BUTYLTIN CONTAMINATION OF SEDIMENTS AND BENTHIC FISH FROM THE EAST, GULF AND PACIFIC COASTS OF THE UNITED STATES *

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Abstract. Butyltin concentrations were determined in sediments, tissues and stomach contents of fish collected in 41 embayments on the East, Gulf and Pacific coasts of the U.S.A. between 1986 and 1991 as part of the National Oceanic and Atmospheric Administration's (NOAA) National Benthic Surveillance Project (NBSP). A total of 99 sediments, 108 fish liver samples from 11 fish species, and 10 composites of fish stomach contents were analyzed for tetrabutylin, tributylin, dibutylin and monobutylin. Tributyltin (TBT) was detected (i.e. > 10 ng/g) in 38 of the sediments samples analyzed and was generally the predominant bulytin present; concentrations of total butyltins ranged from 15 to 1600 ng/g wet weight. The highest concentrations were found in sediments from urban sites, especially sites on the West coast. Many of the fish liver and stomach contents samples also contained butyltins. Tributyltin represented 83 (7.1)% [mean (SEM); n = 15], 64 (6.6)% (n = 12) and 36 (7.8)% (n = 12) of the total butyltins in livers from white croaker, winter flounder and Atlantic croaker, respectively, suggesting possible species differences in biotransformation of TBT. The concentrations of butyltins in stomach contents indicated that diet can be a significant route of exposure of fish to butyltins. Between 1986 and 1991 butyltin concentrations in sediments and fish generally appeared to be declining; however, no statistically significant temporal trends were observed at individual sites or for the sites overall.

1. Introduction

The National Benthic Surveillance Project (NBSP) was initiated in 1984 by the National Oceanic and Atmospheric Administration as a component of its National Status and Trends Program (NS&T). The NS&T was designed to assess and document the status of, and long-term changes in, the environmental quality of the nation's coastal and estuarine waters. Specific objectives of NBSP are to measure concentrations of chemical contaminants (including aromatic hydrocarbons, polychlorinated biphenyls, chlorinated insecticides and selected metals) in sediment and in species of bottom-dwelling fish, as well as to determine prevalences of diseases in these same fish. Results of these determinations for the first several years of the project have been published (McCain *et al.*, 1989; Varanasi *et al.*, 1989; Johnson *et al.*, 1992; Myers *et al.*, 1993; Meador *et al.*, 1994). As the NBSP has matured, the target chemical analytes have been revised to reflect improvements in analytical

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methods and expanded recognition of potentially important xenobiotics. Because of an increasing concern regarding butyltin contamination in the nation's coastal areas, these compounds were added, in 1988, to the suite of chemicals monitored by NBSP.

Tributyltin (TBT), the most toxic butyltin, can enter the marine environment through its use in antifouling paints and its other industrial applications (Snoeij *et al.*, 1987). Tributyltin effectively inhibits the growth of fouling organisms that attach to boat hulls, but also exhibits toxicity toward many non-target organisms. Tributyltin causes detrimental effects in oyster spats and mussel larvae at water concentrations of $\sim$ 50 ng TBT/liter (Hall and Pinkney, 1985; Lapota *et al.*, 1993) and concentrations in this range have been found in environmental water samples (Unger *et al.*, 1986; Dowson *et al.*, 1993).

The Mussel Watch component of the NS&T employs bivalves such as mussels and oysters as monitors of contaminant loading and butyltins have been detected in virtually all bivalve samples examined in this program (Wade *et al.*, 1988, 1990; Uhler *et al.*, 1989). The measurement of butyltins in fish as part of the NBSP expands the knowledge base to another trophic level. The determination of butyltins in the stomach contents of fish potentially could provide information on trophic transfer. Measurements of butyltins in fish also complement data obtained for sediments. The spatial distribution of contaminants, including butyltins, in sediments is frequently very uneven or 'patchy'. Thus, a benefit of measuring contaminants in fish results from the tendency of mobile species to integrate contaminants from a broader geographic area.

Because some marine species, including many fishes, biotransform TBT to the less toxic forms, dibutyltin (DBT) and monobutyltin (MBT) (Lee, 1991; Martin *et al.*, 1989), it is important to measure each of these three butyltins and tetrabutyltin (a contaminant in the manufacture of TBT) in environmental samples. Using a method developed in our laboratory (Krone *et al.*, 1989a), concentrations of the four butyltin were determined in sediments, and fish livers and stomach contents collected at 41 NBSP sites on the U.S. East, Gulf and Pacific coasts. Most of the sampling sites were located in or near urbanized embayments where butyltins would be expected to be elevated. Nonurban sites were also sampled as comparison or reference sites.

2. Methods and Materials

2.1. CHEMICALS

Tetrabutyltin*, tributyltin chloride, dibutyltin dichloride, monobutyltin trichloride, tripropyltin chloride, tin(IV)chloride, tropolone, hexylmagnesium bromide (2 M in

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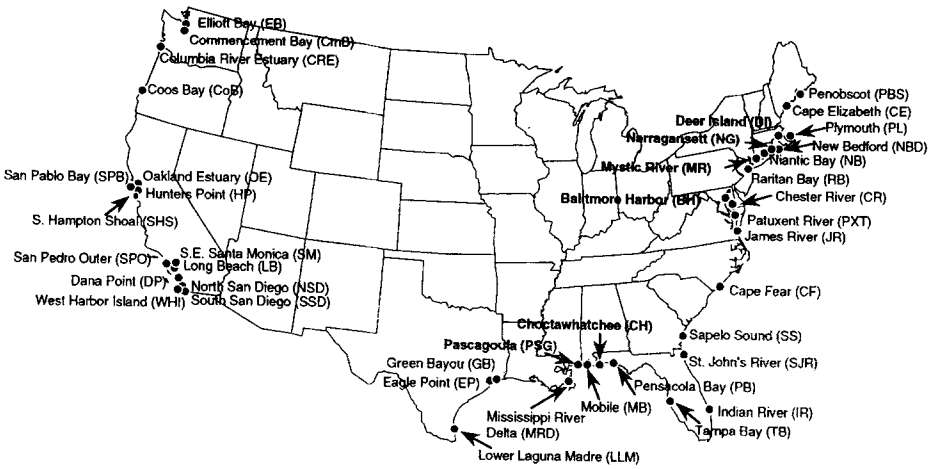

Fig. 1. Chart showing sampling locations and site abbreviations.

diethyl ether; in Aldrich Sure/Seal ™ bottle) and pentylmagnesium bromide (1.5 M in diethyl ether) were obtained from commercial sources (Aldrich, Milwaukee, WI; Alfa Products, Danvers, MA.). Methylene chloride, hexane and pentane were of Burdick and Jackson High Purity grade. All other reagents were of ACS Reagent grade or better. Tripentyltin chloride (TPeT) was synthesized in our laboratory (Krone *et al.*, 1989a). Silica (MCB, Norwood, OH) and alumina (Pierce, Rockford, IL) were heated at 700 °C for 18 h, stored at 170 °C and, before use, cooled to room temperature in a desiccator.

2.2. SAMPLE COLLECTION

Figure 1 shows the locations, names and abbreviations of the sampling sites in this study. Samples collected in 1986, 1988, 1989, 1990 and 1991 from sites on the Pacific coast were analyzed. Samples collected on the East and Gulf coasts in 1989 to 1991 were also analyzed. Sediments were collected (using a modified Van Veen grab) from three stations at each site and three sediment grabs were collected at each station. Surface samples of the top 2 cm of sediment were collected in glass jars, frozen and stored at –20 °C until analyzed. Fish were also captured (using an otter trawl) at each site and were weighed, measured and necropsied within 1 h capture. The excised tissues were immediately frozen and stored at –80 °C until analysis.

2.3. EXTRACT PREPARATION AND ANALYSIS

Composites of fish livers (10 fish per site), stomach contents (10 fish per site), and sediment (the three grabs per station and three stations per site were composited) were analyzed. In selected cases sediment from individual stations at a particular

site were analyzed separately. Details of butyltin analytical methods for sediment and tissues have been described previously (Krone *et al., 1989a*). Briefly, the alkyltin chlorides were extracted from sediments (by tumbling) or tissues (by homogenization) using methylene chloride with tropolone and anhydrous sodium sulfate as complexing and drying agents, respectively. The extracted alkyltins were converted to their *n*-hexyl derivatives through the Grignard reaction and analyzed, following silica/alumina cleanup, by GC with flame photometric detection. Cleanup consisted of chromatographing the sample extracts (following formation of *n*-hexyl derivatives) using a glass column containing 4.5 g each alumina and silica, and eluting with 20 ml pentane. For the liver extracts, an additional Sep-Pak^{TM} cleanup was done prior to GC analysis by loading the appropriate silica/alumina column fraction on an amino Sep-Pak^{TM} and eluting with 3 ml pentane.

Gas Chromatography/Flame Photometric Detector (GC/FPD) was carried out on a Varian model 3700 gas chromatograph equipped with a flame photometric detector (fitted with a 610 nm brandpass filter for tin-selective response), a Varian 8040 autosampler and a PC-based Varian Star integrator. A fused silica capillary column (bonded SE-54, ca. 30 m $\times$ 0.25 mm i.d.) was used with helium carrier gas (2 ml/min). The FPD was operated in dual flame mode with gas flow rates of hydrogen (140 ml/min), air #1 (80 ml/min), air #2 (170/min) and nitrogen make-up gas (30 ml/min). The injector and detector temperatures were maintained at 260 °C and 250 °C, respectively. The initial column temperature was 70 °C and was then increased to 240 °C at 20 °C/min. The final column temperature was held for 4 min. Tripentylmonobutyltin at 1 ng/ul (as tin) was employed as GC internal standard.

2.4. Quality Assurance

Quality control (QC) procedures included the use of recovery standards [TPeT and tripropyltin chloride (TPrT)], calibration standards, method blanks, sediment and tissue reference materials and duplicate analyses of selected samples. Two sediment reference materials (SQI and DUIII) and an oyster reference material (OI) were previously prepared in our laboratory (Krahn *et al.*, 1988). Reference materials and reagent blanks were analyzed with each set of environmental samples. Recovery standards were added to all samples, reagent blanks and spiked blanks. The mean recoveries of TPeT for the sediments and tissue samples were 88 $\pm$ 16% and 78 $\pm$ 26 (mean $\pm$ sd), respectively. All reagent blanks were free of butyltins. Calibration was done by the internal standard method using peak heights and a four concentration calibration curve. Confirmation of peaks identified by GC/FPD was accomplished by reanalyzing about 10% of samples by GC/MS.

2.5. Statistical Analysis

The ralationship between the concentrations of butyltins in sediments and tissues was assessed using the Spearman rank order correlation method (Zar, 1984). The

differences in percent of butyltin present as TBT in tissues for different fish species and sites were compared using one factor ANOVA and Fisher's PLSD (Zar, 1984) on arcsine transformed data. The changes in concentrations of butyltin in sediments over time were examined using the Mann-Kendall test for trend (Gilbert, 1987). Effects were considered significantly different at $\alpha = 0.05$.

3. Results

3.1. Butyltins in sediment

A total of 99 sediment and 108 liver tissue samples from forty-one sites were analyzed for the four butyltins. Table I shows the total butyltin concentrations in sediment and fish livers from 27 sites representing all three U.S. coasts. Samples from 14 other sites did not contain butyltins in sediment or tissues and were not listed in the table. These sites were Penobscot (1990), Cape Elizabeth (1990 and 1991), Plymouth (1989), New Bedford (1988, 1989 and 1991), Niantic (1989), Patuxent River (1991), Cape Fear River (1991), Sapelo Sound (1989), Tampa Bay (1989), Choctawahatchee (1989), Lower Laguna Madre (1991), Dana Point (1986, 1988 to 1991), Southeast Santa Monica (1989, 1990) and Long Beach (1986, 1989, 1990).

The median total butyltin concentration in the 38 sediments which contained butyltins was 130 ng/g wet weight with a range of 15 to 1600 ng/g [mean (SEM) was 210 (45) ng/g]. The median concentration of butyltins in sediments from sites on the Pacific coast was 210 ng/g [mean (SEM) = 390 (170) ng/g]. For sites on the East and Gulf coasts, the medians were 105 and 145 ng/g, respectively. The mean (SEM) for East and Gulf coast sediments were 140 (19) and 97 (14) ng/g, respectively.

The heterogeneous distribution of butyltins in sediments was evident at several sites where samples were analyzed from three individual stations at the site. For example, in 1991, two stations from the North San Diego site had no detectable butyltins, whereas sediment at the third station contained 110 ng/g total butyltins. At the Elliott Bay site in 1991, there was a 35-fold difference between the stations with the highest and lowest total butyltin concentrations (4200 ng/g and 120 ng/g, respectively).

Tributyltin was present in 38 of 99 sediments and represented on average 71% of the total butyltins in sediments. The TBT concentrations ranged from < 10 to 770 ng/g. Dibutyltin and MBT represented, on average, 24% and 6% of the total butyltins in sediments, respectively. However, in some sediments DBT was present at equal to or greater concentrations than TBT, comprising up to 63% of total butyltin (e.g. sites in South San Diego and North San Diego, CA). Significant amounts of MBT were detected (95 ng/g or 41% of total butyltins) in only one sediment sample, from a site in north San Diego, CA. Tetrabutyltin accounted for

TABLE I

Total butyltins in sediment and fish livers

Site	Year	Fish species	Sediment	Liver
			(ng total butyltins/g wet weight	
WEST COAST				
South San Diego	1986	Barred sand bass	510	1400
South San Diego	1988	Barred sand bass	330	na
South San Diego	1989	Barred sand bass	330	1600
South San Diego	1991	Black croaker	240	100
North San Diego	1986	White croaker	230	330
North San Diego	1988	White croaker	260	620
North San Diego	1989	White croaker	220	610
North San Diego	1991	White croaker	35	55
West Harbor Island	1988	White croaker	na	470
San Pedro Outer	1986	White croaker	190	180(0.5)[a]
San Pedro Outer	1988	White croaker	na	210
San Pedro Outer	1989	White croaker	130	< 20
San Pablo Bay	1991	Starry flounder	< 10	97
South Hampton Shoal	1991	White croaker	< 10	48
Hunters Point	1986	White croaker	15	130
Hunters Point	1988	White croaker	60	87
Hunters Point	1989	White croaker	26	< 20
Hunters Point	1990	White croaker	24	< 20
Hunters Point	1991	Starry flounder	20	100(37)[a]
Oakland Estuary	1989	White croaker	110	500
Oakland Estuary	1990	White croaker	110	230
Oakland Estuary	1990	Starry flounder	110	68
Coos Bay	1986		< 10	na
Coos Bay	1988	Starry flounder	92	590
Coos Bay	1989		42	na
Coos Bay	1990	Starry flounder	< 10	160
Columbia River Estuary	1991	Starry flounder	< 10	138(14)[a]
Commencement Bay	1986	English sole	< 10	130
Commencement Bay	1989	English sole	11	< 20
Commencement Bay	1990	English sole	< 10	< 20
Elliott Bay	1986	English sole	1200	720
Elliott Bay	1989	English sole	650	370
Elliott Bay	1990	English sole	240	380
Elliott Bay	1991	English sole	1600	350(7.0)[a]

TABLE I
Continued.

Site	Year	Fish species	Sediment	Liver
			(ng total butyltins/g wet weight	
NORTHEAST				
Baltimore Harbor	1989	White perch	110	< 20
Baltimore Harbor	1990	White perch	98(57)[a]	370(21)[a]
Baltimore Harbor	1991	White perch	< 10	140(3.0)[a]
James River	1991	White perch	< 10	170
Chester River	1990	White perch	< 10	81(80)
Chester River	1991	White perch	< 10	56
Raritan Bay	1988	Winter flounder	< 10	230
Raritan Bay	1989	Winter flounder	140	na
Raritan Bay	1990	Winter flounder	100(45)[a]	560(56)[a]
Narrahagansett	1990	Winter flounder	120	240
Deer Island	1988	Winter flounder	310	na
Deer Island	1990	Winter flounder	< 10	280
Deer Island	1991	Winter flounder	< 10	< 20
Mystic River	1989	Winter flounder	76	na
Mystic River	1990	Winter flounder	< 10	670(57)[a]
SOUTHEAST				
Mobile Bay	1990	Hardhead catfish	< 10	110
Green Bayou (Galveston)	1989	Atlantic croaker	160	860
Green Bayou (Galveston)	1989	Seatrout	160	900
Green Bayou (Galveston)	1989	Spot	160	920
Eagle Pont (Galveston)	1989	Atlantic croaker	< 10	170
Eagle Pont (Galveston)	1989	Seatrout	< 10	140
Eagle Pont (Galveston)	1989	Spot	< 10	100
Mississippi River	1990	Atlantic croaker	< 10	150(7.0)[a]
Pascagoula River	1990	Atlantic croaker	na	80
Pascagoula River	1991	Atlantic croaker	< 10	< 20
Pensacola Bay	1990	Atlantic croaker	na	51(6)[a]
Pensacola Bay	1991	Atlantic croaker	na	< 20
Indian River	1991	Hardhead catfish	< 10	970
St. Johns River	1989	Atlantic croaker	120	71

[a] mean (SEM) for analyses of two separate composites.
na = not analyzed.
Detection Imits are 10 ng/g and 20 ng/g for sediment and tissues, respectively.

3% of total butyltins in the one sediment in which tetrabutyltin was detected (Elliott Bay, WA).

3.2. Butyltins in fish livers and stomach contents

Sixty-eight percent of the liver samples showed the presence of butyltins (detection limits, 20 ng/g wet weight). The total butyltin concentrations in livers of fish containing butyltin ranged from 31 to 1600 ng/g wet weight a mean (SEM) of 330 (36) ng/g. The median concentration in livers was 190 ng/g or about 1.5 times the median total butyltin concentration in sediment. Generally, TBT and DBT were the only butyltins detected in these samples. Tributyltin was detected in 68 of the 108 liver samples (mean (SEM), 180 (18) ng/g wet weight; range 26 to 610 ng/g). In 34 of the 108 samples, DBT was found (210 (29) ng/g; range 17 to 1300 ng/g). Monobutyltin was detected in fish from only one site (South San Diego, CA). All three fish species from this site, barred sand bass, black croaker and diamond turbot, contained MBT in concentrations ranging from 20 to 190 ng/g. In these fish, MBT represented from 14% to 30% of the total butyltins. Table II shows the proportion of total butyltins that was present as TBT in livers of 11 fish species examined in this study.

The proportion of total butyltin present as TBT in livers appeared to vary with species. For example, the percent TBT in white croaker livers was significantly different from the percent TBT present in livers of Atlantic croaker, English sole, barred sand bass, starry flounder, hardhead catfish and spot (Table II). The values for each species represent samples collected at different sites and in several different years. For example, the samples of white croaker were from 7 different sites and as many as 4 different sampling years.

Butyltin were detected in 6 of the 10 stomach content composites that were analyzed. Total butyltins ranged from < 10 to 1800 ng/g wet weight and TBT represented from 47 to 100% of the total butyltins. No butyltins were detected in stomach contents of winter flounder from Raritan Bay, Deer Island and Mystic River, or in stomach contents of white croaker from North San Diego. Figure 2 shows the concentrations of TBT, DBT and MBT in stomach contents, liver and sediment from five sites. These data suggest that organisms in the diet, ingested sediment, or sediment in the intestinal tracts of prey organisms, may be a source of butyltins for fish. Taxonomy of the organisms found in the stomach contents showed molluscs and annelids commonly comprised the majority of organisms by weight except in the stomach contents of white perch from Baltimore, where crustaceans represented 40% of the organisms by weight (Varanasi *et al.*, 1989).

3.3. Comparisons of sediment and tissue butyltins

Livers generally contained higher concentrations of butyltins than sediments from the same site. At only four sites did the sediments, and not tissues, contain butyltins.

TABLE II

Tributyltin as a percentage of total butyltins in livers of fish

Fish species	Composites analyzed[a]	Percent TBT mean (SEM)
White croaker (*Genyonemus lineatus*)	$n = 15$	83(7.1)[b]
White perch (*Roccus americanus*)	$n = 7$	75(7.2)[c]
Winter flounder (*Pleuronectes americanus*)	$n = 12$	64(6.6)[d]
Black croaker (*Cheilotrema saturnum*)	$n = 2$	62(12)
Seatrout (*Cynoscion arenarius*)	$n = 2$	53(11)
Hardhead catfish (*Arius felis*)	$n = 4$	46(5.2)
Starry flounder (*Platichthys stellatus*)	$n = 10$	39(4.6)
Atlantic croaker (*Microgadus undulatus*)	$n = 12$	36(7.8)
English sole (*Pleuronectes vetulus*)	$n = 6$	26(16)
Barred sand bass (*Paralabrax nebulifer*)	$n = 2$	26(6.5)
Spot (*Leiostomus xanthurus*)	$n = 2$	20(20)

[a] Liver from 10 fish comprised each composite.
[b] Significantly different ($p < 0.05$) from hardheaad catfish, starry flounder, Atlantic croaker, English sole, barred sand bass and spot using one factor ANOVA and Fisher's PLSD on arcsine transformed data.
[c] Significantly different ($p < 0.05$) from starry flounder, Atlantic croaker, English sole and spot.
[d] Significantly different ($p < 0.05$) from Atlantic croaker, English sole and spot.

The sediment butyltin concentration was 55 (28) ng/g at these sites, whereas the average total butyltin concentration in the sediment at sites where livers contained butyltins was 260 (65) ng/g. Sediment samples were available in 48 of the instances where fish liver samples contained butyltins. Of these 48 liver samples, 40 contained higher total butyltin concentrations than were present in the sediments from the same site (Table I). In 1991, the year for which the most data were available, samples from a total of 21 sites were analyzed. At six of the sites, mostly on the East and Gulf coasts, no butyltins were detected in sediments or livers. At the remaining sites, butyltin concentrations were greater in liver than sediment in 12 of 15 cases.

A positive Spearman rank order correlation (rho = 0.55; $p < 0.004$) was found between the concentrations of butyltins in sediments and livers when all sites and species were combined. A positive Spearman rank order correlation coefficient (rho = 0.95; $p < 0.006$) was also found between the concentrations of butyltins in sediments and stomach contents.

For sites from all coasts where both tissues and sediments contained butyltins, the mean liver bioaccumulation factor (BAF, ng/g liver wet weight divided by ng/g sediment wet weight) was 2.90 (0.42) [mean (SEM)] with a range of 0.22 to 8.7.

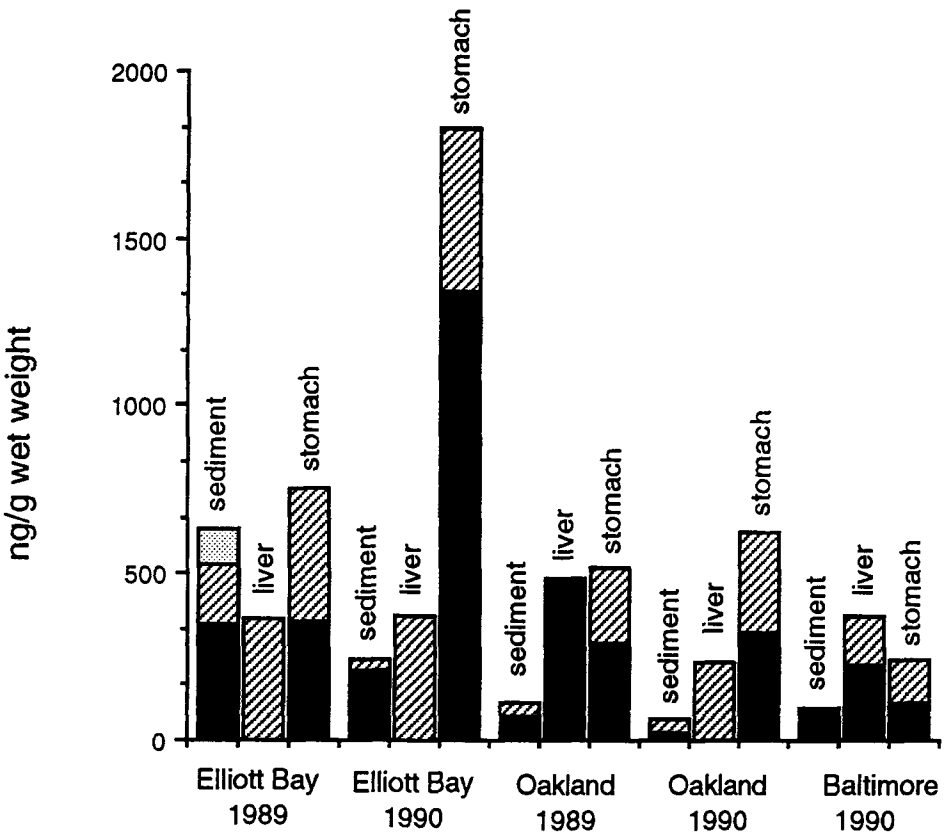

Fig. 2. Tributyltin (■), dibutyltin (▨) and monobutyltin (▦) in sediment, liver and stomach contents collected in 1989 and 1990. English sole were collected in Elliott Bay, white croaker in Oakland and white perch in Baltimore Harbor.

3.4. TEMPORAL TRENDS IN BUTYLTIN CONCENTRATIONS

Table III classifies sediments and liver from seven sites according to the concentration of total butyltins. The table shows, for 1986 and 1991, the number of sites falling into the different concentration classes. The trend is toward greater numbers of sites in the lower concentration classes in 1991 than 1986, most notably when examining butyltins in fish. However, no statistically significant temporal trends in butyltin concentrations were observed at individual sites or for the sites overall.

4. Discussion

Sediment and selected bottom-feeding fishes were employed as monitors of contaminant loading to near-coastal sites. Our results for butyltin concentrations in sediment and fish from 41 coastal sites are generally consistent with the data

TABLE III

Temporal changes in site classification based on total butyltin concentration in sediment and fish livers

Total butyltin concentration	Number of sites in each concentration class			
	Sediment		Fish	
	1986	1991	1986	1991
<10 ng/g	3	3	1	2
10–100 ng/g	1	2	0	2
100–500 ng/g	1	1	3	3
> 500 ng/g	2	1	3	0

reported by Wade *et al.* (1988, 1990) and Uhler *et al.* (1989) for sediments and bivalves, such as mussels and oysters. Wade *et al.* (1988, 1990) measured butyltins in sediments and bivalves from 33 U.S. coastal sites, whereas, Uhler *et al.* (1989) analyzed bivalves from 23 sites. We found that an average of 71% of total butyltins in sediment was represented by TBT. This is in general agreement with the study of Wade *et al.* (1990), which showed that TBT made up an average of 78% of the total butyltins found in the sediment from sites on the three U.S. coasts. The highest sediment butyltin concentrations in our study were found at sites on the Pacific coast, the same pattern that was reported for Mussel Watch Program sediments (Wade *et al.*, 1990). On the other hand, our analyses found butyltins in 38 of 99 (39%) sediments examined, while Wade *et al.* (1990) found 25 of 33 (76%) sediments contained butyltins. Only seven of the sites examined in our study were also investigated by Wade *et al.* (1990). This may partially explain any differences in the percentage of butyltin-containing sediments observed in the two studies.

Butyltins were found in about 65% of liver samples from benthic fish. In contrast, butyltins were detected in virtually all bivalve samples analyzed by Wade *et al.* (1988, 1990) and Uhler *et al.* (1989). Furthermore, the mean concentration of butyltins in bivalves was, on average, 18 times greater than the corresponding sediment concentration, ranging from a ratio of 6.8 at East Coast sites to 57 at a site in Hawaii (Wade *et al.*, 1990). In fish livers, we found the average butyltin concentration was 2.9 times the sediment concentration. A statistically significant positive correlation between the sediment and fish liver butyltin concentrations was found. However, a similar correlation did not exist for sediments and bivalves (Wade *et al.*, 1990). Differences in the sampling sites (as noted above), route of uptake, and varying abilities to biotransform and excrete butyltins may partially explain the apparent dissimilarity in the bioaccumulation factors we observed for fish and those found by Wade *et al.* (1990) for bivalves. Moreover, the BAFs for fish are for liver only, whereas for bivalves, the BAFs are for whole animals.

Among various fish species, a number of factors, including mobility, diet and the heterogeneous distribution of contaminants that often exists in a sediment at a site, could influence the bioaccumulation factors and lead to the 40-fold range we observed in this property. The distribution of contaminants, such as aromatic hydrocarbons (McCain *et al.*, 1989; Varanasi *et al.*, 1989) and butyltins (Krone *et al.*, 1989b), is very often found to be uneven or 'patchy'. In the present study such heterogeneity was found at several sites where sediments from individual stations within the site were analyzed (e.g. Elliott Bay, North San Diego, Hunter's Point). This is consistent with our past studies of Puget Sound marinas, which showed that butyltin concentrations can vary by 3 orders of magnitude over distances of only a few hundred meters (Krone *et al.*, 1989b).

It is generally held that an important attribute of measuring the concentrations of chemical contaminants in fish results from the tendency of mobile species to integrate contaminants from a somewhat broad geographic area. Thus, when butyltins are found in tissues, but not in sediments (such as at the Eagle Point site in Galveston Bay), the results indicate that the fish populations are integrating butyltin contamination over the entire area they inhabit.

The results of our study suggest that species differences in the percentage of total butyltins present as TBT in fish livers may be due to differences in metabolism of TBT. The predominance of DBT in liver of English sole in the present study corroborates results of our pevious study with this species in Puget Sound, Washington, U.S.A. (Krone *et al.*, 1989a). Preliminary results from exposure of English sole and starry flounder to TBT in our laboratory (unpublished data) showed that the concentration of TBT in liver and the ratio of TBT/DBT decreased over a 3 weeks period after a single exposure to TBT. After 7 days, the TBT/DBT ratios in liver for these two species were significantly different [0.56 (0.003) for English sole and 1.4 (0.2) for starry flounder], suggesting differences in TBT metabolism by these two species.

It is possible that factors other than species, such as site characteristics (e.g. sediment total organic carbon (TOC) and percent fines), could contribute to the apparent species differences in proportions of butyltins in liver. However, in those fish species for which data were avalable for multiple sites (white coraker, winter flounder and starry flounder), site differences in the proportions of butyltins in liver were not significant. For example, the TOC and percent fines (particles < 63 μm) varied from 0.44 to 0.97%, and 23 to 34% on a wet weight basis, respectively, in the sediments from North San Diego, Hunters Point and San Pedro. But white croaker collected at these three sites, over several years, did not exhibit statistically significant differences among sites in the proportions of TBT in fish livers ($p > 0.56$). By using data from fish captured at multiple sites and over several years, the inference that species specific factors, rather than sediment characteristics or diet, were responsible for differences in proportions of butyltins is strengthened.

Transfer of butyltins from one trophic level to another is suggested by the finding of butyltins in the stomach contents of fish. Organisms in the diet could

provide a source of butyltins and may influence the proportions of butyltins found in tissues. Laboratory studies by Lee (1985, 1986, 1991) have shown that fish can accumulate butyltins from food and from water. Annilids, arthropods and mollusca were important food organisms found in stomach contents of the fishes analyzed in the present study. Mussels, oysters, crabs, shrimp and oligochaete worms can take up, and often bioconcentrate, TBT from water, food and/or sediment (Lee, 1985, 1986, Wade *et al.*, 1988, 1990; Maguire and Tkacz, 1985). Moreover, studies by Lee (1985) suggested that crustaceans can transform TBT to DBT, MBT and other polar products. Thus, benthic organisms may be an important source of butyltin exposure for bottom-feeding fish and could also influence the proportions of butyltins if organisms which biotransform TBT, such as crustaceans, are part of the diet.

All of the above observations emphasize the need for determining the levels of chemical contaminants, and their metabolites, in tissues and stomach contents of fish, as well as in sediments. Knowledge of the relative tissue concentrations of butyltins is of great importance if the biological impacts of contaminated water and sediments are to be assessed. Moreover, the findings of differing proportions of TBT in livers of some fish species suggest toxicological implications; given equal total butyltin concentrations, the amount of the more toxic butyltin, TBT, may be greater in some species, and potentially exert more detrimental effects than in other species which have greater biotransformation abilities. Additional field and laboratory data will be needed to confirm apparent species differences in butyltin disposition and to determine if factors in addition to biotransformation capacity, such as site characteristics (sediment type, co-occurrence of other contaminants, etc.), diets and mobility may be influencing butyltin patterns in fish tissues.

The half-life of tributyltin in fish is relatively short (about 20 days: Yamada *et al.*, 1994). Thus, the presence of butyltins in fish captured in 1991 suggests that sources of these contaminants still remain in spite of the enactment of the Organotin Paint Control Act in 1988 which banned most uses of tributyltin-containing paints. Nevertheless, the apparent trends toward lower butyltin concentrations seen in sediment and fish suggest that the legislation has had some positive ecological impact. Dowson *et al.* (1993) also found a declining trend in TBT concentrations in sediment, and more so in water, in U.K. river and estuarine systems since a 1987 retail ban on TBT-containing paints in the U.K. Additional years of sampling will be needed to statistically document these trends in both the U.S.A. and U.K.

Our study has assessed butyltin contamination in the subtidal areas of U.S. estuaries, whereas others have monitored the intertidal regions (e.g. Wade *et al.*, 1988 and 1990; Uhler *et al.*, 1990). Together, results of these studies have provided a database that not only documents the presence of butyltins in the nation's coastal areas and demonstrates the bioavailability of butyltins to bottom dwelling fish and bivalves, but also establishes a baseline from which future changes in environmental quality can be measured.

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