

An assessment of chemical contaminants in sediments from the St. Thomas East End Reserves, St. Thomas, USVI

Anthony S. Pait · S. Ian Hartwell · Andrew L. Mason · Robert A. Warner · Christopher F. G. Jeffrey · Anne M. Hoffman · Dennis A. Apeti · Simon J. Pittman

Received: 15 September 2013 / Accepted: 18 March 2014 / Published online: 18 April 2014
© Springer International Publishing Switzerland (outside the USA) 2014

Abstract The St. Thomas East End Reserves or STEER is located on the southeastern end of the island of St. Thomas, USVI. The STEER contains extensive mangroves and seagrass beds, along with coral reefs, lagoons, and cays. Within the watershed, however, are a large active landfill, numerous marinas, resorts, various commercial activities, an EPA Superfund Site, and residential areas, all of which have the potential to contribute pollutants to the STEER. As part of a project to develop an integrated assessment for the STEER, 185 chemical contaminants were analyzed in sediments from 24 sites. Higher levels of chemical contaminants were found in Mangrove Lagoon and Benner Bay in the western portion of the study area. The concentrations of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), zinc, copper, lead, and mercury were above a NOAA Effects Range-Low (ERL) sediment quality guideline at one or more sites, indicating impacts may be present in more sensitive species or life stages. Copper at one site in Benner Bay was above a

NOAA Effects Range-Median (ERM) guideline indicating effects on benthic organisms were likely. The antifoulant boat hull ingredient tributyltin (TBT) was found at the third highest concentration in the history of NOAA's National Status and Trends (NS&T) Program, which monitors the nation's coastal and estuarine waters for chemical contaminants and bioeffects. The results from this project will provide resource managers with key information needed to make effective decisions affecting coral reef ecosystem health and gauge the efficacy of restoration activities.

Keywords St. Thomas East End Reserves · STEER · Chemical contaminants · Sediments · PAHs · Metals · TBT

Introduction

Located on the southeastern end of the island of St. Thomas, US Virgin Islands (USVI), the St. Thomas East End Reserves or STEER (Fig. 1) is a collection of marine reserves and wildlife sanctuaries (MRWS) containing extensive mangroves and seagrass beds, along with coral reefs, lagoons, and cays. The STEER comprises an area of 9.6 km², with approximately 34 km of coastline, and is thought to be one of the most valuable fisheries nursery areas remaining around St. Thomas (STEER 2011). The only perennial stream on the island (Turpentine Gut) flows into Mangrove Lagoon in the west end of the STEER. In addition, there are numerous intermittent streams that discharge stormwater into the

A. S. Pait (✉) · S. I. Hartwell · A. L. Mason · R. A. Warner · C. F. G. Jeffrey · D. A. Apeti · S. J. Pittman
NOAA/NOS/NCCOS Center for Coastal Monitoring and Assessment,
1305 East/West Highway, Silver Spring, MD 20910, USA
e-mail: tony.pait@noaa.gov

A. M. Hoffman
The Nature Conservancy,
St. Thomas, VI, USA

S. J. Pittman
The Marine Institute, Plymouth University,
Plymouth, UK

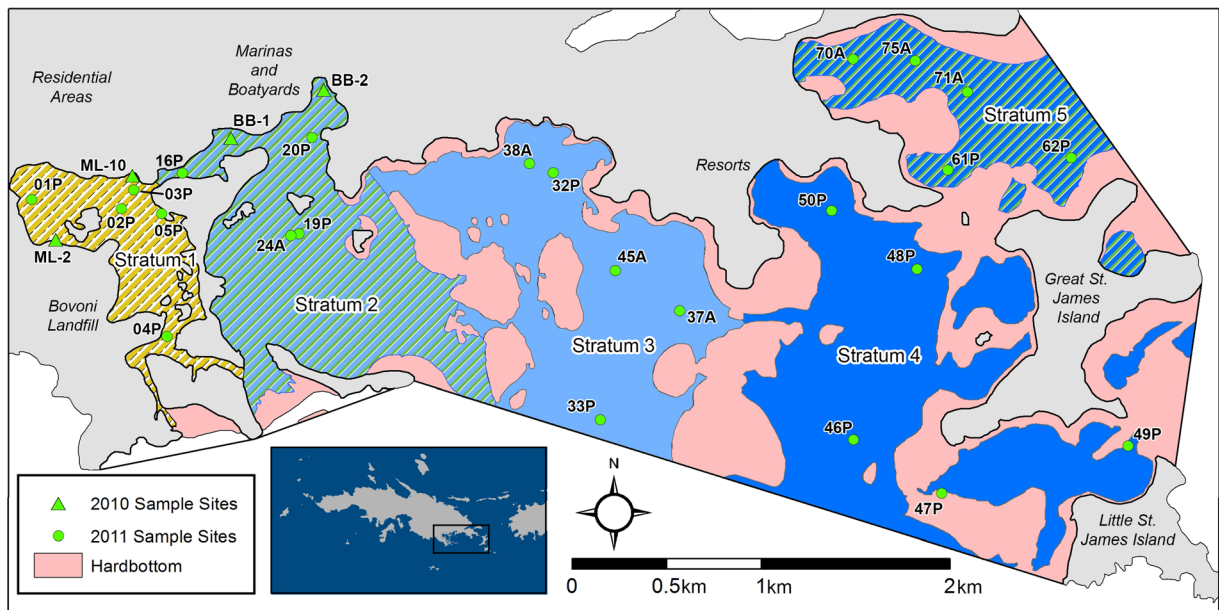


Fig. 1 Map of sediment sampling sites and strata in the STEER

STEER throughout the watershed. Within the watershed are a large active landfill, numerous marinas and boatyards, a number of resorts, various commercial/industrial activities, an EPA Superfund Site, a horse racetrack, and residential areas served by individual septic systems (IRF 1993), all of which can contribute a variety of pollutants to the STEER. Elevated levels of chemical contaminants have been documented in the STEER watershed (EPA 2011).

The USVI Department of Planning and Natural Resources (DPNR) identified the STEER as a priority area and noted the extent of chemical contamination and bioeffects are unknown, but that information is needed to make better informed decisions on coastal resource management. Beginning in 2011, NOAA's National Centers for Coastal Ocean Science (NCCOS) partnered with DPNR Divisions of Coastal Zone Management, Fish and Wildlife, and Environmental Protection, along with the University of the Virgin Islands and The Nature Conservancy with funding from NOAA's Coral Reef Conservation Program (CRCP) to develop an integrated (chemical and biological) assessment for the STEER. This paper details results from the assessment of chemical contaminants in sediments from the STEER.

Materials and methods

A stratified random sampling design was used to characterize the spatial distribution of chemical

contaminants. The STEER was first subdivided into five strata based on habitat and geography (e.g., hard bottom areas, seagrass beds, mangroves, etc.) (Fig. 1). Five sampling points on soft bottom sediments were randomly selected using ArcGIS®. Both primary and alternate sites were identified. Alternate sites were sampled in the event that a primary site was unsuitable due to hard bottom, obstructions, etc. Most of the samples were collected from the charter vessel *Bright Star*. Sites in shallower Mangrove Lagoon were collected using a smaller boat provided by the DPNR Division of Fish and Wildlife.

Sediment collection

Sediments for chemical contaminant analysis were collected using standard NOAA National Status and Trends (NS&T) protocols (Apeti et al. 2012a). A PONAR grab was deployed to collect the samples using a pulley and davit and retrieved by hand. Rocks and bits of seagrass were removed. If a particular grab did not result in 200–300 g of sediment, a second grab was made and composited with material from the first. If enough sediment had not been collected after three deployments of the grab, the site was abandoned and the boat moved on to an alternate site. A series of protocols (Apeti et al. 2012a) were used to avoid contamination of the sediment samples by equipment and cross contamination between samples and sites. All

equipment was rinsed with acetone and then distilled water just prior to use at a site. Personnel handling the samples also wore disposable nitrile gloves. The top 3 cm of sediment was collected from the grab using a stainless steel sediment scoop.

Sediments were placed into two certified clean (I-Chem[®]) 250-mL labeled jars, one for organic chemical analysis, the other for major and trace element analysis, capped, and then kept on ice in a cooler. Sediments for grain size analysis were placed in a Whirl-Pack[®] bag, sealed, and then kept on ice in a cooler. At the end of each day, sediment samples for contaminant analysis were frozen. The Whirl-Pack[®] bags for the grain size analysis were placed in a refrigerator rather than frozen, to avoid altering the grain size structure. Preliminary work during the project planning phase included the collection of nonrandomized samples in May 2010; the sites were selected in consultation with local managers to specifically sample known or potentially contaminated sites. Those results are reported herein for context, but are not included in the statistical comparisons between strata or in the calculation of mean and median concentrations of sediment contaminants in the STEER.

Chemical contaminant analysis

The sediments were analyzed for a suite of 185 organic and inorganic contaminants (Table 1) by TDI-Brooks International, using protocols established by the NS&T Program. The sediment samples were homogenized, dried, and ground using a mortar and pestle. Approximately 15 g of dry sediment was extracted with 100 % dichloromethane using a Dionex Accelerated Solvent Extractor (ASE200). The extracts were reduced in volume and then purified using alumina/silica gel column chromatography. The 59 polycyclic aromatic hydrocarbons (PAHs) were analyzed using gas chromatography/mass spectrometry in the selected ion monitoring mode. The 37 aliphatic hydrocarbons were analyzed by gas chromatography/flame ionization detection. The 31 organochlorine pesticides and 38 polychlorinated biphenyls (PCBs) were analyzed using gas chromatography/electron capture detection. The four butyltins were analyzed using gas chromatography/flame photometric detection after derivatization. A subset of the sediment samples was subsequently reanalyzed using gas chromatography/mass spectrometry for confirmation of the TBT concentrations detected from the initial analysis. Additional information on the analysis of the

sediment samples for organic chemical contaminants can be found in Kimbrough et al. (2006).

After freeze-drying, the sediment samples for trace and major elements were dried to a constant weight, 0.2 g of dried sediment was homogenized and weighed, a 3-mL aliquot of nitric acid was added, and the vials were placed in a digestion block for a total of approximately 6 h. After this period, the vials were removed from the block, and 2 mL of concentrated hydrofluoric acid was added and returned to the block for approximately 2 h. After cooling, 15 mL of 4 % boric acid was added to the vials. The major and trace elements were analyzed using inductively coupled plasma mass spectrometry and atomic-fluorescence spectroscopy. Additional information on the analysis of the sediment samples for trace and major elements can be found in Kimbrough and Lauenstein (2006).

Statistical analysis

The sediment contaminant data from the stratified random sampling were analyzed using JMP[®] statistical software. A Shapiro-Wilk test was first run on individual parameters to see if the data were normally distributed. When data were normally distributed, an analysis of variance (ANOVA) was run followed by pairwise (Tukey's HSD) comparisons. If the data were not normally distributed and a log₁₀ transformation was not effective, Spearman's nonparametric multivariate correlation was used. Some of the data were also subsequently ranked, followed by a Kruskal-Wallis test and pairwise comparisons. Statistical comparisons between strata used data generated from the stratified random sampling. In this paper, when statistical comparisons are made between strata, the stratum number along with the stratum name are used.

NOAA sediment quality guidelines

To put the results of the analysis into context, data from the STEER were compared to data from the NS&T database and also with NOAA numerical sediment quality guidelines (SQG). These guidelines developed by Long and Morgan (1990) and Long et al. (1995) are the effects range-median (ERM), and effects range-low (ERL), which express statistically derived levels of sediment contamination, above which toxic effects would be expected with at least a 50 % frequency (ERM) and below which effects were rarely (<10 %) expected (ERL).

Table 1 Chemical contaminants analyzed in the STEER sediment samples

PAHs (low MW)	PAHs (high MW)	Aliphatics	Organochlorine pesticides	PCBs	Major and trace elements
Naphthalene	Fluoranthene	n-C9	Aldrin	PCB8/5	Aluminum (Al)
1-Methylnaphthalene	Pyrene	n-C10	Dieldrin	PCB18	Antimony (Sb)
2-Methylnaphthalene	C1-Fluoranthenes/Pyrenes	n-C11	Endrin	PCB28	Arsenic (As)
2,6-Dimethylnaphthalene	C2-Fluoranthenes/Pyrenes	n-C12	Heptachlor	PCB29	Cadmium (Cd)
1,6,7-Trimethylnaphthalene	C3-Fluoranthenes/Pyrenes	n-C13	Heptachlor-Epoxide	PCB31	Chromium (Cr)
C1-naphthalenes	Naphthobenzothiophene	i-C15	Oxychlorane	PCB44	Copper (Cu)
C2-naphthalenes	C1-naphthobenzothiophenes	n-C14	Alpha-chlordane	PCB45	Iron (Fe)
C3-naphthalenes	C2-naphthobenzothiophenes	i-C16	Gamma-chlordane	PCB49	Lead (Pb)
C4-naphthalenes	C3-naphthobenzothiophenes	n-C15	<i>Trans</i> -nonachlor	PCB52	Manganese (Mn)
Benzothiophene	Benz[a]anthracene	n-C16	<i>Cis</i> -nonachlor	PCB56/60	Mercury (Hg)
C1-benzothiophenes	Chrysene	i-C18	Alpha-HCH	PCB66	Nickel (Ni)
C2-benzothiophenes	C1-chrysenes	n-C17	Beta-HCH	PCB70	Selenium (Se)
C3-benzothiophenes	C2-chrysenes	Pristane	Delta-HCH	PCB74/61	Silicon (Si)
Biphenyl	C3-chrysenes	n-C18	Gamma-HCH	PCB87/115	Silver (Ag)
Acenaphthylene	C4-chrysenes	Phytane	DDMU	PCB95	Tin (Sn)
Acenaphthene	Benzo[b]fluoranthene	n-C19	2,4'-DDD	PCB99	Zinc (Zn)
Dibenzofuran	Benzo[k]fluoranthene	n-C20	4,4'-DDD	PCB101/90	
Fluorene	Benzo[e]pyrene	n-C21	2,4'-DDE	PCB105	
C1-fluorenes	Benzo[a]pyrene	n-C22	4,4'-DDE	PCB110/77	
C2-fluorenes	Perylene	n-C23	2,4'-DDT	PCB118	
C3-fluorenes	Indeno[1,2,3-c,d]pyrene	n-C24	4,4'-DDT	PCB128	
Carbazole	Dibenzo[a,h]anthracene	n-C25	1,2,3,4-Tetrachlorobenzene	PCB138/160	
Anthracene	C1-dibenzo[a,h]anthracenes	n-C26	1,2,4,5-Tetrachlorobenzene	PCB146	
Phenanthrene	C2-dibenzo[a,h]anthracenes	n-C27	Hexachlorobenzene	PCB149/123	
1-Methylphenanthrene	C3-dibenzo[a,h]anthracenes	n-C28	Pentachloroanisole	PCB151	
C1-phenanthrene/anthracenes	Benzo[g,h,i]perylene	n-C29	Pentachlorobenzene	PCB153/132	
C2-phenanthrene/anthracenes		n-C30	Endosulfan II	PCB156/171/202	
C3-phenanthrene/anthracenes		n-C31	Endosulfan I	PCB158	
C4-phenanthrene/anthracenes		n-C32	Endosulfan sulfate	PCB170/190	
Dibenzothiophene		n-C33	Mirex	PCB174	
C1-dibenzothiophenes		n-C34	Chlorpyrifos	PCB180	
C2-dibenzothiophenes		n-C35		PCB183	

Table 1 (continued)

PAHs (low MW)	PAHs (high MW)	Aliphatics	Organochlorine pesticides	PCBs	Major and trace elements
C3-dibenzothiophenes		n-C36 n-C37 n-C38 n-C39 n-C40	Butyltins Monobutyltin Dibutyltin Tributyltin Tetrabutyltin	PCB187 PCB194 PCB195/208 PCB201/157/173 PCB206 PCB209	

MW molecular weight, *PAH* polycyclic aromatic hydrocarbons, *HCH* hexachlorocyclohexane, *DDMU* 1-chloro-2,2-(p-chlorophenyl)ethylene, *DDT* dichlorodiphenyltrichloroethane, *DDD* dichlorodiphenyl/dichloroethane, *DDE* dichlorodiphenyl/dichloroethylene, *PCB* polychlorinated biphenyl

Results and discussion

A total of 24 samples were collected (Fig. 1) under DPNR Permit STX-032-11 in June 2011. The average water depth at the sites sampled was 7.2 m; the shallowest was 0.6 m at site 1-5P in Mangrove Lagoon. The average surface salinity was 33.2‰; the average bottom salinity was 33.7‰, indicating fairly well mixed waters. The average percent total organic carbon (TOC) in the sediments was 2.49 % and ranged from a low of 0.44 % to a high of 5.44 %. The average percent fines content (sum of percent silt and percent clay) in the STEER sediments was 22.2±4.03 % (mean±standard error). Areas in Mangrove Lagoon and to a certain extent in Benner Bay tended to have a higher proportion of percent fines in the sediments. However, the major sediment grain size class throughout the STEER was sand (68±4.35 %).

Organic contaminants

Total PAHs

Total PAHs refers to the sum of the 59 PAH compounds and compound classes (e.g., anthracene, C1-naphthalenes) analyzed in the STEER sediments (Table 1). The mean total PAH concentration was 145 ±59 ng/g; the median was 6.02 ng/g (Table 2). The highest total PAH concentration was at site 1-3P (1,131 ng/g) in Mangrove Lagoon. From 2010, the concentration of total PAHs at ML-10, also in Mangrove Lagoon, was 951 ng/g. None of the sites sampled in the STEER approached the NOAA ERL (Table 2). A Kruskal-Wallis test run on the ranked data from the stratified random samples indicated a significant difference in total PAHs by stratum ($p=0.0210$); a Tukey’s HSD (highly significant difference) analysis indicated that Mangrove Lagoon (stratum 1) and St. James Bay (stratum 4) were significantly different from each other. Mean total PAH concentration in Mangrove Lagoon (stratum 1) was 437±216 ng/g (Table 3). As will be seen, the pattern of higher concentrations of chemical contaminants in the Mangrove Lagoon and Benner Bay areas, particularly northern Benner Bay, was repeated for a number of other contaminant classes. Land use in the area around Mangrove Lagoon includes an active landfill and residential areas, which likely contribute contaminants to the lagoon. In northern Benner Bay, the presence of marinas and boatyards, with associated

Table 2 Means and medians of chemical contaminants in sediments from the STEER

	Minimum	Maximum ^a	Mean±SE	Median	ERL	ERM	No. samples> ERL	No. samples> ERM
Organics (ng/g)								
Total PAHs	0.93	1,131	145±59	6.02	4,022	44,792	0	0
Total extractable hydrocarbons (µg/g)	1.41	1,104	167±61	23.5	–	–	–	–
Total PCBs	0	65.9	1.00±0.32	0.37	22.7	180	1	0
Total DDT	0	3.61	0.05±0.03	0	1.58	46.1	1	0
Total endosulfan	0	0.63	0.01±0.01	0	–	–	–	–
Chlorpyrifos	0	1.33	0.03±0.02	0	–	–	–	–
Tributyltin (TBT) (ng Sn/g)	0	248	1.85±1.30	0	–	–	–	–
Trace and major elements (µg/g)								
Cadmium (Cd)	0	0.37	0.03±0.02	0	1.2	9.6	0	0
Chromium (Cr)	4.91	40.4	14.1±1.76	11.4	81	370	0	0
Copper (Cu)	1.30	1,010	21.0±7.46	3.75	34	270	10	1
Lead (Pb)	0.37	81.2	5.87±1.90	0.82	46.7	218	1	0
Mercury (Hg)	0	0.34	0.02±0.01	0.01	0.15	0.71	1	0
Nickel (Ni)	4.29	15.1	6.53±0.57	5.08	20.9	51.6	0	0
Zinc (Zn)	0	392	37.3±10.7	11.1	150	410	5	0

ERL effects range-low, ERM effects range-median, – not available

^a Maximum values also include results from the targeted 2010 sampling. Mean and median values were calculated using data generated from the 2011 stratified random samples and did not include data from the 2010 targeted sampling

activities such as repairing and repainting boats, use of fuels and lubricants, etc. are likely sources of at least some of the contaminants found in the sediments in this area. In addition, a highway that winds its way along northern Benner Bay is also a likely source of both organic and inorganic contaminants to the STEER.

In Vieques, Puerto Rico, the mean concentration of total PAHs was 52.3±8.7 ng/g, somewhat below total PAHs found in the STEER sediments (Pait et al. 2010). In southwest Puerto Rico, Pait et al. (2008) reported a mean total PAH concentration in the sediments of 80.6±25.5 ng/g, also lower than the mean found in the STEER.

The ratios of phenanthrene-to-anthracene (P/A) and fluoranthene-to-pyrene (F/P) have been used as screening tools to assess the relative contributions of pyrogenic (combustion-related) versus petrogenic (uncombusted) sources of PAHs (Budzinski et al. 1997). Higher levels of uncombusted PAHs would be more indicative of the presence of spilled fuels, such as gasoline or oil. P/A ratios less than 10 are more indicative of pyrogenic sources; F/P ratios greater than one (1) are also thought to be associated with pyrogenic sources. Most of the sites in the STEER had P/A ratios of less

than 10. While the F/P ratio was close to or above one (1) at most sites indicating pyrogenic sources for the PAHs, three sites in Mangrove Lagoon including 1-2P (0.83), 1-3P (0.70) and 1-5P (0.95) and, in northern Benner Bay, 2-16P (0.80) and 2-20P (0.91) had ratios indicating possible petrogenic contributions to the overall mix of PAHs in the samples. Yunker et al. (2002) and Oros and Ross (2004) have also looked at PAH isomer ratios. The benz-a-anthracene/benz-a-anthracene+chrysene ratio can be used to provide additional information on possible sources of sediment PAHs. Using this approach, three sediment samples from the STEER (1-2P, 1-5P, and 2-19P) had ratios indicating a mix of both petroleum and combustion sources, similar to what was found using the F/P ratio. The ratios for a number of samples from Mangrove Lagoon and northern Benner Bay indicate likely contributions from the combustion of fossil fuels as well as from uncombusted fuels.

Total extractable hydrocarbons

The concentrations of total extractable hydrocarbons (TEH) were approximately an order of magnitude higher than total PAHs. The mean TEH concentration

Table 3 Mean chemical contaminant concentrations by stratum in the STEER

Organics (ng/g)	Stratum				
	Mangrove Lagoon (1)	Benner Bay (2)	Jersey Bay (3)	St. James Bay (4)	Great Bay (5)
Total PAHs	437±216	142±81	133±121	2.1±0.65	8.45±3.38
TEH (µg/g)	624±175	160±83	21.5±6.2	13.1±6.0	14.2±3.6
Total PCBs	1.77±0.50	2.61±1.62	0.26±0.12	0.30±0.06	0.38±0.05
Total DDT	0.05±0.02	0.18±0.14	0.02±0.02	0.01±0.01	0.00
TBT (ng Sn/g)	1.05±0.60	9.63±7.28	0.12±0.12	0.00	0.03±0.03
Trace and major elements (µg/g)					
Cadmium (Cd)	0.1±0.06	0.05±0.05	0.00	0.00	0.00
Chromium (Cr)	26.7±4.4	13.3±2.9	10.1±0.8	11.3±2.7	9.15±1.02
Copper (Cu)	48.4±12.3	55.2±34.5	3.58±1.17	1.76±0.15	2.92±0.56
Lead (Pb)	18.7±5.1	8.81±4.39	1.18±0.35	0.50±0.05	0.74±0.06
Mercury (Hg)	0.061±0.018	0.035±0.019	0.002±0.001	0.001±0.000	0.001±0.000
Nickel (Ni)	10.5±1.7	6.41±0.77	5.18±0.32	5.40±0.65	5.16±0.22
Zinc (Zn)	109±27	57.0±25.3	7.61±2.80	9.81±1.00	6.95±1.12

Means calculated using the stratified random samples

PAHs polycyclic aromatic hydrocarbons, *TEH* total extractable hydrocarbons, *PCBs* polychlorinated biphenyls, *DDT* dichlorodiphenyltrichloroethane, *TBT* tributyltin

in the STEER was 167 µg/g, with the maximum (1,104 µg/g) in Mangrove Lagoon at 1-3P. An ANOVA run on the log10 transformed data indicated that TEH varied by stratum ($p=0.0018$), and a Tukey-Kramer HSD test indicated that Mangrove Lagoon (stratum 1) was significantly different (higher) than Jersey Bay (stratum 3), St. James Bay (stratum 4), and Great Bay (stratum 5). Not surprisingly, a nonparametric correlation run between TEH and total PAHs indicated a very significant positive correlation (Spearman rho=0.6478, $p=0.0006$).

Polychlorinated biphenyls

Total PCBs as defined in this paper is the sum of the 38 congeners analyzed (Table 1). The mean concentration of total PCBs was 1.00±0.32 ng/g; the median was 0.37 ng/g (Table 2). As with the PAHs, there was a pattern of somewhat elevated levels of total PCBs in Mangrove Lagoon and in northern Benner Bay. The highest concentration of total PCBs from the stratified random sampling was 7.2 ng/g (2-20P); from the targeted 2010 sampling, the highest concentration was 65.9 ng/g at BB-2. The concentration of total PCBs at site BB-2 (65.9 ng/g) from the targeted sampling was higher than the PCB ERL (22.7 ng/g), but below the

ERM (180 ng/g) (Table 2). An ANOVA, run on the log10 normalized values, however, indicated no significant variation ($p=0.0573$) in total PCBs concentration across the five strata.

The mean total PCBs concentration found in the sediments in Jobos Bay, Puerto Rico, was 2.09±0.50 ng/g (Pait et al. 2012). In Vieques, that value was 2.86±0.14 ng/g, both higher than what was found in the STEER. In southwest Puerto Rico, the mean total PCBs concentration in sediments was 74.7±47.9 ng/g, due in part to two very high PCB concentrations within Guanica Bay (Pait et al. 2008). If the two sites in Guanica Bay are excluded, the mean for total PCBs in the southwest Puerto Rico study area was 12.1±2.26 ng/g (Pait et al. 2008).

Total DDT

Total dichlorodiphenyltrichloroethane (DDT) as defined here is the sum of the parent isomers (4,4'-DDT and 2,4'-DDT), along with degradation products DDE, DDD, and DDMU. The mean concentration of total DDT in the sediments was 0.05±0.03 ng/g. As with a number of the other chemical contaminants, higher concentrations of total DDT were found in the Benner Bay and Mangrove Lagoon areas. The highest total DDT

concentration from the stratified random samples collected in 2011 was 0.609 ng/g at 2-20P. The highest concentration from the 2010 targeted sampling was 3.61 ng/g at BB-2 (Table 2). In addition, the degradation products DDD and DDE appeared to make up much of the total DDT present, indicating that the parent compound had degraded over time. The concentration of total DDT at BB-2 (3.61 ng/g) from the 2010 targeted sampling was also above the ERL (1.58 ng/g); however, none of the sites sampled had a concentration approaching the DDT ERM of 46.1 ng/g (Table 2). An ANOVA run on log₁₀ normalized data indicated no significant variation ($p=0.2575$) in total DDT across the five strata.

In southwest Puerto Rico, Pait et al. (2008) detected a mean total DDT concentration of 2.10 ± 1.26 ng/g, higher than in the STEER. In Vieques, the mean concentration of total DDT in the sediments was substantially higher, 23.6 ± 16.5 ng/g, due in part to elevated concentrations at four sites (Pait et al. 2010).

Tributyltin

Mono-, di-, tri-, and tetrabutyltin were analyzed in the sediments sampled in the STEER. Tetrabutyltin is an intermediate in the manufacture of tributyltin (TBT) compounds. TBT has had extensive use in the past as an antifoulant on boat hulls and was banned in the USA beginning in 1989. The results of the analysis of TBT are highlighted in Fig. 2. The higher concentrations of TBT and its degradation products, as with a number of the other contaminants analyzed, were found in northern Benner Bay and Mangrove Lagoon. Butyltins, however, were not detected in half of the sediment samples collected in the STEER, primarily from the eastern and more offshore sites (Fig. 2).

The highest concentration of TBT detected in STEER sediments using the stratified random sampling was at site 2-20P in Benner Bay with a concentration of 31 ng Sn/g (note, 1 ng TBT/g dry wt=2.444 ng Sn/g). From the samples collected in 2010, BB-1 and BB-2 were even higher. The concentration of TBT at BB-1 was 77 ng Sn/g; the TBT concentration at BB-2 was quite high, 248 ng Sn/g. A summary of the relative amounts of TBT versus monobutyltin and dibutyltin from the stratified random samples collected in the STEER can be seen in Fig. 3. TBT accounted for between 17 and 55 % of the butyltin present in northern Benner Bay. It can also be seen that Benner Bay

accounted for higher butyltin concentrations and that TBT, dibutyltin, and monobutyltin had similar concentrations, which may indicate more recent deposition of TBT and/or slow degradation of TBT in this environment.

ERL/ERM guidelines have not been developed for TBT. An ANOVA run on the log₁₀ transformed data from the stratified random samples did not indicate any significant differences ($p=0.4368$) in the concentration of TBT between strata. Pait et al. (2008) detected a mean TBT concentration of 0.01 ± 0.01 ng Sn/g in southwest Puerto Rico. In Vieques, Puerto Rico, the mean concentration of TBT was 0.05 ± 0.02 ng Sn/g, and in Jobos Bay, the mean concentration was 0.56 ± 0.28 ng Sn/g. The NS&T median concentration of TBT in sediments is 0.16 ng Sn/g.

The concentration detected at BB-2 (248 ng Sn/g) from the 2010 sampling, represents the third highest TBT detection in the history of NOAA's NS&T Program. The only two higher TBT concentrations were from the Elizabeth River in the southern Chesapeake Bay area and Elliot Bay in Puget Sound (both EPA Superfund sites). The elevated levels of TBT suggest the need for additional work to quantify the distribution of this contaminant in the sediments along with effects (toxicity), including possible endocrine disruption in resident mollusks. Strand et al. (2009) found elevated levels of TBT and its degradation products in several gastropod species in the USVI, as well as imposex at several locations, including Charlotte Amalie Bay in St. Thomas.

Trace elements

Cadmium

Concentrations of cadmium in sediment samples from the STEER were fairly low; cadmium was not detected in 21 of the 24 sediment samples collected in the STEER in 2011. The mean concentration of cadmium in the sediments from the stratified random sampling was 0.028 ± 0.016 µg/g; however, the median was zero. The highest concentration from the stratified random sampling was at 1-3P in Mangrove Lagoon (0.264 µg/g). From the 2010 targeted sampling, the highest concentration detected was at ML-2, with a concentration of 0.371 µg/g. All cadmium concentrations were below the NOAA ERL. Because of the low number of

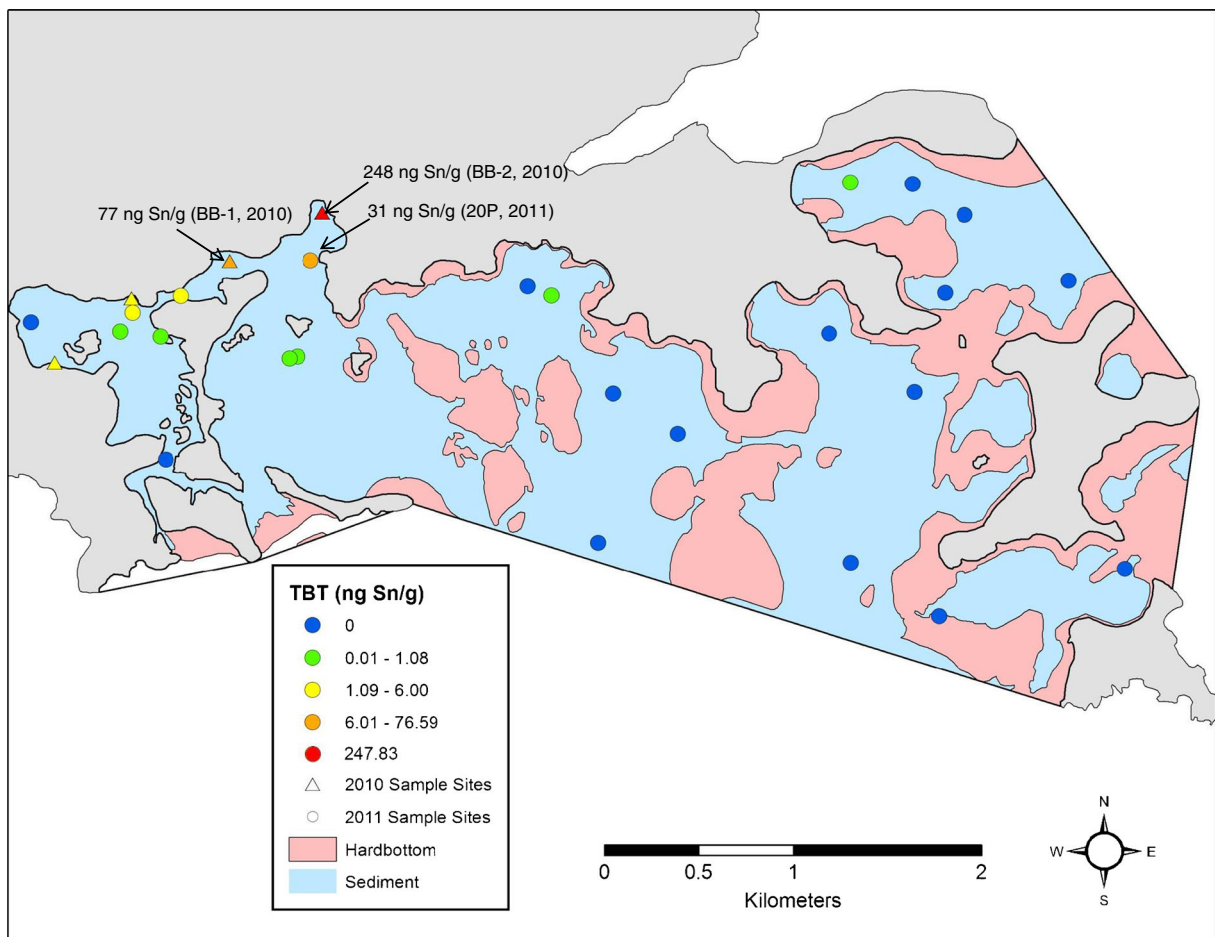


Fig. 2 Tributyltin (TBT) detected in STEER sediments

detections of cadmium in the STEER, no analysis by stratum was carried out.

Chromium

Somewhat elevated concentrations of chromium were also detected in Mangrove Lagoon and Benner Bay. The mean concentration of chromium in the STEER from the stratified random sampling was $14.1 \pm 1.76 \mu\text{g/g}$; the median was $11.4 \mu\text{g/g}$. The highest concentration of chromium in the sediments from the stratified random sampling was $35.7 \mu\text{g/g}$ at site 1-1P, also in Mangrove Lagoon. The three highest levels of chromium from the stratified random sampling were all from Mangrove Lagoon. From the 2010 samples, the highest chromium concentration was $40.4 \mu\text{g/g}$ at BB-2, similar to the concentration of chromium in Mangrove Lagoon. The concentration of chromium was below the NOAA ERL. An ANOVA carried out on the log10 transformed data

indicated that chromium varied significantly ($p=0.0090$) by stratum, and a subsequent pairwise comparison (Tukey’s HSD) indicated that chromium in Mangrove Lagoon (stratum 1) was significantly different (higher) than Jersey Bay (stratum 3), St. James Bay (stratum 4), and Great Bay (stratum 5). This can also be seen in Table 3.

In southwest Puerto Rico, Pait et al. (2008) calculated a mean chromium concentration of $31.2 \mu\text{g/g}$, higher than in the STEER. In Vieques, mean chromium levels in the sediment were also somewhat higher, $22.5 \mu\text{g/g}$ (Pait et al. 2010).

Copper

The results of the analysis of copper are highlighted in Fig. 4. The mean concentration in the sediments was $21 \pm 7.46 \mu\text{g/g}$; the median was $3.75 \mu\text{g/g}$. The highest copper concentration from the stratified random

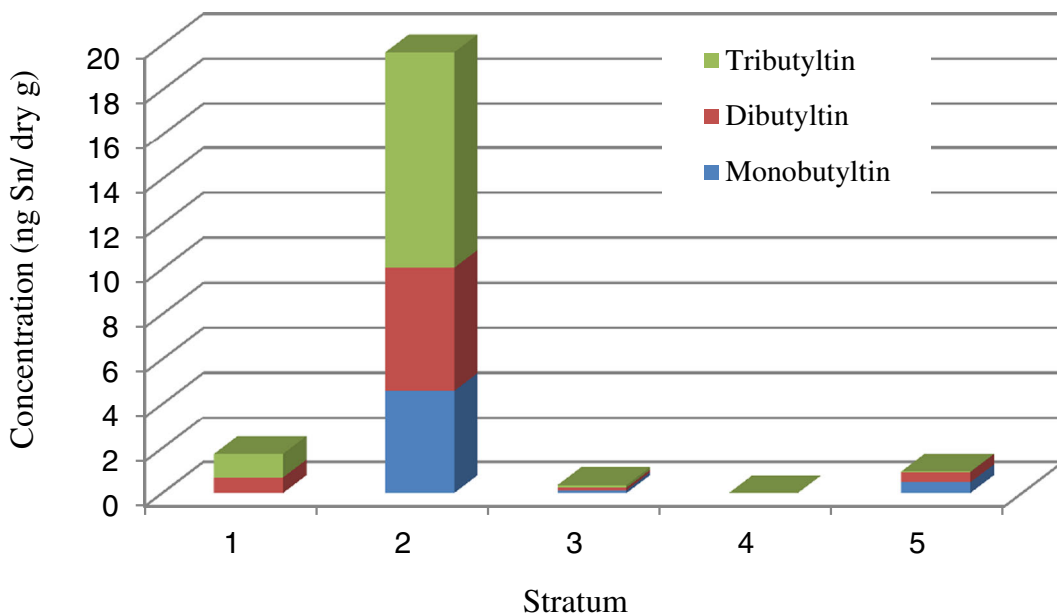


Fig. 3 Mean butyltins in STEER sediments by stratum

sampling was 155 $\mu\text{g/g}$ at site 2-20P, followed by 69.9 $\mu\text{g/g}$ at site 1-1P in Mangrove Lagoon. From the targeted sampling in 2010, the lowest concentration was 60.6 $\mu\text{g/g}$ at ML-10. At BB-1, the concentration of copper in the sediment was 145 $\mu\text{g/g}$. At BB-2, the copper concentration was quite high, 1,010 $\mu\text{g/g}$. The ERL for copper is 34 $\mu\text{g/g}$; the ERM is 270 $\mu\text{g/g}$. From the stratified random sites, six sites (2-20P, 1-1P, 1-3P, 1-2P, 2-16P, 1-5P) exceeded the ERL, but none exceeded the ERM for copper. All four of the 2010 targeted sites (i.e., BB-1, BB-2, ML-2, and ML-10) were above the NOAA ERL for copper. At site BB-2 (1,010 $\mu\text{g/g}$), the level of copper substantially exceeded the copper ERM of 270 $\mu\text{g/g}$, indicating that effects on benthic organisms are likely in this area. The copper concentration at BB-2 is also one of the 10 highest concentrations of copper in sediments detected by NOAA's NS&T Program. A Kruskal-Wallis test run on the ranked values from the stratified random sampling indicated a significant difference ($p=0.0001$) across the strata. A Tukey-Kramer HSD analysis revealed that Mangrove Lagoon (stratum 1) and Benner Bay (stratum 2) had significantly higher copper levels than the other three strata.

Marinas and boatyards are a major land use adjacent to the northern portion of Benner Bay. Copper has been used for years in antifoulant paint systems on boat hulls. Activities such as the mooring of vessels with hulls painted with copper-containing paints, along with the

cleaning, scraping, and repainting of boat hulls, and subsequent runoff containing paint chips and dust, as might occur during a rainstorm, could lead to elevated concentrations of this metal in the STEER. The elevated levels of TBT in the sediments in this same area, and lower levels of TBT in Mangrove Lagoon, support the possibility that the copper found in the sediments in the northern part of Benner Bay are related to the use of both copper and TBT in boat-related activities. A nonparametric correlation analysis between copper and TBT in the STEER also showed a significant positive correlation (Spearman $\rho=0.7078$, $p=0.0001$). For copper, inputs into Mangrove Lagoon from Turpentine Gut, runoff from residential areas, and inputs from the adjacent Bovoni Landfill could also be contributing sources.

Lead

The mean lead concentration was 5.87 ± 1.90 $\mu\text{g/g}$; the median was 0.82 $\mu\text{g/g}$ (Table 2). The highest concentration of lead in the sediments from the stratified random sampling was 31 $\mu\text{g/g}$ at 1-2P in Mangrove Lagoon. The highest concentration from the 2010 targeted sampling was 81.2 $\mu\text{g/g}$ at BB-2 in Benner Bay. The ERL for lead is 46.7 $\mu\text{g/g}$; the ERM is 218 $\mu\text{g/g}$. None of the 2011 stratified random sites had a concentration above the ERL. However, BB-2 (81.2 $\mu\text{g/g}$) from the 2010 targeted sampling had a lead concentration above

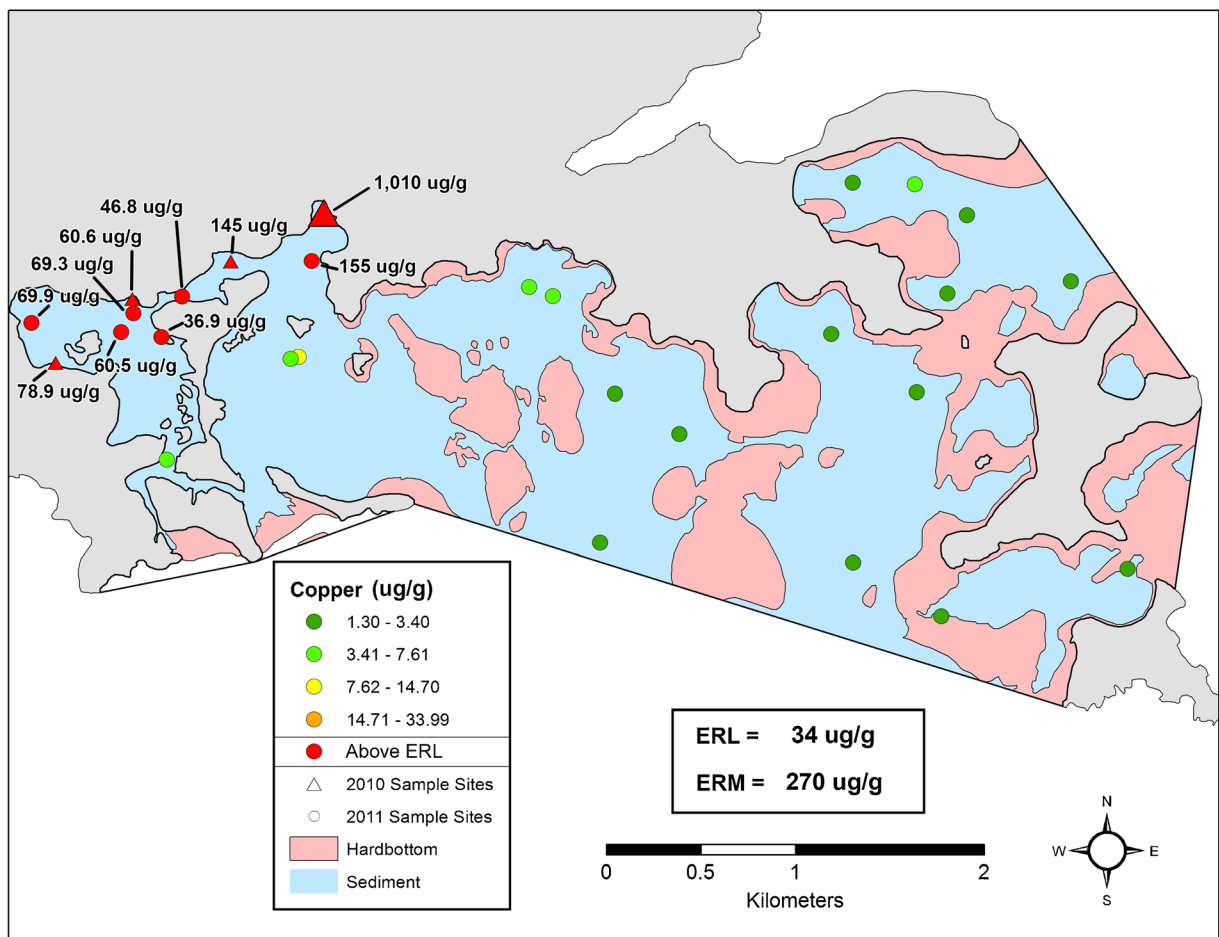


Fig. 4 Copper detected in STEER sediments

the ERL, but still well below the ERM of 218 $\mu\text{g/g}$. A Kruskal-Wallis test showed a significant ($p < 0.0001$) difference in the concentration of lead across the STEER, and a Tukey’s HSD test indicated that Mangrove Lagoon (stratum 1) was significantly higher than lead in Jersey Bay (stratum 3), St. James Bay (stratum 4), and Great Bay (stratum 5), similar to a number of the other contaminants assessed in this study. Table 3 also shows the mean lead concentrations by stratum.

In southwest Puerto Rico, Pait et al. (2008) detected a mean lead concentration of 1.93 $\mu\text{g/g}$, less than the mean found in the STEER. In Vieques, the mean lead concentration was 5.42 $\mu\text{g/g}$, close to that in the STEER. In Jobos Bay, the mean concentration of lead in the sediments sampled was 7 $\mu\text{g/g}$ (Apeti et al. 2012b), also similar to the STEER.

Mercury

The mean concentration of mercury from the stratified random sampling was $0.019 \pm 0.01 \mu\text{g/g}$; the median was 0.01 $\mu\text{g/g}$. The highest concentration of mercury from the stratified random sampling was in Mangrove Lagoon at site 1-1P (0.109 $\mu\text{g/g}$). From the 2010 targeted sampling, the highest concentration was at BB-2 (0.34 $\mu\text{g/g}$) in northern Benner Bay. As with a number of the other contaminants, higher concentrations of mercury were found in northern Benner Bay and Mangrove Lagoon. There was one exceedence of the ERL (0.150 $\mu\text{g/g}$) for mercury at BB-2 (0.34 $\mu\text{g/g}$) in northern Benner Bay, with a concentration twice as high as the ERL, but below the ERM (0.71 $\mu\text{g/g}$). A Kruskal-Wallis test run on the ranked mercury values indicated a

significant difference ($p < .0001$) between strata, and a Tukey's HSD test indicated that mercury in Mangrove Lagoon (stratum 1) and Benner Bay (stratum 2) was higher than in Jersey Bay (stratum 3), St. James Bay (stratum 4), and Great Bay (stratum 5).

The mean sediment concentration of mercury found in southwest Puerto Rico was $0.004 \mu\text{g/g}$ (Pait et al. 2008). In Vieques, Pait et al. (2010) found a mean mercury concentration of $0.019 \mu\text{g/g}$, the same as in the STEER. Apeti et al. (2012b) detected a mean concentration of $0.042 \mu\text{g/g}$ mercury in sediments from Jobos Bay, higher than was found in the STEER.

Zinc

The mean zinc concentration from the stratified random sampling was $37.3 \pm 10.7 \mu\text{g/g}$; the median was $11.1 \mu\text{g/g}$ (Table 2). The highest concentration of zinc from these collections was at site 1-2P, with $159 \mu\text{g/g}$. From the 2010 targeted sampling, the highest zinc concentration was $392 \mu\text{g/g}$ in Benner Bay (BB-2), followed by $192 \mu\text{g/g}$ in BB-1, also in Benner Bay. In Jobos Bay, Apeti et al. (2012b) found a mean zinc concentration of $54.7 \mu\text{g/g}$, somewhat higher than in the STEER. There were two sites (1-2P and 1-3P) from the stratified random sampling that exceeded the ERL ($0.150 \mu\text{g/g}$). From the 2010 targeted sampling, three of the four sites (BB-2, BB-1, and ML-2) analyzed exceeded the ERL. None of the sites exceeded the ERM; however, BB-2 ($392 \mu\text{g/g}$) from the 2010 targeted sampling was fairly close to the zinc ERM of $410 \mu\text{g/g}$. In the marine boating industry, zinc anodes are used to protect vital engine and boat parts (e.g., propellers, struts, rudders, outboard and inboard engines) and are a component in some antifoulant paint formulations. Zinc is also used in batteries and in alloys such as brass. The elevated levels of zinc in the sediments in northern Benner Bay could be indicative of boat-related use. A Kruskal-Wallis test indicated zinc varied significantly ($p = 0.0006$) by stratum, and the Tukey-Kramer HSD test indicated that Mangrove Lagoon (stratum 1) and Benner Bay (stratum 2) were significantly different (higher) than Great Bay (stratum 5). This can also be seen in Table 3.

In southwest Puerto Rico, Pait et al. (2008) detected a mean zinc concentration of $8 \mu\text{g/g}$, below the mean found in the STEER. In Vieques, Pait et al. (2010) calculated a mean zinc concentration of $34.4 \mu\text{g/g}$, similar to what was found in the STEER.

Normalization of trace elements

Concentrations of trace metals were normalized to aluminum to assess locations where unusually high concentrations of trace metals may indicate anthropogenic inputs, above that expected as background. From this analysis, copper, zinc, and mercury were found at a few selected sites at concentrations above that which would be predicted based upon background aluminum levels. All of these sites were in either Mangrove Lagoon or Benner Bay. It should also be noted that the concentrations of aluminum and iron were considerably higher in Mangrove Lagoon and Benner Bay than in the other strata, likely indicating that terrestrial sources of sediment are more dominant there than in the rest of the STEER.

Correlations between contaminants

A series of nonparametric correlations (Spearman's) were run between the various contaminants and classes and the sediment parameters. Organic contaminants including total PAHs, total PCBs, TEH, TBT, and total butyltins were correlated ($p \leq 0.05$) with one another. A number of the sediment samples from Mangrove Lagoon and northern Benner Bay had elevated concentrations of contaminants, indicating land uses in these areas are most likely associated with the input of these contaminants. In addition, the lower flushing of waters in and out of this part of the STEER, along with the smaller sediment grain sizes (i.e., silts and clays) that can trap contaminants, likely contributed to the elevated levels in these areas as well. The trace and major elements were significantly correlated with each other, indicating both anthropogenic and natural inputs.

Summary and conclusions

The degradation of coral reef ecosystems worldwide has led to intensive efforts to understand and mitigate the stressors responsible for their decline. The role of pollution is often cited as a major factor, but the degree to which pollution, and more specifically, chemical contaminants, impacts coral reef and associated habitats is largely unknown. Because of this, coral reef managers may be missing an important and, in some locations, critical piece of information to effectively manage and, where needed, initiate restoration efforts.

Elevated levels of chemical contaminants were primarily found in Mangrove Lagoon and in northern Benner Bay. There is a large active landfill adjacent to Mangrove Lagoon that likely contributes a variety of contaminants through runoff, groundwater seeps, and perhaps from atmospheric deposition (e.g., from tire/trash fires). Mangrove Lagoon also receives input from various commercial/industrial sources, as well as from adjacent residential/urbanized areas in the watershed via Turpentine Gut. Land use around northern Benner Bay appears dominated by marina/boatyard activities, which is also a likely a source of chemical contaminants to the STEER.

Tributyltin was found at high concentrations in sediments from three sites in the northern Benner Bay area (two from the targeted 2010 sampling). The level of TBT detected at one site in Benner Bay was the third highest quantified by NOAA's NS&T Program. The presence of high concentrations of TBT likely represents the results of past application of TBT, mooring of vessels that contain TBT, along with the cleaning and scraping of hulls that may have had TBT applied at some point. There are, however, no established guidelines for TBT in sediment.

Copper and zinc were elevated at several locations in Benner Bay and Mangrove Lagoon. Copper was above the NOAA ERM at one site from the 2010 targeted sampling, indicating that impacts to benthic organisms and within the broader food web are likely. This would also appear to be associated with marina activities, including the mooring of vessels, along with the cleaning and scraping of the hulls and subsequent transport of these materials into northern Benner Bay. The locations where the three highest copper concentrations were found were also the locations of the three highest TBT concentrations. Elevated copper concentrations in Mangrove Lagoon may also indicate inputs from surrounding land areas, a degree of transport from Benner Bay, or a combination of these and other processes. A number of other chemical contaminants analyzed for this project, including zinc, lead, copper, mercury, total PCBs, and total DDT, were above ERLs at one or more sites in the STEER, indicating that impacts may be occurring in some of the more sensitive species or life stages that may be present.

Anthropogenic stressors, concentrated in Benner Bay and Mangrove Lagoon, are most likely impacting the ecology of the STEER, including the health of juvenile and adult species, and perhaps the spawning of fish and

invertebrates. The information generated from this project is being used to highlight challenges to resource managers to protect and, where needed, restore this ecologically and economically important area.

Acknowledgments The authors wish to acknowledge the support from NOAA's Coral Reef Conservation Program (CRCP) for this project. We would also like to thank Jean-Pierre Oriol, Director of the Department of Planning and Natural Resources (DPNR) Division of Coastal Zone Management, Roy Pemberton, Director of DPNR Division of Fish and Wildlife, Jeanne Brown of The Nature Conservancy, Tyler Smith, Sandra Romano, Renata Platenberg, Kevin Brown, and Frank Galdo, Jr. of the University of the Virgin Islands (UVI), and Rob Ferguson and Marlon Hibbert of NOAA's CRCP for help with the planning, logistics, and fieldwork along with interpretation of results for this project. Sybille Sorrentino of Virgin Island Ecotours graciously provided a base of operations for our fieldwork. Finally, we would like to thank Captain Bobby Vante of the *Bright Star* for his skill and patience in getting us to the sampling sites within the St. Thomas East End Reserves.

References

- Apeti, D. A., Hartwell, S. I., Johnson, W. E., & Lauenstein, G. G. (2012a). *National Status and Trends Bioeffects Program: field methods* (p. 52). Silver Spring, MD: NOAA National Centers for Coastal Ocean Science, Center for Coastal Monitoring and Assessment. NOAA NCCOS Technical Memorandum 135.
- Apeti, D. A., Whittall, D. R., Pait, A. S., Dieppa, A., Zitello, A. G., & Lauenstein, G. G. (2012b). Characterization of land based sources of pollution in Jobos Bay, Puerto Rico: status of heavy metal concentration in bed sediments. *Environmental Monitoring and Assessment*, *184*, 811–830.
- Budzinski, H., Jones, I., Bellocq, J., PiCrard, C., & Garrigues, P. (1997). Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry*, *58*, 85–97.
- EPA (U.S. Environmental Protection Agency). 2011. Remediation system evaluation. Tutu Wellfield Superfund Site, St. Thomas, U.S. Virgin Islands. Office of Solid Waste and Emergency Response (5102G). Final Report. EPA-542-R-11-008. 37 pp.
- IRF (Island Resources Foundation). 1993. Mangrove Lagoon/Benner Bay area of particular concern (APC) and area for preservation and restoration (APR) management plan: a comprehensive analytic study. Prepared by Island Resources Foundation, St. Thomas, Virgin Islands, for USVI DPNR/CZM Program. 32 pp.
- Kimbrough, K. L., & Lauenstein, G. G. (Eds.). (2006). *Major and trace element analytical methods of the National Status and Trends Program: 2000–2006* (p. 19). Silver Spring, MD: NOAA Technical Memorandum NOS NCCOS 29.
- Kimbrough, K. L., Lauenstein, G. G., & Johnson, W. E. (Eds.). 2006. Organic contaminant analytical methods of the National Status and Trends Program: update 2000–2006. NOAA Technical Memorandum NOS NCCOS 30. 137pp.

- Libes, S. M. (1992). *An introduction to marine biogeochemistry*. New York, NY: Wiley. 734 pp.
- Long, E. R., MacDonald, D. D., Smith, S. L., & Calder, F. D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19, 81–97.
- Long, E. R., & Morgan, L. G. (1990). *The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program* (p. WA175). Seattle: NOAA Technical Memorandum NOS OMA 52.
- Oros, D. R., & Ross, J. R. M. (2004). Polycyclic aromatic hydrocarbons in San Francisco estuary sediments. *Marine Chemistry*, 86, 169–184.
- Pait, A. S., Whittall, D. R., Jeffrey, C. F. G., Caldow, C., Mason, A. L., Lauenstein, G. G., & Christensen, J. D. (2008). Chemical contamination in southwest Puerto Rico: an assessment of organic contaminants in nearshore sediments. *Marine Pollution Bulletin*, 56, 580–606.
- Pait, A. S., Mason, A. L., Whittall, D. R., Christensen, J. D., & Hartwell, S. I. (2010). Assessment of chemical contaminants in sediments and corals in Vieques. In Bauer and Kendall (Ed.), *An ecological characterization of the marine resources of Vieques, Puerto Rico part II: field studies of habitats, nutrients, contaminants, fish, and benthic communities* (p. 174). Silver Spring, MD: NOAA Technical Memorandum NOS NCCOS 110.
- Pait, A. S., Whittall, D. R., Dieppa, A., Newton, S. E., Brune, L., Caldow, C., Mason, A. L., Apeti, D. A., & Christensen, J. D. (2012). Characterization of organic chemical contaminants in sediments from Jobos Bay, Puerto Rico. *Environmental Monitoring and Assessment*, 184(8), 5065–5075.
- STEER. 2011. St. Thomas East End Reserves management plan. Edited by J. Brown, A. Holecek, J. Murray, L. Noori, J.P. Oriol, J. Pierce, R. Platenberg, S. Romano, D. Russo, & C. Settar. 99 pp.
- Strand, J., Jørgensen, A., & Tairova, Z. (2009). TBT pollution and effects in molluscs at US Virgin Islands, Caribbean Sea. *Environmental International*, 35, 707–711.
- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33, 489–515.