greater lipid content. Fish and shrimp lipid content within species varied significantly among sites ($P < 0.05$), with the exception of lipid content in Sirajo Goby (P = 0.34, N = 6; Fig. 3). Thus, PCB and mercury concentrations in fish and shrimp were normalized by lipid content to provide a comparative basis among sites (Fig. 3). An urban site (4U) had the greatest mercury and PCB concentrations after lipid normalization.

3.5. Contaminant criteria and guidelines

All contaminant concentrations measured in the water and sediment of Puerto Rico streams were less than the EPA recommended water quality criteria and the Office of Pesticide Programs' aquatic life benchmarks for the protection of plants, invertebrates, and fish. All organic contaminants, mercury, lead, selenium, cadmium, and zinc measured in sediment were less than consensus-based guidelines (MacDonald et al., 2000). Sediment analyzed from all sites exceeded the consensus-based TEC for copper, but were below the consensus-based PEC (MacDonald et al., 2000; Fig. 2). Nickel sediment concentrations exceeded the consensus-based TEC at five agricultural and both industrial sites, with four of these sites also exceeding the consensus-based PEC (MacDonald et al., 2000; Fig. 2). Two agricultural sites (9A and 10A) exceeded the SEL by 4 orders of magnitude, and sampling at another agricultural site (7A) revealed exceedances with a mean concentration almost 2 orders of magnitude above the SEL (Persaud et al., 1993; MacDonald et al., 2000; Fig. 2).

Some concentrations of mercury, cadmium, chlordane, DDTs, dieldrin, and PCBs measured in fish and shrimp from Puerto Rico rivers exceeded EPA consumption limits (Table 1). EPA human consumption limits were not available for zinc, nickel, lead, or copper. Mercury consumption guidelines were the most frequently exceeded contaminant threshold for fish tissue, with most at the 16 meals per month limit (non-cancer). Bigmouth Sleeper from an urban site had the greatest mercury concentrations among all native fish or shrimp species and they exceeded the EPA consumption limit recommended for 3 meals per month. However, the greatest mercury fish tissue concentration measured was in an exotic species (Channel Catfish) from an agricultural site, also exceeding the 3 meals per month limit. Chlorinated pesticides were generally detected at low concentrations in fish

Table 1
Fish and shrimp contaminant concentrations (ppm wet weight) from Puerto Rico (USA) stream sites exceeding EPA consumption limit recommendations using non-cancer endpoints (U.S. Environmental Protection Agency, 2000).

Contaminant	Site	Species	Concentration (ppm)			Meals	
			Mean	SD	Range	Mean	Range
Cadmium	1R	*Macrobrachium* spp.	0.204			12	
	2I	*Macrobrachium* spp.	0.194			12	
	9A	*Macrobrachium* spp.	0.184			12	
Mercury	8A	*Ictalurus punctatus*	0.282			3	
	4U	*Gobiomorus dormitor*	0.145	0.065	0.077 – 0.233	4	8-4
	4U	*Eleotris perniger*	0.077	0.025	0.049 – 0.092	8	16-8
	8A	*Lepomis auritus*	0.074			12	
	4U	*Anguilla rostrata*	0.068	0.065	0.017 – 0.141	12	UR[a] – 4
	9A	*Agonostomus monticola*	0.065			12	
	6A	*Awaous banana*	0.063			12	
	11A	*Anguilla rostrata*	0.059			16	
	7A	*Eleotris perniger*	0.041	0.011	0.033 – 0.0523	16	UR – 16
	10A	*Awaous banana*	0.040			16	
	13A	*Anguilla rostrata*	0.040			16	
	2I	*Gobiomorus dormitor*	0.039			16	
	13A	*Macrobrachium* spp.	0.038			16	
	7A	*Agonostomus monticola*	0.035	0.024	0.013 – 0.056	16	UR-16
	4U	*Awaous banana*	0.032	0.040	0.012 – 0.092	16	UR-8
	7A	*Anguilla rostrata*	0.029	0.023	ND[b] – 0.049	UR	UR-16
	3I	*Gobiomorus dormitor*	0.027	0.020	0.011 – 0.053	UR	UR-16
	1R	*Sicydium* spp.	0.023	0.018	0.013 – 0.050	UR	UR-16
	7A	*Awaous banana*	0.020	0.018	0.011 – 0.047	UR	UR-16
	1R	*Anguilla rostrata*	0.020	0.011	0.013 – 0.036	UR	UR-16
	1R	*Gobiomorus dormitor*	0.017	0.013	0.011 – 0.036	UR	UR-16
Dieldrin	4U	*Anguilla rostrata*	0.014	0.013	ND – 0.024	UR	UR-16
PCBs	4U	*Agonostomus monticola*	0.025	0.005	0.019 – 0.030	4	8-4
	4U	*Anguilla rostrata*	0.025	0.006	0.019 – 0.031	4	8-4
	4U	*Eleotris perniger*	0.011	0.003	0.008 – 0.014	16	16-12
	2I	*Anguilla rostrata*	0.009			16	
	4U	*Awaous banana*	0.008	0.004	0.005 – 0.013	16	UR-12
	7A	*Anguilla rostrata*	0.006	0.002	0.005 – 0.009	16	UR-16
	3I	*Anguilla rostrata*	0.004	0.003	0.001 – 0.008	UR	UR-16
	7A	*Agonostomus monticola*	0.004	0.002	0.003 – 0.006	UR	UR-16

[a] UR = unrestricted number of meals per month.
[b] ND = below detection limits.

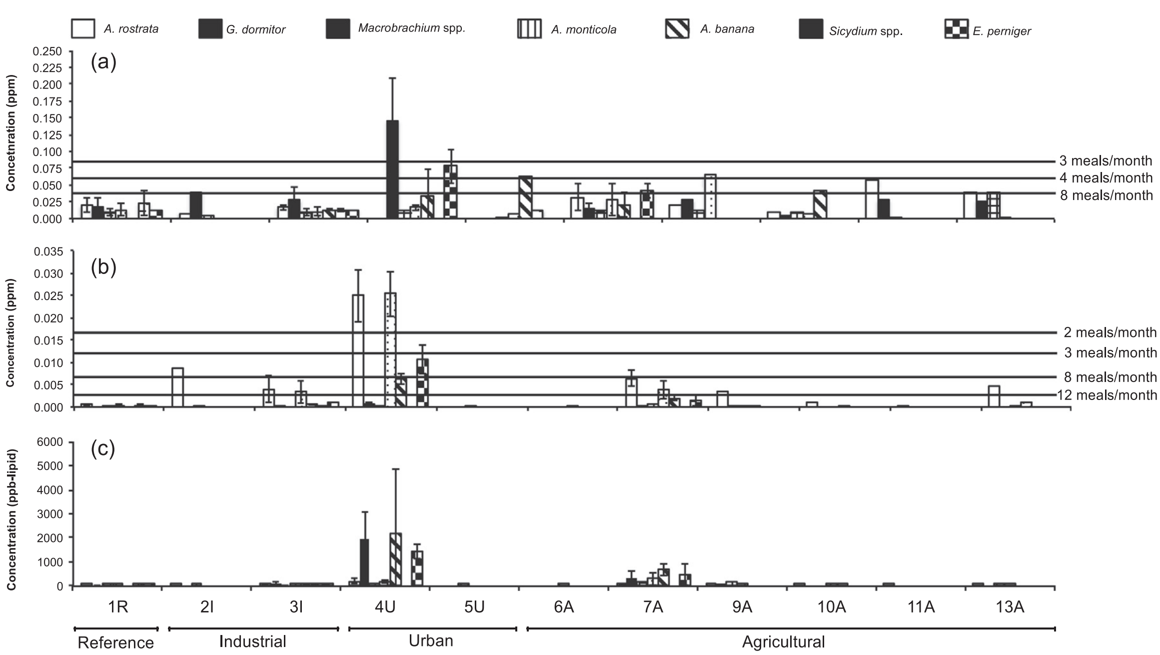

Fig. 3. Concentrations of (a) mercury (ppm wet weight), (b) PCBs (ppm wet weight), and (c) PCBs (ppb lipid-corrected) in fish and shrimp taxa from Puerto Rico streams with EPA monthly consumption limits (U.S. Environmental Protection Agency, 2000) denoted by the horizontal lines.

Table 2
Comparison of aquatic contaminants (ppb wet weight) in fish tissue among aquatic ecosystems, including U.S. lakes (Stahl et al., 2009), U.S. streams (Gilliom et al., 2006; Scudder et al., 2009), Puerto Rico (USA) streams (this study), one Cuba river (Rosa et al., 2009), and Hawaii (USA) streams (Gilliom et al., 2006). Benchmark exceedance concentrations are 300 ppb for mercury, 12 ppb for PCBs, 67 ppb for chlordanes, and 69 ppb for DDTs (U.S. Environmental Protection Agency, 2000).

Water body	Mercury			Sum of PCBs			Sum of chlordane			Sum of DDTs		
	Median (ppb)	Max. (ppb)	Threshold exceeded (%)	Median (ppb)	Max. (ppb)	Threshold exceeded (%)	Median (ppb)	Max. (ppb)	Threshold exceeded (%)	Median (ppb)	Max. (ppb)	Threshold exceeded (%)
U.S. lakes												
Predators	285	6605	49	2	705	17	ND[a]	100	< 1	2	1481	< 2
Benthic feeders	69	596	< 5	14	1266	50–75	27	378	< 5	13	1761	10–25
U.S. streams												
Overall	169	1950	27	–	–	–	ND	1790	13	33	9494	34
Urban	–	–	–	–	–	–	46	1790	39	63	2200	47
Agricultural	–	–	–	–	–	–	5	445	12	64	9494	49
Undeveloped	–	–	–	–	–	–	< 1	634	2	7	2148	13
Hawaii streams	–	–	–	–	–	–	17	1790	30	10	361	15
PR streams												
Overall	13	282	0	< 1	31	8	ND	15	0	0	12	0
Reference	13	50	0	< 1	1	0	ND	ND	0	0	< 1	0
Urban	19	233	0	7	31	8	< 1	15	0	0.6	12	0
Industrial	13	53	0	< 1	9	0	ND	2	0	0	2	0
Agricultural	18	282	0	< 1	9	0	ND	3	0	0	10	0
Cuba river	–	375	4	–	–	–	–	–	–	–	–	–

[a] ND = below detection limits.

tissue; however, dieldrin concentrations in American Eel from the urban site (4U) were above all human consumption limits for cancer endpoints (i.e., 0 meals per month). There were few threshold exceedances for DDTs; River Goby from an agricultural site (7A) and American Eel from an urban site (4U), both exceeded the EPA consumption limits recommended for 16 meals per month for cancer endpoints. Mountain Mullet from site 4U had the greatest concentrations of PCBs, exceeding the recommended consumption limit for 1 meal per month for cancer endpoints (4 meals for non-cancer endpoints). No Bigmouth Sleeper, Sirajo Goby, or *Macrobrachium* spp. exceeded human consumption limits for PCBs.

4. Discussion

Overall, Puerto Rico streams are relatively less polluted than water bodies of other tropical regions and the United States (Table 2). The maximum advisable concentration for mercury (300 ppb wet weight) was never exceeded in this study; a study of mercury in a Cuban river revealed only 4% of the samples exceeding the criterion for mercury (Rosa et al., 2009). Other researchers have found that 27% of streams and 49% of predatory fish in lakes in the United States exceeded this criterion (Scudder et al., 2009; Stahl et al., 2009). Concentrations of PCBs were lower in Puerto Rico streams relative to other regions with 8% of all samples exceeding 12 ppb wet weight compared to 50–75% of benthic feeding fish from lakes in the United States exceeding this same benchmark (Stahl et al., 2009). Only 5% of samples exceeded the U.S. Geological Survey's National Water Quality Assessment Program (NAWQA) benchmark$_{low}$ (6 ppb wet weight) for DDTs; however, 63% and 76% of all samples for Hawaii (USA) and U.S. streams exceeded this concentration, respectively.

Only several specific instances from this study revealed pollution in the stream ecosystems of Puerto Rico, but it was not widespread or associated with a particular land use type. Nickel concentrations in sediment at three agricultural sites exceeded the severe effect level, indicating that sediment contamination at these sites may be problematic for the majority of sediment-dwelling organisms (MacDonald et al., 2000). An urban site (4U) in the San Juan metropolitan area generally had the greatest concentrations of contaminants, including the greatest concentrations of PAHs, chlordanes, and PCBs in sediment and the greatest mercury, PCB, and dieldrin in native fishes. This site also had the greatest concentrations of current use and chlordane pesticides and PAHs in water. Likewise, the other urban site (5U) also seemed to be relatively contaminated. The sediment was relatively low in organic carbon, but it had the third greatest concentration of PAHs and chlordane in water and second greatest concentrations of PCBs and PAHs in sediment. Native fish species were not available for comparison with the other urban site because they were not present at this site, due to the presence of a downstream dam (Kwak et al., 2007). In urban areas, there may be a greater input of pesticides for mosquito control, maintenance of right-of-ways, golf courses, and domestic lawns (Miles and Pfeuffer, 1997). A greater amount of contaminants may also be released into urban streams as a result of runoff from impervious surfaces (Klein, 1979; Holland et al., 2003).

Nickel and copper were the only contaminants to exceed sediment quality guidelines. Nickel was highly elevated at three agricultural sites, even after normalization by iron concentration, total organic carbon, and percent clay. These high levels could be due to applications of nickel-based fungicides or from illegal disposal of various electroplated items (Rowell, 1968; Tandon et al., 1977; Hunter and Arbona, 1995). Elevated levels of copper may be owing to the natural geology of the island, pesticide applications, or they may be associated with transportation, as copper is a major component of automobile brake pads (Gasser et al., 2009), and all sampling sites were near road stream crossings.

Findings at three sites were contrary to expectations considering their land use and potential pollution sources. The reference site (1R) was relatively contaminated with metals, which was unexpected because it was located within a predominately forested watershed of the El Yunque National Forest. This unexpected finding may be attributed to persistent legacy effects of past land use or management practices (Harding et al., 1998; Kwak and Freeman, 2010). This area was historically mined for gold, copper, and chalcopyrite and was also farmed as a coffee plantation (Cardona, 1984). There were also unexpected findings at two industrial sampling sites. Site 2I was downstream of a nonoperational oil refinery and was expected to contain greater concentrations of PAHs in sediment and water, but levels in both media were low. Site 3I was located near a cement production facility and was expected to be a significant source of mercury, yet low mercury levels were detected there. These unexpected findings at the industrial stream sites may be related to hydrology and temporal changes.

4.1. Contaminants and island hydrology

Although streams of Puerto Rico receive substantial amounts of pollution from a variety of sources (Hazen, 1988; Hunter and Arbona, 1995; Stallard, 2001; Neal et al., 2009), results indicate that these stream ecosystems are not severely polluted, with the sporatic exception of nickel in sediment and PCBs and dieldrin in fish tissue. Hydrology may be an important factor limiting contaminant bioaccumulation in the stream ecosystems of Puerto Rico. If so, lentic ecosystems in Puerto Rico would be expected to show better evidence of pollution. Lentic and lotic environments differ in chemistry, hydrology, and ecology, which consequently have been shown to affect bioaccumulation. For example, fish from lentic systems have been found to bioaccumulate selenium at a rate 10 times greater than fish from lotic environments exposed to similar concentrations (Adams et al., 2000). Lentic systems form sediment from organic matter that is constantly being recycled within the system along with any associated contaminants and reside there due to long hydraulic retention times (Jeffries and Mills, 1990; Simmons and Wallschläger, 2005). In contrast, lotic systems create high flushing rates that limit sedimentation of contaminated organic matter and the subsequent exposure of benthos and detrital components of the ecosystem, thus reducing bioaccumulation (Van Derveer and Canton, 1997; Adams et al., 2000; Simmons and Wallschläger, 2005). The lotic ecosystems of Puerto Rico experience frequent flushing flows from recurring high rainfall flood events and hurricanes, and thereby have reduced deposition and long-term retention of contaminants. In addition, lotic systems have a greater redox potential than lentic systems, due to constant aeration from flowing water (Simmons and Wallschläger, 2005). Reducing conditions can form metal species that are less bioavailable than those more oxidized metal species (Lenz and Lens, 2009). Additionally, the streams studied were shallow, facilitating chemical degradation by photolysis, depending upon the compound.

Streams in Puerto Rico tend to be well incised and narrow and may have less potential for bioaccumulation because they lack connections to environments similar to lentic systems, such as floodplains. Most of the sites sampled also lack a connection to reservoirs because the native species targeted for sampling are only found downstream of reservoirs due to their diadromous life history (Cooney and Kwak, 2013). Conversely, non-native Channel Catfish from site 8A collected upstream of a reservoir had the greatest concentrations of mercury in this study. It is likely that Channel Catfish from this site migrated upstream from the reservoir where they had been exposed to greater contaminants. Relationships with benthic habitats, as illustrated by this Channel Catfish example, and other microhabitat affinities, likely play a minimal role in these streams because they are shallow and the substrate appears low in organic content and thus, organic pollutants.

Similarly, bioaccumulation in coastal areas is also influenced by habitat type because sheltered intertidal shores and creeks allow for accumulation of fine sediments, providing sinks for contaminants (Rawlins et al., 1998). Although, most Caribbean islands have little continental shelf with effective mixing and dispersal of terrestrial-based pollution (Rawlins et al., 1998), several deep oceanic basins in the Caribbean receive little flushing, making them vulnerable to contaminant accumulation (Ross and DeLorenzo, 1997). Impoundments and estuaries of Puerto Rico may be more polluted than the stream habitats sampled, as suggested by other studies. For example, a study of coastal sediments revealed that Guanica Bay, Puerto Rico, had elevated levels of PCBs and DDT (Pait et al., 2008). In contrast, another study generally found low concentrations of mercury in biota at three estuaries in Puerto Rico (Burger et al., 1991). High levels of contaminants in fish tissue were found in marine and some reservoir fish of Puerto Rico (Rodríguez and González, 1981). Although, a contaminant survey of Redear Sunfish *Lepomis microlophus* and sediment in the Dos Bocas Reservoir, Puerto Rico, showed little evidence of contamination problems (Neal et al., 2005).

5. Conclusions

Contrary to expectations, stream ecosystems in Puerto Rico were not severely polluted (albeit prior to the devastating impact of hurricanes Irma and Maria in September 2017), especially when compared with other water bodies in tropical ecosystems and the United States. Several exceptions were nickel in sediment at agricultural sites and PCBs and dieldrin at an urban site. All fish species contained variable concentrations of contaminants, but among those sampled, the Bigmouth Sleeper may be most suitable for human consumption in a recreational sport fishery. They have low levels of organic contaminants and rare occurrences of mercury contamination. These findings comprise the first comprehensive study of contaminants among species and sites in the freshwater ecosystems of Puerto Rico, and findings may provide insight for other tropical island ecosystems. These results improve understanding relative to land use patterns and may assist water and natural resource agencies in identifying areas of concern, planning to improve ecological and human health, and development of freshwater fisheries.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.envres.2017.11.053.

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