Source Determination of Benzotriazoles in Sediment Cores from Two Urban Estuaries on the
Atlantic Coast of the United States

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Abstract

Benzotriazoles (BZTs) are used in a broad range of commercial and industrial products, particularly as metal corrosion inhibitors and as ultraviolet (UV) light stabilizer additives in plastics and polymers. In this study, dated sediment cores from two east coast estuaries were analyzed for commonly used BZTs. In Narragansett Bay, UV stabilizing BZTs (UV-BZTs) were present at high levels from 1961 on, reflecting their patent date, local production and long-term preservation in sediment. In Salem Sound, UV-BZTs were present at concentrations consistent with other coastal marine locations not influenced by BZT production. Anticorrosive BZTs (AC-BZTs) were found in both cores, with the highest levels reported to date present in Narragansett Bay, indicating sorption to, and preservation in, sediments. This study revealed both classes of BZTs have remained structurally intact over time in coastal sediment cores, demonstrating their resistance to degradation and persistence in environmental compartments.

Key words: Emerging contaminant, benzotriazole, UV stabilizer, sediment core, corrosion inhibitor, persistent chemical

Introduction

The long-term global production of chemicals has resulted in the release and accumulation of many compounds in the environment. The fate and effects of many legacy pollutants such as PCBs and chlorinated pesticides have been studied extensively and are relatively well understood (e.g., NRC 2001). Conversely, many other contaminants whose potential risks are not known and are not regulated have been designated as chemicals of emerging concern (Daughton, 2004). Benzotriazoles (BZTs) are a class of chemical that has been in high volume production and use for more than five decades, yet information about their environmental behavior, distribution and long-term fate is limited (Davis et al., 1977). Currently, most BZTs in production are used as product additives for either ultraviolet stabilization or anticorrosive protection (Cantwell et al., 2015).

The majority of BZTs are used as ultraviolet stabilizing additives (UV-BZTs) in plastics, films, polymers, synthetic coatings and paints (Zhang et al., 2011). The UV-BZT stabilizers have a hydrogen on the triazole's 2-H position and, without exception, have a phenol ring attached (Figure 1a). These molecules often contain multiple functional groups based on the intended end use. Because of their insolubility in water and relatively high octanol-water partition coefficients (K_{OW}) (Table 1), some of these UV-BZTs may exhibit behaviors characteristic of legacy persistent organic pollutants (POPs), with some evidence of preservation and persistence in sediments (Reddy et al., 2000). For example, the Environmental Ministry of Japan has identified several UV-BZTs as POPs (e.g., UV-320) or potential POPs (e.g., UV-327), banning or limiting their production or usage in that country (Nakata et al., 2009).

Conversely, the anticorrosive benzotriazoles (AC-BZTs), used for metal protection, are fewer, less structurally complex and lower in molecular weight than the UV-BZTs (Davis et al., 1977).

The corrosion inhibiting AC-BZTs (Figure 1b) have a hydrogen located in the 1-H position on the triazole moiety and may contain other functionalities, such as CH₃ or Cl, in one or more positions on the molecule. They were patented in the 1950s for the prevention of discoloration of metal surfaces (Shaefer, 1952), and then, subsequently, for use as corrosion inhibitors in heat transfer fluids (Meighen, 1957) and lubricants (Donaldson et al., 1965; Malec, 1975). They also have been used extensively as corrosion inhibitors in aircraft deicing fluids (Chan et al., 1995) and machine dishwashing detergents (Christie et al., 1997). These uses have resulted in the release of large quantities of AC-BZTs to surface and ground waters (Novak et al., 2000; Breedveld et al., 2002). In particular, their use as a detergent additive results in sustained input to domestic waste water treatment plant (WWTP) streams (Kolpin et al., 2002; Voutsas et al., 2006; Loos et al., 2009; Reemtsma et al., 2010; Vetter and Lorenz, 2013). Due to their high aqueous solubility and low K_{OWS} (Table 1), removal efficiency of AC-BZTs is generally less than 70% during secondary wastewater treatment (Asimakopoulos et al., 2013a). They are also resistant to degradation during water treatment processing (Reemtsma et al., 2010) and are potentially toxic to aquatic organisms (Pillard et al., 2001; Li, 2013).

The first measurements of UV-BZTs in the aquatic environment were published by Jungclaus et al. (1978) and Lopez-Avila and Hites (1980), who measured the release of UV-BZTs and other chemicals to Narragansett Bay, RI, USA as a result of chemical manufacturing production. More recently, studies have reported UV-BZT sediment concentrations from rivers and coastal waters of China and Japan (Nakata et al., 2009), as well as elsewhere in the U.S. (Zhang et al., 2011), providing information on the presence and environmental levels of BZTs in areas not associated with their production. Tissue concentration data for several UV-BZTs exist for a number of marine species, including shellfish (Pruell et al., 1984; Nakata et al., 2012), fish (Kim

et al., 2011) and porpoises (Nakata et al., 2010), confirming their bioavailability and bioaccumulation in living organisms. Recently, several AC-BZTs have been identified and measured in human urine using liquid chromatography-tandem mass spectrometry (Asimakopoulos et al., 2012). A follow up study involving human subjects from seven countries found AC-BZT urine concentrations as high as 24 ng/mL, indicating that usage of these compounds is resulting in human exposure and uptake of these compounds (Asimakopoulos et al., 2013b).

The objective of this study was to measure the spatial and temporal trends of BZTs in two urbanized estuaries and develop a better understanding of their behavior, long-term persistence, and potential for imparting adverse ecological effects in coastal ecosystems. Sediment cores from two locations were analyzed for both UV- and AC-BZTs to provide an estimate of the extent of BZT contamination present. Site 1 is located in upper Narragansett Bay, RI (Figure 2), an estuary with a documented history of being impacted by the production of UV-BZTs as well as industrial and domestic wastewater discharges (Jungclaus et al., 1978). The second site is in the center of Salem Sound, MA, USA (Figure 3), a coastal urban estuary within Massachusetts Bay without any known direct sources of BZTs. In this study, a total of eight BZTs were measured based on their designations as high production volume (HPV) chemicals and early dates of production (Table 1). Two of these are AC-BZTs: 1H-Benzotriazole (1-H-BZT) and 1H-Benzotriazole, 5-methyl- (TT). The other six are phenolic, UV-BZTs: Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl- (UV-P); Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)- (UV-PS); Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)- (UV-328); Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl)-4-methyl- (UV-326); Phenol, 2-(5-chloro-

2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-1 (UV-327); and Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)- (UV-320).

Materials and Methods

Sampling Locations-Radiometric Dating Sediment geochronologies for each core were developed using a Constant Initial Concentration (CIC) model fit to unsupported ^{210}Pb activities (Appleby and Oldfield, 1992) and confirmed through the use of time-stratigraphic peaks for fallout of fission-produced ^{137}Cs (Bopp et al., 1982). Supported and unsupported (excess) sediment ^{210}Pb lead activities in core sections were determined by gamma γ -spectroscopy while ^{137}Cs activities in the cores were determined by γ -spectroscopy. Detailed information on sample preparation, chemical and radiochemical analysis methods, geochronologies, and radionuclide profiles can be found in Cantwell et al. (2010).

The Narragansett Bay (NB) core site is located in 6 m of water in the upper Providence River below the Fields Point WWTP (Figure 2). In the NB core, the CIC model fit to excess ^{210}Pb activities resulted in an average apparent sediment accumulation rate of 2.2 cm/yr. There is a peak in the ^{137}Cs profile likely corresponding to the 1963 fallout maxima. In addition, this site was dredged in 1940 to a depth that penetrated into glacial clays, providing a time reference for the bottom of the core. No dredging has been conducted in the immediate vicinity of the coring site since 1940. Assuming a constant sediment accumulation rate and using the ^{137}Cs peak as a specific date horizon results in an accumulation rate of 2.4 cm/yr.

The average depth of Salem Sound (SS) is 9.15 m, and two sediment cores were collected adjacent to the South Essex Sewage District outfall pipe in May 2010. No known dredging activities have occurred in the vicinity of the core site due to the proximity of the outfall piping.

The first core was split, logged, and subsampled for all chemical analyses. The second core was subsampled vertically for samples to be used in radiometric analyses. An age model was developed using ^{210}Pb , ^{137}Cs , ^7Be , and ^{14}C data. An age model was calculated with the ^{210}Pb data using the CIC model. The base of the age model was constrained with a calibrated (Marine09) AMS radiocarbon date (^{14}C) taken from bivalve shell fragments at core depth 72.5 cm. The sample was analyzed at the NSF-Arizona AMS Laboratory (Tucson, Arizona, USA). A local marine reservoir correction ($\Delta R = 60 \pm 15$) was used based on the only local bivalve (*Mya arenaria*) listed in the CALIB marine reservoir correction database (Beverly, MA; distance 4 km) (McNeely 2006; Reimer et al., 2009). Below the dating limit of ^{210}Pb , the age model was extended by fitting the line through the mid-point of the calibrated ^{14}C age. The calculated sedimentation rate for the upper portion of this core is 0.22 cm/yr.

Sediment Extraction. Two extraction procedures were used to measure the UV- and AC-BZTs in the sediments. The UV-BZTs were extracted by way of accelerated solvent extraction (ASE) using a Dionex ASE model 200 (Thermo Scientific, Chelmsford, MA, USA). Stainless steel extraction cells were loaded with approximately 0.25–1 g of freeze dried sediment mixed with sufficient diatomaceous earth to fill the cell prior to the addition of deuterated phenanthrene (50 ng) as an internal standard (IS). Samples were extracted using a 1:1 mixture of hexane/acetone over three five minute static cycles at 120 °C and 1800 psi, and were evaporated to 2 mL before the addition of 5 mL of iso-octane. Extracts were further reduced to approximately 1 mL prior to being loaded onto solid phase silica cartridges (Waters Corporation, Milford MA, USA). Cartridges were eluted with 6 mL of a 90:10 mixture of hexane/diethyl ether, exchanged to hexane, reduced to 1 mL and stored at -5 °C until analysis by GC/MS. The 1-H-BZT and TT were also extracted from sediments using the ASE. Extractions cells were

loaded with approximately 1 g of freeze dried sediment mixed with sufficient diatomaceous earth to fill the cell prior to the addition of deuterated 1-H-BZT as an IS. Samples were extracted using 100% methanol over three five minute static cycles at 100°C and 1500 psi. Narragansett Bay sediment core extracts were passed through GF/C filters at this point, but other extracts did not require this extra filtration step. Extracts were evaporated to 0.5 mL and then diluted with 10 mL of Milli-Q water prior to being loaded onto Oasis HLB extraction cartridges (Waters Corporation, Milford MA, USA). The cartridges were dried under vacuum after being washed with 6 mL of 5% methanol in Milli-Q. The extracts were then eluted with 6 mL of methanol, evaporated to dryness and reconstituted with 1 mL of an 80:20 mixture of Milli-Q/methanol. At this point, extracts were filtered using a 0.22 µm centrifuge tube filter before being transferred to LC/MS vials.

Analysis. Analysis of UV-BZTs was performed on an Agilent 6890 gas chromatograph equipped with a 5973 mass selective detector (Agilent Technologies, Wilmington, DE, USA) operated in select ion monitoring mode. Analytes were quantified with either a high or low range (based on extract concentration) six point calibration curve, with calibrations (with a linear coefficient of determination of $r^2 = 0.99$ or better as the minimum acceptance criteria) performed prior to each analysis. All sediment extractions were performed alongside process blanks and replicate samples in each run. Blank values were below the method detection limit (1.3 ng/g based on 1 g dry sediment), while replicate samples were extracted and analyzed with the relative percent deviation always below 5%. Continuing calibration verification standards were measured as part of each instrument run and were within 10% of stated concentrations. Analysis of the AC-BZTs was performed on a Waters Acquity Ultra-Performance Liquid Chromatography with a Waters Xevo TQD tandem mass spectrometer operated in positive electrospray ionization

(ESI) mode. Separation of 4-methyl benzotriazole and 5-methyl benzotriazole was not possible using the described method and therefore they are reported together as tolyltriazole (TT). These methylated benzotriazoles are isomers and are present in equal proportion in commercial technical mixtures generically known as tolyltriazole (CAS 29385-43-1). An isotopically labeled compound, 1H-benzotriazole-d4 (CDN isotopes), was used for internal standard quantification of target analytes. Procedural blanks were below the method detection limit of 0.9 and 0.5 ng/g for 1-H-BZT and TT, respectively, based on a sample mass of 1 g dry weight. Further information on analytical procedures can be found in Supplemental Materials.

Results and Discussion

Ultraviolet Benzotriazoles

Narragansett Bay A combination of relatively high and consistent sedimentation rates coupled with excellent radiometric dating permitted an accurate historical reconstruction of BZT release and accumulation at our site in Narragansett Bay. The discharge and behavior of UV-BZTs in the environment were initially studied in this area in the 1970s by Jungclaus et al., 1978; Lopez-Avila, 1979; and Lopez-Avila and Hites, 1980. Briefly, these compounds were produced at a chemical manufacturing facility until operations ceased in 1985 (Reddy et al., 2000). This facility was located on the Pawtuxet River and released its wastewater directly to the Pawtuxet River, which discharges to Narragansett Bay. Until now, limited information existed on the production and fate of these compounds in the environment. In the core, which is approximately 2.5 km from the mouth of the Pawtuxet River, measurable concentrations of UV-P start in 1961 at 1,600 ng/g (dry), climbing rapidly and peaking at more than 26,000 ng/g by 1972 (Figure 4). Above this peak in the core, concentrations steadily decline to 1,500 ng/g by 1991. From this time to the surface, which corresponds to October 2007, concentrations remain in the range of

1,000 ng/g, reflecting a sustained and uniform accumulation rate at this site during this period of time. Measurable concentrations of UV-326 also appear in 1961. From 1961, concentrations climb to a maximum in the core of over 7,100 ng/g in 1966, declining to approximately 300 ng/g by 1974. A subsequent, smaller peak of 4,200 ng/g appears at a depth corresponding to 1991. This spike is surprising since the facility that produced the UV-BZTs ceased operations in 1985 and no apparent explanation exists for why only this compound would respond in this manner. Elevated levels of UV-328 also start in 1961, but remain at or below 1,000 ng/g until 1970 when concentrations climb and peak at 74,000 ng/g by 1976. Lopez-Avila (1979) reported 1970 as the starting date for production of UV-328 at this facility; however, it is apparent from the core data that this compound was being discharged to the environment commencing in 1961. After a slight dip to 45,000 ng/g, concentrations again climb to 73,000 ng/g by 1982, with a steep decline by the mid-1980s, which again is attributed to the manufacturing facility's closure. Following another decline into the early 1990s, concentrations remain between 3,000–6,000 ng/g to the surface. Similarly, levels of UV-327 rapidly build from approximately 1961, peaking at 73,000 ng/g by 1966. A secondary peak of 51,000 ng/g is present in 1972, confirming long-term production and release of this compound to the environment. This temporal response of UV-327 corresponds well with production dates of this compound (1962–1972) reported by Lopez-Avila (1979) and provides further confirmation of the accuracy of our age model. From this date onward, concentrations steadily decline to the early 1990s where they remain relatively constant (i.e., 2,000 ng/g $\pm$ 750 ng/g) to the surface. Finally, UV-320 was the last compound to appear in the core at a depth corresponding to 1966, and had the lowest concentrations of all UV-BZTs with a maximum of 600 ng/g by 1972. Subsequent concentrations drop to 78 ng/g by 1978 and show a continuous decline to 30 ng/g in 1989, remaining below this concentration to the top of

the core. UV-PS was detected at a depth corresponding to approximately 1975, but at levels below the limit of quantitation and not reported here. This compound was found to be present in Pawtuxet River sediments in the 1970s by Jungclaus et al. (1978), but not in estuarine waters or sediments measured by Lopez-Avila (1979), which would explain its low levels and its limited presence in the core.

Examination of U.S. patent records reveals that UV-P, UV-PS, and UV-320 were issued patents in 1961 for their light absorbing properties as additives to plastics, polymers and other materials (Heller et al., 1961). The appearance of UV-P and UV-320 in the core aligns well with their patent date. For UV-PS, the data from this core as well as previous information (Jungclaus et al., 1978) suggests that little of this compound was released to the environment here and may be indicative of its magnitude of production at the facility. Although not identified in the original patent literature, UV-326 is also present in 1961, providing further evidence that 1961 is the baseline for UV-BZT production at this facility and the start of their release into Narragansett Bay. The temporal responses of each of the compounds in the NB core provides insight into the long-term fate and transport of these compounds. Lopez-Avila and Hites (1980) collected shallow cores (e.g., 21 cm) in 1977 at a number of sites below our core location in Narragansett Bay. One site was close to NB (~2 km), with reported levels of UV-P, UV-327 and UV-328 that are in good agreement with our measured core concentrations for that time period. For example, at a depth corresponding to 1977 in the NB core, concentrations of UV-P, UV-327 and UV-328 were 10,000, 10,300 and 44,000 ng/g, respectively, while Lopez-Avila and Hites (1980) reported 6,000, 11,000 and 21,000 ng/g, respectively. This comparison also provides a good indication of the persistence of these compounds, which have been sequestered for more than four decades in the sediments.

Concentrations at the surface of the NB core (October 2007) remain highly elevated for UV-P, UV-327 and UV-328 at 1,400, 2,700 and 3,400 ng/g, respectively, long after the facility had ceased operations. Examining post-production (1985–2007) UV-BZT concentrations in the core reveals continuous long-term deposition and accumulation at this site. This is illustrated by UV-P, UV-327 and UV-328, which had the highest levels in the core during their production years (Lopez-Avila, 1979). It is suspected that these high post-production levels are due to resuspension and transport of previously released UV-BZTs, which are now likely bound to sediments based on their reported log K_{OWS} (Table 1). Not surprisingly, the duration and magnitude of the discharge of UV-BZTs, particularly UV-327 and UV-328, has resulted in their widespread distribution in sediments at elevated levels throughout greater Narragansett Bay (Hartmann et al., 2005). The contemporary accumulation of UV-BZTs at high levels at our site indicates that they are still being released into the Bay, with the most plausible source for them being the historically contaminated sediments from within the Pawtuxet River (Lopez-Avila, 1979). Evidence of this comes from suspended sediments collected in sediment traps deployed at the mouth of the Pawtuxet River, which discharges to Narragansett Bay (Figure 1). Sediment trap samples collected during eight, two week deployments in 2012 revealed average water column sediment concentrations of UV-P, UV-327 and UV-328 at 18,300, 13,600 and 4,300 ng/g, respectively. These levels are well above those measured at the surface of the core. Suspended sediment mass fluxes exiting the mouth of the Pawtuxet River during a one year period (2012) have been estimated (Cantwell et al., 2014), and using these records along with sediment trap data resulted in calculated annual fluxes of 91, 68 and 21 kg for UV-P, UV-327 and UV-328, respectively, entering the upper part of Narragansett Bay. While substantial evidence for the source of UV-BZTs to Narragansett Bay already existed, these sediment trap

and flux values explain the high post-production concentrations and confirm the sediments of the Pawtuxet River as the historical, current and continuing source of UV-BZTs to the coring location and likely other parts of Narragansett Bay.

Salem Sound At the Salem Sound site, four of the six UV-BZTs were present in the core (UV-P, UV-326, UV-327, UV-328), while UV-PS and UV-320 were below levels of detection (Figure 5). Examining the trend of UV-P reveals that it is present down-core prior to its patent date of 1961 (e.g. 11 cm) based on the core chronology. This early appearance is also noted for UV-327 and UV-328, which were present in the NB core at 1961. This indicates that physical disruption (e.g., resuspension, bioturbation) of the sediment may have occurred at some point in time, partially disturbing the sediment at some depths within the core. The UV-BZTs extend down-core to approximately 15 cm, which based on the core dating is prior to the 1950s, well before any of these compounds were patented or produced. The ^{137}Cs data shows a clear, well-defined peak above and below the 1963 maxima, indicating the absence of any significant post-sedimentation disturbance from 11 cm to the surface of the core. The mixed zone at or below 11 cm precludes the use of this core for confirmation of UV-BZT release dates to the environment. However, it still provides valuable information on recent trends (< 11 cm) and abundances for each of the UV-BZTs. Another benefit of the data from this location is that the direct influences of BZT production are absent (unlike the NB core) and environmentally relevant concentrations of BZTs in a representative coastal ecosystem can be elucidated. For UV-P, measurable concentrations remain below 10 ng/g throughout the core, with a small but consistent declining trend observable from 9 cm (1970) to the surface (2010) (Figure 5). For UV-326, measureable concentrations appear at 11 cm, further up-core than the other BZTs, indicating it was released to this location later than the other UV-BZTs. This later appearance also indicates that UV-326

deposition started after the mixing occurred in the core. Up-core, UV-326 levels remain relatively constant between 5–10 ng/g until an increase to a core maximum of 24 ng/g at 4 cm (~1990). From 4 cm to the surface (2010), concentrations drop by about half to 12 ng/g. Elevated levels of UV-328 are present in the mixed zone (> 11 cm) and increase up-core to 36 ng/g at 9 cm (1970), the highest level of all UV-BZTs measured in this core. From 9 cm depth, concentrations decline up-core to 16 ng/g at a depth of 5 cm (~1990), where levels eventually decline to 4 ng/g at the surface (2010). Finally, UV-327 is also present in the mixed zone of the core (> 11 cm) below 5 ng/g, increasing to a maximum of 16 ng/g at 9 cm depth (~1970). There is a second, smaller peak in the core at 5 cm measuring 12 ng/g, and from there concentrations slowly decline to 3 ng/g at the surface (2010).

One trend common to all the UV-BZTs at this site was their decline in concentration commencing at a depth between 4–5 cm and continuing to the surface of the core. This may have been due to an upgrade from primary to secondary level treatment at the South Essex Sewerage District (SES D) WWTP in 1997. Further down the core at approximately 8 cm, a similar response can be seen, particularly for UV-327 and UV-328, which may have been the result of an upgrade of the SES D to primary treatment in 1977. This upgrade in treatment is also reflected in the total organic content (TOC) of the core which starts to decline at 8 cm depth (Figure S1). Using the dates of the two WWTP upgrades and the corresponding depths where the declines are observed in the BZTs establishes an annual sedimentation rate of 0.22 and 0.37 cm/yr at 1977 and 1998, respectively. These values agree well with the rate of 0.22 cm/yr that was based on the radiometric dating techniques. This also demonstrates that the treatment level of WWTPs influences the amount of UV-BZTs released to the environment and provides further evidence that the sediments in the upper 11 cm of this core are relatively undisturbed.

Information on the presence and abundance of UV-BZTs in sediment is limited, particularly for marine sediments. A recent study from the Ariake Sea and Omuta River in Japan (Nakata et al., 2009) reports UV-BZTs in surface sediments and provides an opportunity to compare contemporary concentrations from two spatially diverse locations. For example, our concentrations of UV-320 at SS near the surface (2.4 ng/g) are consistent with those reported by Nakata et al. (2009) (0.3–2.3 ng/g) for eleven surface coastal sediments. Levels of UV-326 at the surface in SS were approximately 12 ng/g and are also in good agreement with those reported in the Ariake Sea, which range from 1.5–12 ng/g across their sample sites. Surface concentrations of UV-328 at SS are 4 ng/g, while those in the Ariake range from 2.6 to 16 ng/g. Finally, UV-327 is 3 ng/g at the surface of our core, which is close to values in the Ariake Sea ranging from 1.6 to a high of 9 ng/g. Nakata et al. (2009) also measured the same UV-BZTs in riverine sediments from the Omuta River, which discharges to the Ariake Sea. In general, UV-BZT levels were higher in the river sediments (2.6–320 ng/g), possibly reflecting their proximity to source inputs of the BZTs. Overall, surface concentrations from SS correspond well with the Ariake Sea coastal sediments, and offer important information on what may be considered representative levels of UV-BZTs in urban estuaries not impacted by BZT production, unlike Narragansett Bay. Further, these findings provide support for the assertion that UV-BZTs are ubiquitous and are accumulating, albeit at low levels, in marine sediments at urbanized coastal locations.

Currently, the sources of UV-BZTs in urban estuaries and the environment in general are poorly understood. In the case with NB, release of UV-BZTs to the environment was associated with their manufacturing. However, in the case of locations such as SS, one assumption is that WWTPs are the primary pathway of these compounds to the environment. Recent data of UV-

BZTs in WWTP effluents provide an estimate of current trends and evidence of their relative contribution to receiving waters. In Portugal, dissolved individual effluent concentrations of UV-327 and UV-328 ranged from 21–31 ng/L (Montesdeoca-Esponda et al., 2012), while in Spain they ranged from 4–13 ng/L (Carpinteiro et al., 2012). Overall, these concentrations reflect the physico-chemical properties (e.g., K_{OW}) of the UV-BZTs and their low solubility in water.

What remains unclear is the source of the UV-BZTs that are present in WWTP influents. Individual influent concentrations of UV-326, UV-327 and UV-328 at five WWTPs in Japan (Nakata and Shinohara, 2010) were similar, ranging from 5.6–78 ng/L, while UV-326 was measured at approximately 25 ng/L in an influent in Australia (Liu et al., 2012). Based on measured low influent concentrations to WWTPs and considering that UV-BZTs are used primarily as plastics additives, one hypothesis is that UV-BZTs are migrating out of the plastic products. Thus, their environmental presence is likely due to their diffusion out of products during and following their intended use. The equation below was initially derived and used by the European Union to approximate the volatilization rate of chemical plasticizers added to plastic films during their product use (EU, 2002):

$$\text{Percentage loss due to volatilization} = 1 \times 10^6 \times V_p \times N$$

V_p = vapor pressure of UV-P = 1.13×10^{-6} mm Hg (BASF 2010)

N = service life (assuming 10 years)

Using the vapor pressure of UV-P to determine volatility loss results in an estimate of over 11% over 10 years, suggesting that long-term diffusion from plastics could be a potentially important source of UV-BZTs to the environment. In addition to volatilization, there is desorption of the UV-BZTs into natural waters during their service life. Some UV-BZTs (UV-P, UV-326, UV-

327 and UV-328) have been measured in residential house dusts at relatively high levels (22–657 ng/g) (Carpinteiro et al., 2010), providing evidence that some household plastic products are releasing UV-BZTs to the surrounding environment. Of five UV-BZTs found in house dust by Kim et al. (2012), UV-234 (not measured in this study), UV-326 and UV-328 (which were also the most abundant UV-BZTs in the SS core) had the highest concentrations. Potential UV-BZT migration from plastics has also been investigated for UV-P in polyethylene terephthalate (PET) (Monteiro et al., 1999). Findings revealed that these compounds readily migrate into food products and thus are likely not molecularly bound to the plastic structure. The diffusive behavior of the UV-BZTs appears remarkably similar to polybrominated flame retardants (PBDEs), which were also used extensively in plastics. Most PBDEs are not molecularly bound to the plastic matrix, allowing them to partition from one environmental phase to another, and have also been found in residential house dusts (Stapleton, 2005), WWTP influents (desJardin et al., 2006) and in sediments (Christensen and Platz, 2001) at similar levels as UV-BZTs. Overall, these similarities suggest that both classes of compounds have similar sources and pathways to the environment, thus making diffusion and migration of UV-BZTs out of plastic materials and products an important source to environmental compartments and, potentially, human exposure (Kim et al., 2012).

Anticorrosive BZTs

Narragansett Bay The down-core trends of the AC-BZTs in the NB core are unusual and suggest a number of discrete events may have occurred that influenced the levels present (Figure 6). While it is difficult to interpret with absolute certainty, it is possible to elucidate local events and larger scale trends from these data. For example, the presence of AC-BZTs predates the UV-BZTs, with trace amounts of 1-H-BZT and TT present down to the bottom of the core,

which corresponds to 1940. Concentrations of both compounds increase modestly up-core until approximately 1960, when 1-H-BZT increases abruptly. The increase of 1-H-BZT continues to a maximum of 240 ng/g in 1974. A slow but sustained decrease then occurs and continues to approximately 1995, where concentrations of 1-H-BZT are approximately 14 ng/g. From this point in time to the surface (2007), the levels remain relatively constant between 10–13 ng/g. The temporal trend and behavior of 1-H-BZT in the core is intriguing in several respects. Sediment data on AC-BZTs are extremely limited and the data reported show 1-H-BZT ranges from 0.38–33 ng/g (Zhang et al., 2011) in river sediments. The sediment levels of 1-H-BZT in NB are, to our knowledge, the highest reported to date in aquatic sediments. It is unlikely that 1-H-BZT was inadvertently produced along with one or more of the UV-BZTs because of the different positions of the hydrogen on the triazole moiety (e.g., 1-H for AC-BZTs and 2-H for UV-BZTs). The concentrations in NB suggest that 1-H-BZT may have been produced locally. The company that produced the UV-BZTs at this site also held patents associated with 1-H-BZT, which would make this assertion plausible (Aiken et al., 1965; Casalongo, 1972). Further, the concentration trend of 1-H-BZT aligns well with the time period when UV-BZTs were being produced and discharged (i.e., 1961–1985), suggesting that they may have been produced at this facility. Finally, the sediment levels of 1-H-BZT are extremely high relative to its physico-chemical characteristics, given this chemical has a log K_{OW} of 1.44 and aqueous solubility of $5.96E+06$ $\mu\text{g/L}$. The distribution of BZTs in the sediment cores is assumed to be dictated by equilibrium partitioning of the individual chemicals between the sediment particle, primarily the TOC, and the interstitial water. In the NB core, TOC was relatively uniform, ranging from 5.3–7.6 % (Figure S1). For the UV-BZTs, which have moderate to high log K_{OW} s (e.g., 4.31–7.25) and elevated sediment concentrations (Figures 4, 5), this model appears to describe their

behavior fairly accurately. Conversely, the AC-BZTs have relatively low log K_{OW} s (e.g., 1.44–1.71) but are also concentrated in the sediments (Figures 6, 7). Further, the estimated log K_{OC} for a representative AC-BZT, 1-H-BZT, is 1.22 when calculated using a linear free energy relationship based on log K_{OW} (Schwarzenbach et al., 2003). However, an empirical K_{OC} measured as the ratio of sediment concentrations (normalized for TOC content) and interstitial water concentrations for 1-H-BZT in sediments from the Narragansett Bay station resulted in a log K_{OC} of 4.70, a value four orders of magnitude higher than the equilibrium partitioning models predicts. Currently, it is not clear why the empirical K_{OC} is so high; it may be related to the interaction of the AC-BZTs with inorganic constituents of the sediments, which the basic equilibrium partitioning model does not consider (Chiaia-Hernandez et al., 2012). In any event, it is a key observation from this investigation and may explain why these seemingly water soluble AC-BZTs (Table 1) are accumulating and persisting for decades in marine sediments like the more hydrophobic UV-BZTs.

Concentrations of TT are also present at the bottom of the core (i.e., 1940) but remain below 5 ng/g up to the 1970s, with a sustained increasing peak at 21 ng/g in the early 1980s. From this time to the surface, concentrations exhibit a slow decline to 11 ng/g. Based on the low levels of TT, it is apparent that it was not produced locally. However, the increase at approximately 1972 may be due to the incorporation of AC-BZTs into domestic automatic dishwasher detergent formulations. Patents for dishwasher detergents with benzotriazoles as corrosion inhibitors started to be issued in the early 1970s (Casalongo, 1972), supporting the temporal trend of TT observed in this core. Unfortunately, any corresponding increase of 1-H-BZT due to its use in dishwashing detergents is obscured by the elevated levels present in the core during this period. Following its peak in the 1970s, concentrations of 1-H-BZT display a sustained decline, and by

1995 levels of 1-H-BZT and TT become roughly equivalent, suggesting that contemporary inputs from WWTP effluents containing AC-BZTs (likely from dishwashing detergent use) are the primary and more recent source to the sediment. This observation is substantiated by measured water column concentrations of 1-H-BZT and TT in samples taken at the core site in August 2014. These averaged 38 and 43 ng/L for 1-H-BZT and TT, respectively, making it likely that the discharges from WWTPs are the contemporary source of these compounds to estuarine waters and sediments (Asimakopoulos et al., 2013a).

Salem Sound In contrast to NB, the concentrations of AC-BZTS throughout the SS core were low, remaining below 5 ng/g for both compounds (Figure 7). Concentrations of 1-H-BZT are measureable well into the mixed sediment zone (> 11 cm), with levels just under 3 ng/g, and display a declining trend to the surface of the core, which is less than 1 ng/g. Concentrations of TT are low as well and show somewhat greater variability throughout the core's length when compared to 1-H-BZT. There is, however, a TT peak at approximately 1973, which, as noted previously, is approximately when AC-BZTs were patented for dishwasher detergent formulations (Casalongo, 1972). This peak is the highest level measured in the core (4.2 ng/g), although a corresponding increase in 1-H-BZT is not apparent. Overall, the mean concentrations and ratios between the two compounds throughout the core are similar (2.01 ng/g 1-H-BZT, 1.71 ng/g TT). Concentrations of both AC-BZTs are also similar to those reported by Chiaia-Hernandez et al. (2012) in Lake Greifensee, Switzerland (1.4 ng/g 1-H-BZT, 0.8 ng/g TT). Levels at the SS site and in the surface sediments of NB likely reflect WWTP effluent release to the environment and subsequent removal to the sediment.

Summary

In NB, UV-BZTs were present at high levels from 1961 on, reflecting their patent date, local production and long-term preservation, while UV-BZTs at SS were much lower, comparing well with concentrations observed at other coastal locations around the world. The AC-BZTs also were present back to the 1940s based on the NB data, confirming early production, use and preservation in sediment. Sediment concentrations of 1-H-BZT at NB were highly elevated despite its high aqueous solubility, suggesting an unexplained complexation or sorption mechanism may be responsible. The AC-BZTs at SS were very low, but were measurable down-core, with concentrations similar to those reported at other locations globally.

By all accounts, BZTs meet the USEPA's definition as contaminants of emerging concern: unregulated chemicals present in the environment that have been have not been detected or are being detected at levels that may be significantly different than expected, and whose potential environmental and human health risks are largely unknown (USEPA 2015). Research needs include identification of the primary sources and pathways of UV-BZTs to the environment, as well as an improved understanding of their behavior (e.g., transformation, degradation). For AC-BZTs, their low removal efficiency following WWTP processing, their demonstrated persistence in sediments and their potential toxicity at low levels justify further investigation.

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Literature Cited

- Aiken, J.K., Howard, D.K., Popplewell, A.F., 1965. Inhibiting copper corrosion, British Patent 994,409.
- Appleby, P. G., Oldfield, F., 1992. Applications of lead-210 to sedimentation studies. In Uranium-series disequilibrium: applications to earth, marine, and environmental sciences. 2. ed.
- Asimakopoulos, A. G., Ajibola, A., Kannan, K., Thomaidis, N. S., 2013a. Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece. *Sci. Tot. Env.* 452, 163-171.
- Asimakopoulos, A. G., Bletsou, A. A., Wu, Q., Thomaidis, N. S., Kannan, K., 2012. Determination of benzotriazoles and benzothiazoles in human urine by liquid chromatography-tandem mass spectrometry. *Anal. Chem.*, 85 (1), 441-448.
- Asimakopoulos, A. G., Wang, L., Thomaidis, N. S., Kannan, K., 2013b. Benzotriazoles and benzothiazoles in human urine from several countries: A perspective on occurrence, biotransformation, and human exposure. *Environ. Int.* 59, 274-281.
- BASF, 2010. Material safety data sheet Tinuvin P. CAS Number 2240-22-4. Version 1.2 revision 2010/05/12
- Breedveld, G. D., Roseth, R., Hem, L., Sparrevik, M., 2002. Triazoles in the Terrestrial Environment. NGI Report No. 20001103-1.
- Bopp, R. F., Simpson, H. J., Olsen, C. R., Trier, R. M., Kostyk, N., 1982. Chlorinated hydrocarbons and radionuclide chronologies in sediments of the Hudson River and Estuary, New York. *Environ. Sci. Technol.* 16 (10), 666-676.
- Cantwell, M.G., Wilson, B.A., Zhu, J., Wallace, G.T., King, J.W., Olsen, C.R., Burgess, R.M., Smith, J.P., 2010. Temporal trends of triclosan contamination in dated sediment cores from four urbanized estuaries: Evidence of preservation and accumulation. *Chemosphere* 78 (4), 347-352.
- Cantwell, M.G., Perron, M.M., Sullivan, J.C., Katz, D.R., Burgess, R.M., 2014. Assessing changes in contaminant fluxes following dam removal in the Pawtuxet River. *Environ. Monit. Assess.* 186 (8), 4841-4855.
- Cantwell, M. G., Sullivan, J.C., Burgess, R.M., 2015. Benzotriazoles: History, Environmental Distribution, and Potential Ecological Effects, Chapter 16, p. 513-545. In: Eddy Y. Zeng (Ed.), *Comprehensive Analytical Chemistry 67, Persistent Organic Pollutants (POPs): Analytical Techniques, Environmental Fate and Biological Effects*. Elsevier B.V., Amsterdam, Netherlands.

- Carpinteiro, I., Abuin, B., Rodriguez, I., Ramil, M., Cela, R., 2010. Pressurized solvent extraction followed by gas chromatography tandem mass spectrometry for the determination of benzotriazole light stabilizers in indoor dust. *J. Chromatogr. A* 1217 (24), 3729-3735.
- Carpinteiro, I., Ramil, M., Rodríguez, I., Nogueira, J.M.F., 2012. Combining stir-bar sorptive extraction and large volume injection-gas chromatography-mass spectrometry for the determination of benzotriazole UV stabilizers in wastewater matrices. *J. Sep. Sci.* 35 (3), 459-467.
- Casalonga, A., 1972. Corrosion inhibitors containing derivatives of benzotriazole, French Patent 2,114,478.
- Chan, S. K., Hubred, G. L., Todd, H. E. 1995. Deicer/anti-icer compositions for aircraft. US Patent 5,435,930.
- Chiaia-Hernandez, A. C., Krauss, M., Hollender, J., 2012. Screening of lake sediments for emerging contaminants by liquid chromatography atmospheric pressure photoionization and electrospray ionization coupled to high resolution mass spectrometry. *Environ. Sci. Technol.* 47 (2), 976-986.
- Christensen, J. H., Platz, J., 2001. Screening of polybrominated diphenyl ethers in blue mussels, marine and freshwater sediments in Denmark. *J. Environ. Monit.* 3 (5), 543-547.
- Christie, J. A., Macbeath, F. S., Turner, J. C., 1997. Machine dishwashing composition containing oxygen bleach and paraffin oil and benzotriazole compound silver tarnishing inhibitors. US Patent 5,698,504.
- Daughton, C.G, 2004. Non-regulated water contaminants: emerging research. *Environ. Impact Assess. Rev.* 24, 711-732.
- Davis, L. N., Santodonato, J., Howard, P., Saxena, J., 1977. Investigation of selected potential environmental contaminants: benzotriazoles. Final Report prepared for Office of Toxic Substances, US Environmental Protection Agency: Washington, DC.
- desJardins Anderson, T., MacRae, J. D., 2006. Polybrominated diphenyl ethers in fish and wastewater samples from an area of the Penobscot River in Central Maine. *Chemosphere*, 62 (7), 1153-1160.
- Donaldson, E., Fowler, B.T., Tims, J.M., 1965. Lubricating greases, British Patent 984,488.
- EU (European Union), 2002. Risk assessment report: bis(pentabromodiphenyl)ether). European Chemicals Bureau, Luxembourg, Belgium.

- Hartmann, P. C., Quinn, J. G., Cairns, R. W., King, J. W., 2005. Depositional history of organic contaminants in Narragansett Bay, Rhode Island, USA. *Mar. Pollut. Bull.* 50 (4), 388-395.
- Heller, H., 1961. Ultra-violet light-absorbing composition of matter, US Patent 3,004,896.
- Jungclaus, G., Avila, V., Hites, R., 1978. Organic compounds in an industrial wastewater: a case study of their environmental impact. *Environ. Sci. Technol.* 12 (1), 88-96.
- Kim, J.-W., Isobe, T., Ramaswamy, B.R., Chang, K.-H., Amano, A., Miller, T.M., Siringan, F.P., Tanabe, S., 2011. Contamination and bioaccumulation of benzotriazole ultraviolet stabilizers in fish from Manila Bay, the Philippines using an ultra-fast liquid chromatography–tandem mass spectrometry. *Chemosphere* 85 (5), 751-758.
- Kim, J.-W., Isobe, T., Malarvannan, G., Sudaryanto, A., Chang, K.-H., Prudente, M., Tanabe, S., 2012. Contamination of benzotriazole ultraviolet stabilizers in housedust from the Phillipines: Implications on human exposure. *Sci. Tot. Env.* 424, 174-181.
- Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., Buxton, H. T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance. *Environ. Sci. Technol.* 36 (6), 1202-1211.
- Li, M.-H., 2013. Acute toxicity of industrial endocrine-disrupting chemicals, natural and synthetic sex hormones to the freshwater planarian, *Dugesia japonica*. *Toxicol. Environ. Chem.* 95 (6), 984-991.
- Liu, Y.-S., Ying, G.-G., Shareef, A., Kookana, R.S., 2012. Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. *Environ. Pollut.* 165, 225-232.
- Loos, R., Gawlik, B. M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide survey of polar organic persistent pollutants in European river waters. *Environ. Pollut.* 157 (2), 561-568.
- Lopez-Avila, V., 1979. Ph.D. Dissertation: Organic compounds in an industrial wastewater: a case study of their environmental impact. Massachusetts Institute of Technology, Cambridge, MA.
- Lopez-Avila, V., Hites, R. A., 1980. Organic compounds in an industrial wastewater. Their transport into sediments. *Environ. Sci. Technol.* 14 (11), 1382-1390.
- Malec, R.E., 1975. Lubricating oil compositions containing trialkyl-substituted phenols and benzotriazole, US Patent 3,900,410.

- McNeely, R., 2006. Geological Survey of Canada, Current Research (Online) no. 2006-G. Natural Resources Canada.
- Meighen, A., 1957. Heat exchange compositions. US Patent 2,803,603.
- Monteiro, M., Nerin, C., Reyes, F. G. R., 1999. Migration of Tinuvin P, a UV stabilizer, from PET bottles into fatty-food simulants. *Packag. Technol. Sci.* 12 (5), 241-248.
- Montesdeoca-Esponda, S., Sosa-Ferrera, Z., Santana-Rodríguez, J., 2012. On-line solid-phase extraction coupled to ultra-performance liquid chromatography with tandem mass spectrometry detection for the determination of benzotriazole UV stabilizers in coastal marine and wastewater samples. *Analytical and Bioanalytical Chemistry* 403 (3), 867-876.
- Nakata, H., Murata, S., Filatreau, J., 2009. Occurrence and concentrations of benzotriazole UV stabilizers in marine organisms and sediments from the Ariake Sea, Japan. *Environ. Sci. Technol.* 43 (18), 6920-6926.
- Nakata, H., Shinohara, R.-i., 2010. Concentrations of benzotriazole UV stabilizers and polycyclic musks in wastewater treatment plant samples in Japan. *Interdisciplinary Studies on Environmental Chemistry-Environmental Research in Asia*, 239-245.
- Nakata, H., Shinohara, R.-i., Murata, S., Watanabe, M., 2010. Detection of benzotriazole UV stabilizers in the blubber of marine mammals by gas chromatography-high resolution mass spectrometry (GC-HRMS). *J. Environ. Monit.* 12 (11), 2088-2092.
- Nakata, H., Shinohara, R.-I., Nakazawa, Y., Isobe, T., Sudaryanto, A., Subramanian, A., Tanabe, S., Zakaria, M.P., Zheng, G.J., Lam, P.K.S., Kim, E.Y., Min, B.-Y., We, S.-U., Viet, P.H., Tana, T.S., Prudente, M., Frank, D., Lauenstein, G., Kannan, K., 2012. Asia-Pacific mussel watch for emerging pollutants: Distribution of synthetic musks and benzotriazole UV stabilizers in Asian and US coastal waters. *Mar. Pollut. Bull.* 64 (10), 2211-2218.
- Novak, L. J., Holtze, K., Kent, R. A., Jefferson, C., Anderson, D., 2000. Acute toxicity of storm water associated with de-icing/anti-icing activities at Canadian airports. *Environ. Sci. Technol.* 19 (7), 1846-1855.
- National Research Council (NRC). 2001. A Risk-Management Strategy for PCB-Contaminated Sediments. National Academy Press, Washington, DC.
- Pillard, D. A., Cornell, J. S., DuFresne, D. L., Hernandez, M. T., 2001. Toxicity of Benzotriazole and Benzotriazole Derivatives to Three Aquatic Species. *Water Res.* 35 (2), 557-560.
- Pruell, R.J., Hoffman, E.J., Quinn, J.G., 1984. Total hydrocarbons, polycyclic aromatic hydrocarbons and synthetic organic compounds in the Hard shell clam, *Mercenaria mercenaria*, purchased at commercial seafood stores. *Mar. Environ. Res.* 11 (3), 163-181.

- Reddy, C. M., Quinn, J. G., King, J. W., 2000. Free and bound benzotriazoles in marine and freshwater sediments. *Environ. Sci. Technol.* 34 (6), 973-979.
- Reemtsma, T., Miehe, U., Duennbier, U., Jekel, M., 2010. Polar pollutants in municipal wastewater and the water cycle: Occurrence and removal of benzotriazoles. *Water Res.* 44 (2), 596-604.
- Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk, R.C., Buck, C.E., Burr, G.S., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Hajdas, I., Heaton, T.J., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., McCormac, G., Manning, S.W., Reimer, R.W., Richards, D.A., Southon, J.R., Talamo, S., Turney, C.S.M., van der Plicht, J., Weyhenmeyer, C.E., 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. *Radiocarbon*, 51 (4), 1111-1150.
- Schaeffer, J.R., 1952. Detergent compositions containing metal discoloration inhibitors. US Patent 2,618,606.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. *Environmental Organic Chemistry*. John Wiley and Sons, Inc., Hoboken, NJ, USA.
- Stapleton, H. M., Dodder, N. G., Offenberger, J. H., Schantz, M. M., Wise, S. A., 2005. Polybrominated diphenyl ethers in house dust and clothes dryer lint. *Environ. Sci. Technol.* 39 (4), 925-931.
- USEPA 2015. United States Environmental Protection Agency. Water: Contaminants of Emerging Concern. Accessed 5/06/2015. <http://water.epa.gov/scitech/cec/>.
- Vetter, W., Lorenz, J., 2013. Determination of benzotriazoles in dishwasher tabs from Germany and estimation of the discharge into German waters. *Environ. Sci. Pollut. Res.* 20, 4435-4440.
- Voutsas, D., Hartmann, P., Schaffner, C., Giger, W., 2006. Benzotriazoles, alkylphenols and bisphenol A in municipal wastewaters and in the Glatt River, Switzerland. *Environ. Sci. Pollut. Res.* 13 (5), 333-341.
- Zhang, Z., Ren, N., Li, Y.-F., Kunisue, T., Gao, D., Kannan, K., 2011. Determination of benzotriazole and benzophenone UV filters in sediment and sewage sludge. *Environ. Sci. Technol.* 45 (9), 3909-3916.

Table 1. Select attributes of benzotriazole compounds*

Compound	Molecular Weight	Log K_{OW}	Aqueous Solubility (µg/L)	Henry's Law Constant (atm-m³/mol)	Estimated Log K_{OC} (µg/g OC)
1-H-BZT	119.13	1.44	5.96E+06	1.47E-07	1.22
TT	133.15	1.71	3.07E+06	1.62E-07	1.42
UV-P	225.25	4.31	2.56E+04	6.12E-14	3.34
UV-PS	267.33	4.36	1.36E+04	1.43E-13	3.38
UV-328	351.50	7.25	1.48E+01	6.52E-13	5.52
UV-326	315.81	5.55	6.84E+02	1.17E-13	4.26
UV-327	357.89	6.91	2.63E+01	2.74E-13	5.26
UV-320	323.44	6.27	1.50E+02	3.70E-13	4.79

*Estimation Programs Interface Suite. v 4.11. United States Environmental Protection Agency, Washington, DC, USA

Figure 1a Ultraviolet stabilizing benzotriazoles

UV-P

UV-PS

UV-328

UV-326

UV-327

UV-320

Figure 1b Anticorrosive benzotriazoles

1-H-benzotriazole

1-H-benzotriazole, 4-methyl-

1-H-benzotriazole, 5-methyl-

Figure 2 Narragansett Bay

Figure 3 Salem Sound

Figure 4 UV-BZTs in Narragansett Bay sediments

Figure 5 UV-BZTs in Salem Sound sediments

Figure 6 AC-BZTs in Narragansett Bay sediments

Figure 7 AC-BZTs in Salem Sound sediments