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An assessment of butyltins and metals in sediment cores from the St.Thomas East End Reserves, USVI

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Abstract

Tributyltin (TBT) concentrations near a marina complex in Benner Bay on St. Thomas US Virgin Islands were elevated relative to other areas in a larger study of the southeastern shore of the island. At the request of the USVI Coastal Zone Management Program sediment cores and surface sediment samples were collected to better define the extent and history of TBT deposition in the vicinity of Benner Bay. The sediment cores were sectioned into 2 cm intervals and dated with ^{210}Pb and ^{137}Cs. The core sections and the surface samples were analyzed for butyltins and 16 elements. Deposition rates varied from 0.07 -5.0 mm/yr, and were highest in the marina complex. Core ages ranged from 54 to 200 yrs. The bottoms of the cores contained shell hash, but the top layers all consisted of much finer material. Surface concentrations of TBT exceeded 2,000 ng Sn/g (dry weight) at two locations. At a depth of 8 cm TBT exceeded 8,800 ng Sn/g in the marina complex sediment. Based on the ratio of tributyltin to total butyltins, it appears the marina sediments are the source of contamination of the surrounding area. There is evidence that vessels from neighboring islands may also be a source of fresh TBT. Copper concentrations increase over time up to the present. Gradients of virtually all metals and metalloids extended away from the marina complex. NOAA sediment quality guidelines were exceeded for As, Pb, Cu, Zn and Hg.

Key words: Tributyltin; metals; sediment cores; contamination; US Virgin Islands

Introduction

The St. Thomas East End Reserves (STEER) is a collection of Marine Reserves and Wildlife Sanctuaries located on the southeastern end of the island of St. Thomas, U.S. Virgin Islands. As part of a larger study of the STEER (Pait et al. 2013; 2014) utilizing a Sediment Quality Triad approach, a series of sediment toxicity bioassays were conducted along with a characterization of the benthic infaunal community, and analyses of a broad suite of chemical contaminants. Higher levels of chemical contaminants were found in the western portions of the STEER than in the eastern parts. The benthic infaunal communities in the west appeared to be severely diminished. Bioassays indicated significant sediment toxicity in the western side using multiple tests. A variety of contaminants, including tributyltin (TBT) were identified at elevated concentrations in specific locations.

For 40 years TBT was used as a prime ingredient in anti-fouling paint applied to the hulls of boats and ocean going ships. By the mid-1960s it had become the most popular anti-fouling paint worldwide. Although the paints were effective, the TBT slowly leached out into the marine environment where it was highly toxic to a wide range of organisms.

The formulation of TBT paints changed over time from simple contact by surface leaching, to a polymer base through which the biocide discharge rate is regulated by reacting with water. TBT-based paints were extremely effective and long lasting. By the late 1970s TBT paints were commonly used on both commercial and recreational vessels.

Negative aspects of TBT were suspected in the late 1960s when it was recognized that the release of organotin into aquatic environments was impacting non-target organisms. Toxic

effects in some species occur at 1 ng per liter of water (Bray and Langston 2006). TBT is toxic to bacteria, fungi, algae, mollusks and crustaceans. There are implications of effects on cetaceans and bioaccumulation in the human food chain. A galvanizing event occurred in the late 1970s and early 1980s, when oyster crops in Arcachon Bay, France, failed. Subsequent research identified that TBT had caused decreased spatfall, unnatural shell thickening and abnormal structure that weakened the shells. Similar observations were seen in UK oyster stocks. Away from hull cleaning operations, TBT sediment concentrations were higher in harbors with many small boats than in industrial harbors with commercial ships (Bryan and Gibbs 1991; Page et al. 1996). In 1982, France banned TBT use on recreational vessels less than 25 m long. Subsequent work showed that TBT was an endocrine disruptor in marine gastropods causing masculinization (imposex) in females and widespread population decline. By the early 1990s, many nations had partial or complete bans on TBT. In 1999, the International Maritime Organization (IMO), came to agreement that TBT would be phased out between 2003 and 2008, with a total ban of organotin antifouling coatings by 1st January 2008. The U.S. ratified the agreement in 2012. Since the ban, copper-based paints have largely replaced TBT paints. However, while the agreement requires compliance from the developed nations, much of the developing world are not signatories. Also, TBT is still used as a slimicide in power plant cooling towers and other industrial heat exchange equipment, as a wood preservative, and a molluscicide to prevent Schistosomiasis. It was reportedly still available in bottom paint as recently as 2014 in the Caribbean and Central America through U.S. outlets (Turner and Glegg 2014).

TBT is a persistent and bioaccumulative compound. Degradation pathways proceed from tributyltin to dibutly-, to monobutyl-, and finally to elemental tin. The reported half-life in estuarine waters range from days to weeks (Omae 2005). TBT is strongly sorbed to sediment however. Also, paint chips from boat hulls that ultimately are flushed into a water body, serve as a reservoir for release into the sediment. The half-life of TBT in sediments is years, and in anaerobic sediments extends into decades (Matthiessen 2013). Thus, high concentrations may persist in older buried sediments where uncontrolled releases have occurred in the past. This material may or may not become bioavailable depending on local sediment deposition rates and subsequent disturbance (e.g. dredging).

In 2013 we undertook a study to assess the distribution of TBT and other heavy metal residues in sediments in the STEER in more detail at the request of the USVI Coastal Zone Management Program. In addition, sediment cores were taken in selected locations based on previous sampling in the area (Pait et al. 2013, 2014) to assess the record of TBT concentrations over time. This information will help inform management decisions and strategies for maintenance/restoration projects.

Methods

Benner Bay is in the central portion of the STEER (Figure 1) The north shore of Benner Bay contains extensive marina facilities for recreational boats, and is adjacent to a channel leading to Mangrove Lagoon. The channel has mooring lines for boats to shelter from hurricanes and is also the site of many anchored and derelict boats. Surficial sediment samples were collected at six locations in Benner Bay leading away from the main marina facility on two transects, one through an offshore boat anchoring area (S1-3) and one out the approach channel (S4-6) (Figure

1). Sediment core samples were collected at four locations starting from the marina complex toward the southwest down the channel leading to Mangrove Lagoon (Figure 1). The history of TBT contamination along this gradient would shed light on whether the marinas are the source of TBT or if there are other potential sources. A seventh surface sample was taken at one core location (BB2) as a check on gear bias.

Sediments were collected using standard NOAA National Status and Trends (NS&T) protocols including quality assurance/quality control (QA/QC) (Apeti et al. 2012). A single PONAR grab (0.04 m^2) was deployed by hand to collect the surface samples. The top 3 cm of sediment were collected from the grab using a stainless steel sediment scoop. Only surface sediment was used for chemical analyses to assess current depositional conditions.

Sediments were placed into certified clean (I-Chem®) 250 ml labeled jars, capped and then kept on ice in a cooler. Sediments for grain size analysis were placed in a WhirlPack® bag and sealed. At the end of each day, sediment samples for contaminant analysis were frozen.
The corer was a standard design (Aquatic Research Instruments) for collection of undisturbed cores of the sediment and mud-water interface. The corer drove a seven cm diameter polycarbonate tube into the sediment with a hand-held weight. A one way check valve seated in the core head allowed water and sediment to move through the core barrel. During retrieval the check valve automatically seats, creating a partial vacuum and retains the sample in the core barrel. The core was capped and returned to the dock where it was extruded in 2 cm sections by means of a plunger provided with the corer. Each section was placed into a certified clean (I-Chem®) 250 ml labeled jar and homogenized. A sub-sample was removed for grain size

126 analysis. Sediments for grain size analysis were placed in a WhirlPack® bag, sealed and then
127 kept refrigerated. Sediment samples for elemental and TBT analyses were frozen.
128
129 The surface sediments and core sections were analyzed for a suite of 16 major and trace
130 elements, grain size and butyltin compounds (mono-, di-, tri- , and tetra- butyl tin). Tetrabutyltin
131 is only present at trace levels, left over from the manufacturing process. The major and trace
132 elements were analyzed using inductively coupled plasma mass spectrometry and atomic-
133 fluorescence spectroscopy. Detailed descriptions of the NS&T protocols, including quality
134 assurance/quality control (QA/QC) used in the analysis can be found in Kimbrough and
135 Lauenstein (2006). The butyltins were analyzed using gas chromatography/flame photometric
136 detection after derivatization with hexyl-MgBr.
137
138 Subsamples of the core sections were also analyzed for ^{210}Pb and ^{137}Cs activity to estimate the
139 age and deposition rates of the sediments down the core length. ^{210}Pb measurements were
140 carried out via analysis of its short-term daughter product ^{210}Po, measured by alpha spectroscopy
141 (Palinkas and Nittrouer 2007). Age models were fit to the data, as appropriate, to determine
142 sediment accumulation rates (Appleby and Oldfield 1978; Carroll and Lerche 2003; Hancock et
143 al. 2000). ^{137}Cs measurements are used as a check on calculated age profiles by providing date
144 "markers". ^{137}Cs resulted from atomic bomb testing. The first appearance of ^{137}Cs in sediments
145 marks the year 1954, which is the year when global concentrations generally achieved detectable
146 levels. The other ^{137}Cs marker is the concentration maximum in the year 1963, after which
147 atmospheric testing ceased. ^{137}Cs measurements were performed using gamma spectroscopy.
148 Dry, ground sediment from each sampling interval (~3-5 g) was sealed in 60-mL plastic jars. The

gamma emissions from each sample was counted for approximately 24 hours using a calibrated Canberra germanium detector, using the 661 KeV photopeak of the gamma spectrum. Sediment accumulation rates were calculated from both the depth of first appearance and maximum activity.

Core depths varied and were limited by the depth of dense and/or shell hash layers which was the depth of refusal for the corer (Figure 2). Cores from 16P, BB1, and B3 were 16, 20 and 16 cm deep, respectively. Two cores were taken at BB2. The first core was 28 cm deep, but the core above 18 cm was disturbed by air bubbles during handling. A second core sample was taken but was only 14 cm deep so there is a break in the data. There was only enough material to do butyltins and the radiochemical analyses on the 18-20 cm section.

Results and discussion

Butyltin concentrations for the surface samples and the top 2 cm layer of the cores are shown in Table 1. The concentration of total butyltins at BB2 (and S7) was orders of magnitude above all other stations. There is a clear gradient of butyltins from BB2 out into Benner Bay and down the channel toward Mangrove Lagoon. Differences between BB2 and S7 values are within analytical variability of the method, indicating no gear bias.

Plots of ^{210}Pb and ^{137}Cs activities with depth are shown for each core in Figure 3. The age of each layer of the cores as calculated by the ^{210}Pb and ^{137}Cs methods are shown in Table 2. The sections representing 1963 (upper) and 1954 (lower) are highlighted. These represent 50 and 59 years before 2013 respectively. The average ages determined by the ^{137}Cs method appear to more closely reflect years before present (YBP). Years at 16P, BB1 and BB2 are over

172 estimated while B3 is underestimated by the ^{210}Pb method. It is unclear which ^{137}Cs
173 accumulation rate to use at BB2 so the most recent marker (1963) was used.
174
175 Core 16P shows the best profile of all the cores , showing the characteristic shape of logarithmic
176 ^{210}Pb decay with depth until the background activity (0.1 disintegrations per minute {dpm}/g) is
177 reached (Figure 3). For ^{137}Cs, the depth of first appearance (1954) is 6-8 cm; the depth of
178 maximum activity (1963) is 4-6 cm. The accumulation rate calculated from the ^{210}Pb data is 0.73
179 mm/yr. Calculated accumulation rates based on the ^{137}Cs data are 1.0-1.4 mm/y and 0.8-1.2
180 mm/y, respectively. The ^{137}Cs rates are slightly higher than from the ^{210}Pb data, indicating
181 somewhat younger sediment at depth. This becomes more obvious when the TBT data is plotted
182 vs YBP (years before present).
183
184 The accumulation rate in core BB1 calculated from the ^{210}Pb data is 0.6 mm/y. For ^{137}Cs, the
185 depth of first appearance (1954) is 6-8 cm, yielding an accumulation rate of 1.0-1.4 mm/y. The
186 depth of maximum ^{137}Cs activity (1963) is 2-4 cm, yielding an accumulation rate of 0.4-0.8
187 mm/y.
188
189 The ^{210}Pb data for core B3 are subject to interpretation. The core was not long enough to reach
190 the background ^{210}Pb concentration, so the background activity was assumed to be equal to that
191 used for 16P and BB1 (0.1 dpm/g). The background concentration within a small region should
192 be the same. Also, there is some question as to whether all data points reflect sedimentation, and
193 thus should be used in the rate calculation, or whether the upper 4 data points reflect mixing and
194 should be neglected in the rate calculation. The accumulation rates are 3.2 mm/y (all data) or 1.6

mm/y (only the lower 4 data points). For ^{137}Cs data, the depth of first appearance (1954) is 8-10 cm, yielding an accumulation rate of 1.4-1.7 mm/y. This is in agreement with the ^{210} Pb rate from the lower four points. There are two depths, above and below the 6-8 cm interval, with identically high activities that could be considered the depth of maximum ^{137}Cs activity (1963). The first, at the top of the higher-activity layer, is 4-6 cm and yields an accumulation rate of 0.8-1.2 mm/y. One could also assume a typical profile shape and assume that the sediment in the 6-8 cm interval has anomalously low activities. If 6-8 cm is used as the depth of maximum activity, the accumulation rate would be 1.2 mm -1.6 mm/y. However, the anomaly in the ^{210}Pb data occurs at the 6-8 cm depth interval, so it may be an event-related disturbance of the sediment layer is responsible. Station B3 is in the center of the channel leading into the marina facilities. In depositional environments sediments are continually laid down and compacted by overlying sediment. In a continuous sequence, the age of the sediment can be estimated and the history of chemical contamination can be recreated. Bioturbation by burrowing organisms will tend to mix the surface layers as they accumulate and may blur the history. Also, powerful storms, like hurricanes, may scour out whole sections, or, conversely bury layers with large deposits from runoff or resuspension. Human activities such as dredging and spoil disposal may cause breaks in the historical record. Activities on land that alter sediment delivery from runoff may increase or decrease the rate of sedimentation over time. Given the anomalies, it is likely that the calculated ages for the deeper sediment sections are underestimated.

The ^{210}Pb profile for core BB2 is also subject to interpretation because of the break in the data set. Accumulation rates were calculated both using all points, and the lower points. Accumulation rates are 3.5mm/y for all data points and 1.2 mm/y for only the lower points. A

218 background value of 0.1 dpm/g was used, consistent with cores 16P and BB1, since the core does
219 not appear to be long enough for ^{210}Pb activities to have reached background activities. There is
220 an anomaly at the 6-8 cm depth interval, which may be an event-related disturbance of the
221 sediment layer similar to core B3. Station BB2 was in the heart of the marina facilities, adjacent
222 to the boat ramp and travel lift.
223
224 Samples down to 12 cm had no detectable ^{137}Cs. The remaining samples were counted with
225 detections in the 20-22 cm and 22-24 cm intervals. However, these detections occurred at the
226 659 keV photopeak (part of gamma spectrum); the photopeak that represents ^{137}Cs is 662 keV. In
227 practice, a deviation of ± of ~2 keV is accepted when evaluating gamma spectra, using
228 information about sample and site to guide decisions. Thus, the 20-22 and 22-24 sections are
229 considered borderline; they would likely be recorded as detectable ^{137}Cs, unless more evidence
230 suggested otherwise. It is difficult to determine whether these detections represent the depth of
231 first appearance or maximum activity. Using the point as a first occurrence (1954) yields an
232 accumulation rate of 4.23 mm/yr. Using the point as a maximum (1963) occurrence yields an
233 accumulation rate of 5.0 mm/yr.
234
235
236 The characteristics of the sediment have changed dramatically over the years in some core
237 locations. Figure 4 shows the proportion of fine grained (silt + clay) and gravel-sized (>4 mm)
238 particles in the cores over time. All the cores show a much higher percentage of gravel-sized
239 material at the bottom of the cores than the top. These particles were not gravel, but were in fact
240 shell hash (Figure 2). The shift toward fine-grained material is most dramatic at BB2. Station

BB2 is surrounded by bulkheads and sits beneath constant boat activity. It is next to the main marina ramp. While BB2 was the deepest core, it covers the shortest time span due to the much higher accumulation rate (Table 2). Recall that there were anomalies in the cores from BB2 and B3 and that the calculated accumulation rates in the lower half of the cores was much lower than in the top half. A much lower accumulation rate in the deeper, older, layers at BB2 is logical as recent human activity has clearly drastically altered the bottom sediment characteristics. Note also that the most dramatic shifts have occurred in the last 50-75 years.

Reviews done in the 1980s to evaluate the potential outcomes of declaring the STEER a NOAA National Marine Sanctuary noted that Mangrove Lagoon and Benner Bay were dominated by turtle grass beds in the 1960s, but in the 1970s the bottom was becoming mud, and was converting to a calcareous macroalgae-dominated benthic community (NOAA, 1981). Extensive shoreline development, increasing boating activity, pollution from terrestrial runoff and sewage discharges were all impacting Benner Bay water quality by the early 1970s (Grigg et al., 1971). The watersheds immediately adjacent to Benner Bay that drain into it are the Nadir and Compass Pt. subwatersheds. More recent assessments describe the Nadir shoreline and watershed as being “a highly dense chain of marinas and commercial properties that transitions to single family residential area moving uphill”, and Compass Pt. includes “a residential area that extends from the top of the subwatershed down to Benner Bay; the main gut flows behind single family homes on the hillside, then under or on the road through the marina complex” (Horsley Witten Group, 2013).

The concentrations of total butyl tins are shown in Figure 5. The peak concentrations occur at less than 50 years ago, which is consistent with historical use patterns. There are low concentrations of butyltins in sections below 50 years ago which may reflect the initial buildup of TBT contamination and/or an indication of how deep sediments are churned by storms and bioturbation. Butyltin concentrations are vastly higher at BB2 which also shows a peak in the past, albeit more recently than in the other cores. The break in the data unfortunately occurs where the use of TBT was initiated so it is impossible to conclude if concentrations were even higher in the past, or if TBT use continued into more recent years. Concentrations have declined in recent years. Nevertheless, the observed concentrations at depth are vastly higher than anywhere else in Benner Bay or the rest of the STEER.

Concentrations of this magnitude have only been observed in a few places (Page et al. 1996, 24-12,400 ng/g - Maine , USA; Shim et al. 2002, 33-19,780 ng/g – S. Korea; Diaz et al. 2002, 123-6,692 and 574-1,970 – NE and SE Spain; EVS, 1999, 8-6,200 - Seattle, USA. All of these studies were sampling in marinas and/or ship yards for the purpose of locating hot spots. Our data is reported as ng/g of tin, as opposed to TBT which has a 60% higher molecular weight than elemental tin. Of 1,506 data points in the NS&T data base with TBT sediment analyses, the median total butyltin value is 0.95 ng Sn/g (dry weight), the average is 8.9 ng Sn/g. The highest value is 990 ng Sn/g from Elliott Bay, a Superfund site in Puget Sound sampled in 1989.

There was relatively little butyltin in the B3 core. Neither is there evidence of large historical changes over the years. Relative to the ^{137}Cs date markers, the ^{210}Pb analyses severely underestimated the age of the B3 sediments unlike the other cores (Table 2). There are obvious

discontinuities in both the ^{137}Cs and ^{210}Pb records (Figure 5). It's location is in the middle of the channel leading into inner Benner Bay. What events or processes (e.g. storms, dredging, etc.) may have contributed to the history of deposition at this location is unknown. The concentrations of the major soil elements of aluminum, iron, and silicon all show a major shift at B3 in the mid-1940s (Figure 6), which coincides with the discontinuity in the ^{210}Pb and ^{137}Cs anomalies (Figure 3). Interestingly, the same is true for all the trace metals as well (not shown). Clearly, some event or change in circulation or terrestrial input occurred then.

Another puzzling aspect is the percentage of tributyltin as a proportion of total butyltins in the sediment. While the concentration of butyltins is decreasing over time, the proportion of tributyltin is increasing at 16P, BB1 and B3 up to the present, indicating continuing fresh inputs (Figure 7). The peak concentrations at BB2 in the marina are only 4-10 cm deep. The proportion of tributyltin at those depths is 50-70%. Prop wash from boats and storm-driven tidal currents may be the source of fresh tributyltin at the outer stations. Unlike BB2, the proportions below 10 cm depth in the cores at 16P, BB1 and B3 are meaningless as the concentrations are essentially zero and they date back to before TBT existed. Station 16P was located behind a mangrove island in the middle of the waterway between Benner Bay and Mangrove lagoon (Figure 1). There are moored boats, but no marina facilities in the immediate vicinity, so the TBT load there is likely drifting in from other areas. The currents in the waterway are highly variable and dependent on tidal flux and wind driven currents. The last tropical storm to hit St. Thomas was Irene in 2011, which passed just south of the island with sustained gale force winds and heavy rain.

Chemical results from the top sections in the cores and the surface sediment grabs illustrate consistent gradients away from inner Benner Bay for almost all constituents. Elemental concentrations for the surface samples and the top layer of the cores are shown in Tables 3 and 4. With three exceptions (Se, Sb, Si) the highest metals concentrations are all found at BB2. The concentration of Cu was orders of magnitude higher at station BB2 than all other stations. Copper concentrations exceeded the NOAA sediment quality guideline ERM (effects range median) (Long et al. 1995) by 5X at BB2. Zinc also exceeded the ERM at BB2. Mercury was an order of magnitude higher at BB2 than all other stations except S1. Arsenic, Pb, Hg, and Zn exceeded the ERL at multiple stations. Aluminum, silicon, and iron are the most common elements in the earths' crust. Decreasing gradients of these element leading away from Benner Bay all indicate a greater contribution of land-based sediment material close to the shoreline, as opposed to marine sources. Metals concentrations were higher in general at the stations located closest to shore and declined further out into Benner Bay. The pattern of calcium decreasing from offshore toward Benner Bay and Mangrove Lagoon locations in the 2011 data are consistent with this interpretation (Pait et al. 2013). All of these observations, plus the historical patterns revealed in the cores indicate a disturbed habitat that is heavily and increasingly impacted by land-based sediment input and chemical contamination from boating related activities.

The gradient of butyltins in the surface from BB2 out into Benner Bay and down the channel toward Mangrove Lagoon clearly illustrate the impact of boating related activities (Table 1). Surface concentrations in the marina complex are one to two orders of magnitude higher than anywhere else. Butyltins at S1 leading out of the harbor were higher than at core B3 and those

stations further out. Stations 2-6 were laid out on two transects leading away from core B3 on different routes. Concentrations of TBT drop off rapidly further out. The one exception was station S6 that had a total butyltins concentration of 231 ug Sn/g. Station S6 was taken on the edge of the channel leading out to open waters. The spike in concentration at that point, was almost as high as seen at S1. Notably, the percentage of tributyltin (relative to total butyltins) at that site was 93.7%, indicating fresh contamination. This strongly suggests a recent spill or perhaps grounding of a freshly painted vessel. It is unclear why butyltins are elevated at 16P and BB1, unless there are other sources in the area as well.

There is also a strong gradient of copper leading away from the marina complex (Table 4). Copper-based bottom paints were used before the advent of TBT, which themselves contained copper, and copper-based paints have replaced the TBT paints. Note also, that copper at Station S6 is not elevated, in contrast to TBT. The concentration of copper in the cores show a clear increase in concentrations over time at all locations (Figure 8), including at B3. Copper concentrations exceeded the ERL at all surface stations.

Conclusions

The inner reaches of northern Benner Bay are severely degraded by marina operations, shoreline development and watershed changes. Sediment dynamics and sediment quality are, and have been for decades, heavily impacted. The benthic community was once a thriving ecosystem as evidenced by the remnants of shelled species, that, at the bottom of some cores exceeded the volume of sediment present. That community has vanished and was smothered by very fine sediment that accumulates at rates an order of magnitude above normal rates. There are no

355 previous reports prior to Pait et al. (2013) on the condition of the benthic community in these
356 areas. The only evidence that exists is what can be inferred from the cores. The sediment within
357 the marina complex is unlike anything found anywhere else in the STEER.
358
359 The sediment is highly contaminated with butyltin paint residues, copper, and other metals. The
360 sediment is contaminated below the surface as well. Dredging new or deeper channels will
361 spread these contaminants over a wide area. Dredging for remediation purposes is advisable, but
362 will be expensive to do with methods that will properly prevent dredge spoil release to the water
363 column. Otherwise, the benthic community will likely never recover and environmental damage
364 will expand as contaminants are diffused over an even increasing area. Matthissen (2013)
365 reported that benthic communities do not recover from TBT contamination until the
366 concentration of butyltins is reduced to 10-40 ng/g. The concentration of butyltins at a depth of
367 6-8 cm was 8,871 ng Sn/g at station BB2.
368
369 The system may be receiving fresh inputs of TBT as evidenced by the percentage of tributyltin
370 residues at station S6. The system is dynamic. Between sampling in 2011 and 2013, the
371 concentration of TBT had more than doubled at station BB2. Copper had increased by 50%.
372 What event(s) may have caused such large changes in such a short time are unknown.
373 Hurricanes, as well as vessel groundings, prop wash, and pile driving are all likely activities
374 present at a marina that would stir up the bottom, and bring up contaminants from deeper in the
375 sediment column.
376
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Fig 1 Map showing the north shoreline of Benner Bay. Sediment cores were collected at locations marked with pins, surface sediment samples were collected at locations marked with circles. Inset shows location on St Thomas Island

Fig 2 Photograph of a core from Benner Bay illustrating the change in texture from shell hash to fine grained sediment over time

Fig 3 Plots of ^{210}Pb and ^{137}Cs activities with depth for core (a) 16P, (b) core BB1, (c) core B3, and (d) core BB2

Fig 4 Proportion of fine grained (silt + clay) and gravel-sized particles in the cores over time

Fig 5 Concentration (ng Sn/g) of total butyltins as a function of time

Fig 6 Changes in major element concentrations over time at station B3

Fig 7 Percent tributyltin as a proportion of the total butyltins as a function of time and core depth

Fig 8 Copper concentrations as a function of time

Table 1. Concentrations of butyltins and metals in surface samples of sediments and the top layer of the cores

Table 2. Estimated ages of sections within sediment cores from the STEER and the calculated accumulation rates. Sections indicating markers for the years 1954 and 1963 are highlighted. The accumulation rates for the ^{137}Cs method are the average of the 1954 and 1963 values, except the BB2 core.

Table 3. Major element concentrations (ppm) in surface sediments from Benner Bay, St Thomas USVI.

Table 4. Trace element concentrations (ppm) in surface sediments from Benner Bay, St Thomas USVI, and NOAA sediment quality guidelines (ERM, ERL).

Table 1 Concentrations of butyltins (in nanogram of Sn per gram of dry weight) in sediments from Benner Bay, St Thomas USVI

Site	Monobutyltin	Dibutyltin	Tributyltin	Tot BT	%Tri BT
16P	6.61	10.43	66.4	83.5	79.6
B3	13.3	11.2	12.4	36.9	33.6
BB1	12.6	28.2	40.0	80.8	49.5
BB2	940	700	1102	2741.2	40.2
S7	692	592	993	2277.4	43.6
S1	72.6	68.7	134	275.0	48.6
S2	25.7	9.74	12.2	47.6	25.6
S3	7.61	3.93	4.01	15.6	25.8
S4	6.25	5.07	6.24	17.6	35.5
S5	11.2	8.29	5.57	25.0	22.2
S6	8.33	6.21	217	231.3	93.7

Proportion of tributyltin to total butyltin (Tot BT) is also shown

Table 2 Estimated ages of sections within sediment cores from the STEER and the calculated accumulation rates

Mean Core Depth cm	16P		BB1		B3		BB2		
	^{210}Pb age	^{137}Cs age	^{210}Pb age	^{137}Cs age	^{210}Pb age	^{137}Cs age	^{210}Pb age	^{137}Cs age 1954	^{137}Cs age 1963
1	13.7	9.1	16.7	11.1	3.1	6.7	2.9	2.4	2.0
3	41.1	27.3	50.0	33.3	9.4	20.0	8.7	7.1	6.0
5	68.5	45.5	83.3	55.6	15.6	33.3	14.5	11.8	10.0
7	95.9	63.6	116.7	77.8	21.9	46.7	20.3	16.5	14.0
9	123.3	81.8	150.0	100.0	28.1	60.0	26.1	21.3	18.0
11	150.7	100.0	183.3	122.2	34.4	73.3	31.9	26.0	22.0
13	178.1	118.2	216.7	144.4	40.6	86.7	37.7	30.7	26.0
15	205.5	136.4	250.0	166.7	46.9	100.0			
17			283.3	188.9					
19			316.7	211.1			55.1	44.9	38.0
21							60.9	49.6	42.0
23							66.7	54.4	46.0
25							72.5	59.1	50.0
27							78.3	63.8	54.0
Rate mm/yr	0.73	1.10	0.60	0.90	3.20	1.50	3.45	4.23	5.0

Sections indicating markers for the years 1954 and 1963 are highlighted. The accumulation rates for the ^{137}Cs method are the average of the 1954 and 1963 values, except the BB2 core

Table 3 Major element concentrations (ppm) in surface sediments from Benner Bay, St Thomas USVI

Site	Al	Fe	Si
16P	38,600	23,200	140,000
B3	21,400	11,700	57,000
BB1	48,900	27,000	222,000
BB2	64,700	36,200	141,000
S1	29,500	17,100	62,600
S2	26,500	15,000	76,400
S3	7660	4760	22,700
S4	13,300	7810	32,600
S5	12,400	6840	29,800
S6	9450	6210	26,200

Table 4 Trace element concentrations (ppm) in surface sediments from Benner Bay, St Thomas USVI, and NOAA sediment quality guidelines (ERM, ERL)

Site	Ag	As	Cd	Pb	Sb	Sn	Cr	Cu	Mn	Ni	Zn	Se	Hg
16P	0.00	11.00	0.16	15.7	0.46	1.99	16.8	92.9	176.0	5.28	118.0	0.75	0.061
B3	0.00	10.00	0.09	17.4	0.22	1.76	10.3	97.4	94.1	3.12	92.9	0.34	0.050
BB1	0.00	9.64	0.23	25.4	1.00	3.32	19.7	88.7	200.0	5.09	145.0	0.61	0.096
BB2	0.27	16.40	0.28	129.0	0.73	22.20	61.5	1520.0	225.0	8.86	574.0	0.52	0.410
S1	0.08	9.67	0.08	119.0	1.49	5.25	18.9	373.0	115.0	4.40	206.0	0.24	0.126
S2	0.00	6.96	0.08	24.1	0.19	3.06	15.9	115.0	124.0	3.32	104.0	0.24	0.083
S3	0.00	3.44	0.07	7.8	0.10	0.82	2.5	51.7	38.9	2.59	47.5	0.00	0.030
S4	0.00	5.08	0.07	10.2	0.13	1.21	6.1	50.6	61.7	3.01	52.7	0.24	0.032
S5	0.00	3.96	0.00	15.9	0.12	1.20	5.1	54.8	55.3	2.57	49.4	0.15	0.033
S6	0.00	4.46	0.07	7.5	0.09	0.90	4.4	41.6	49.30	2.37	45.4	0.09	0.03
ERM	3.7	70.0	9.6	218.0			370	270		51.6	410		0.71
ERL	1.0	8.2	1.2	46.7			81	34		20.9	150		0.15

Fig. 1 Map showing the north shoreline of Benner Bay. Sediment cores were collected at locations marked with circles, surface sediment samples were collected at locations marked with squares. Inset shows location on St Thomas Island

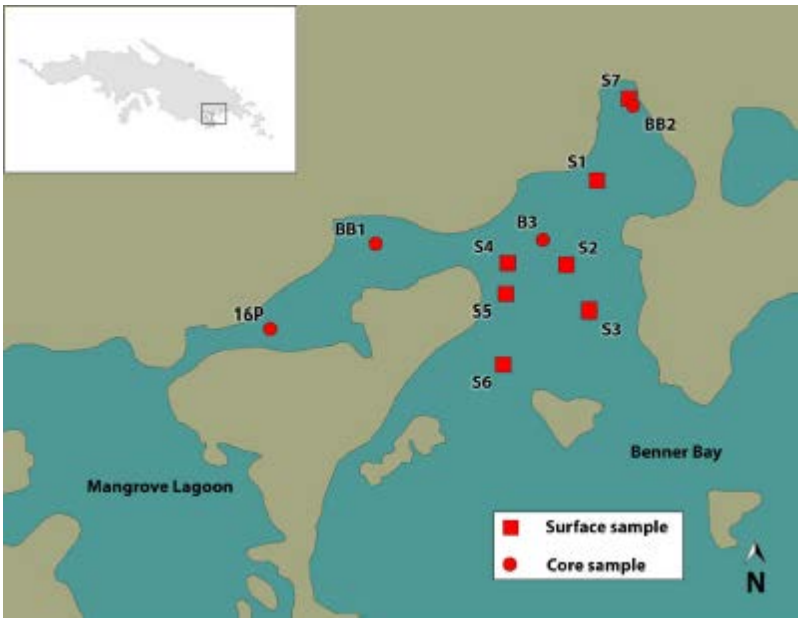

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Fig. 3 Plots of 210Pb and 137Cs activities with depth for core a 16P, b core BB1, c core B3, and d core BB2

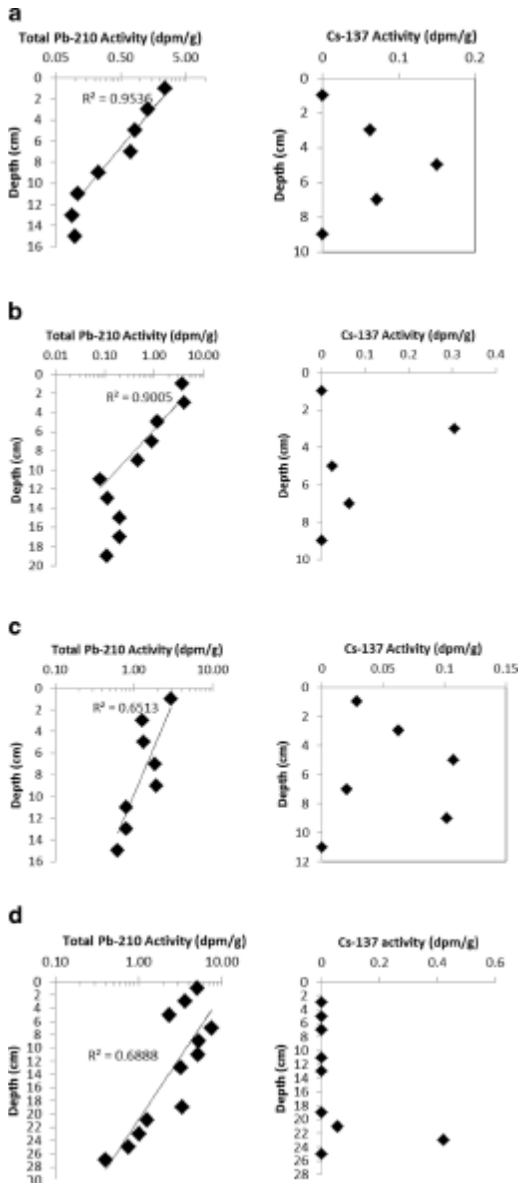

Fig. 4 Proportion of fine-grained (silt + clay) and gravel-sized particles in the cores over time

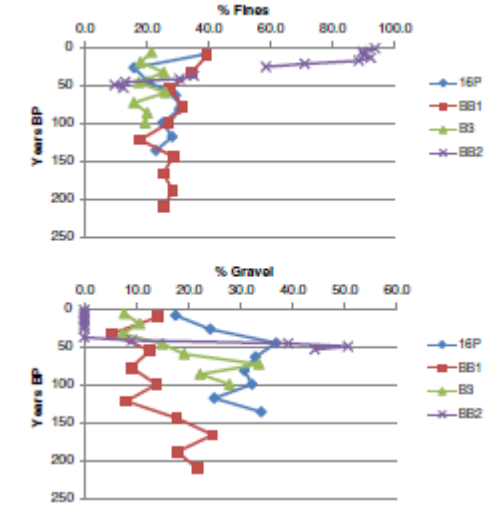

Fig. 5 Concentration (in nanogram of Sn per gram) of total butyltins as a function of time

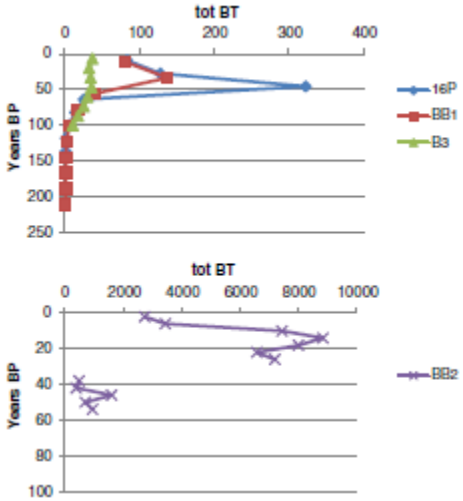

Fig. 6 Changes in major element concentrations over time at station B3

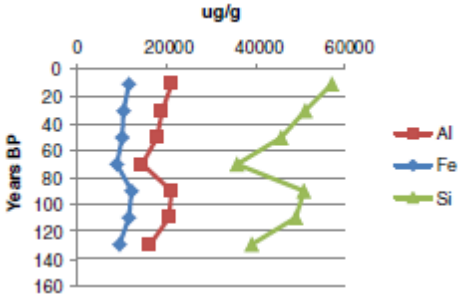

Fig. 7 Percent tributyltin as a proportion of the total butyltins as a function of time and core depth

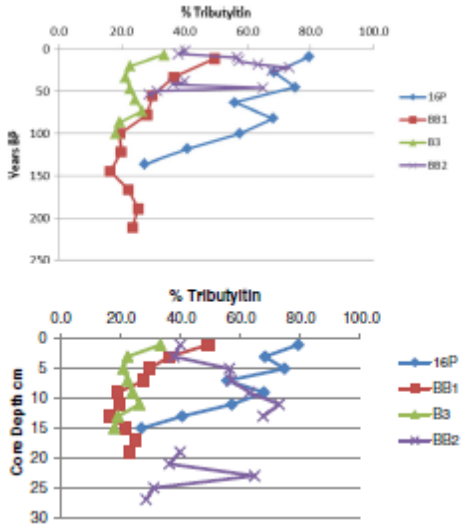

Fig. 8 Copper concentrations as a function of time