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Historical Perspective on the Environmental Bioavailability of DDT and Its Derivatives to Gulf of Mexico Oysters

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■ DDT and its metabolites, DDD and DDE, were analyzed in 479 oyster samples from the Gulf of Mexico between 1986 and 1988 as part of the National Status and Trends "Mussel Watch" (NS&T) Program. DDT and/or its derivatives were found in every sample analyzed in concentrations ranging over 2 orders of magnitude. DDT accounted for 3–6% of the total DDT burden in oysters. The remaining percentage was approximately equally distributed between DDD and DDE. After the first 3 years of the NS&T program, the geographical distribution of total DDT along the northern coast of the Gulf of Mexico has been well defined. Based on 3 years of data, there were only a few sites that had statistically significant monotonic changes in concentrations with time. However, when the present data set is compared to historical data for the Gulf of Mexico, a general decrease is observed. The rate of DDT disappearance, as monitored by Gulf of Mexico oysters, is comparable with its decline in other marine environments.

Introduction

The National Oceanic and Atmospheric Administration's (NOAA's) National Status and Trends "Mussel Watch" (NS&T) Program is designed to monitor the current status and long-term effect of selected organic and inorganic environmental contaminants, e.g., chlorinated pesticides, polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), and trace metals, along the U.S. coasts by measuring their concentrations in bivalves and sediments over a number of years. The ultimate goals of the NS&T program are to define the geographical distributions of contaminants, identify "problem" areas, and determine trends in concentrations. The rationale for the "Mussel Watch" approach using different bivalves, e.g., mussels, oysters, and clams, has been summarized by different authors (*1–8*) and its concept has been applied to many national (*5*, *9*) as well as international (*7*, *10*, *11*) programs.

Overviews of the initial results for the first years of the NS&T program have already been reported (*12–15*). A more complete data set and extensive interpretation of the chlorinated hydrocarbon data in oyster and sediment samples from the Gulf of Mexico is published elsewhere (*16*). This report focuses on DDT [1,1′-(2,2,2-trichloroethylidene)bis[4-chlorobenzene]] and its derivatives, DDD [1,1′-(2,2-dichloroethylidene)bis[4-chlorobenzene]] and DDE [1,1′-(2,2,2-trichloroethenylidene)bis[4-chlorobenzene]], which, in spite of the ban of DDT in the United States in the early 1970s, have been reported to be present in sediments and marine animals from the Gulf of Mexico in numerous studies carried out over the past 15 years (*17–29*). DDT, DDD, and DDE concentrations in oysters resulting from the first 3 years (1986–1988) of the NOAA's NS&T program for the Gulf of Mexico portion are presented here and compared to historical Gulf coastal-wide data sets (*27*, *29*).

Methods

Sampling. The site locations for the 1986, 1987, and 1988 samplings are shown in Figure 1. Samples were collected from three stations within each site over 2–3-

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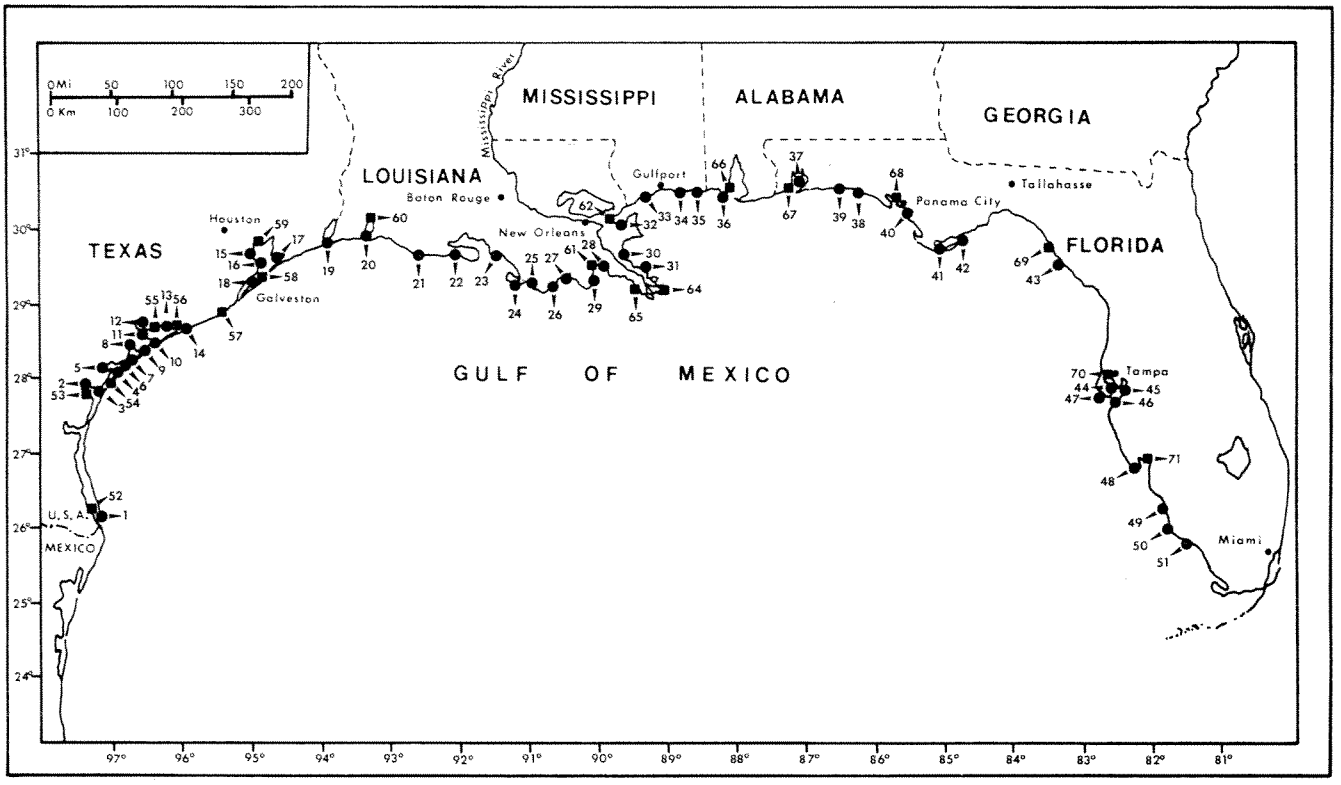

Figure 1. Gulf of Mexico sampling site locations. Shown are sites sampled from 1986 to 1988 (●) and sites added to the 1988 sampling program (■). See Table II for a complete site identification.

month periods starting in late December or early January. Stations were approximately 100–1000 m apart. Oysters (20 per station) were pooled in precombusted jars and frozen until analysis. During 1986 and 1987, oyster samples were collected at 49 and 48 sites with a total of 147 and 143 samples, respectively. The sites sampled during the first 2 years of the NS&T program were chosen to avoid known point sources of contaminant inputs. During 1988, 19 new sites were added to the original sampling program to provide more information for areas located closer to suspected contamination sources. During the third sampling period, 189 oyster samples were collected from a total of 63 sites.

Extraction and Separation. The analytical procedure used was adapted from a method developed by MacLeod et al. (*30*). Extraction and separation procedures are described in more details in Sericano et al. (*16*). Briefly, approximately 15 g of wet tissue is extracted, after the addition of anhydrous Na_2SO_4, with methylene chloride in a homogenizer (Tekmar Tissumizer). A small subsample is removed from the total volume for lipid weight determination. Each set of 8–10 samples is accompanied by a complete system blank and spiked blank or reference material that are carried through the entire analytical procedure. Before extraction 4:4 dibromooctafluorobiphenyl (DBOFB) is added to all samples, blanks, and reference material as internal standard. Tissue extracts are fractionated by silica–alumina column chromatography. The sample extracts are eluted from the column with pentane (f1, aliphatic hydrocarbons) and pentane–methylene chloride (1:1) (f2, chlorinated hydrocarbons and PAHs). The second fraction is further purified by Sephadex LH-20 column chromatography to remove lipids (*31*). The sample is eluted from the column with 140 mL of a mixture of cyclohexane–methanol–methylene chloride (6:4:3). The first 40 mL is discarded and the next 100-mL fraction is collected. Samples extracts are finally concentrated on a 75 °C water bath, under N_2 flow, to a volume of 0.5–1 mL, in hexane, for gas chromatographic analysis.

Gas Chromatography. DDT and its metabolites were determined by gas chromatography with an electron capture detector (GC-ECD, ^{63}Ni) using a 30-m DB-5 fused-silica capillary column (0.25-μm film thickness, 0.25-mm i.d., J&W Scientific), as previously described (*16*). Isomers of the DDT, DDD, and DDE were quantitated against authentic standards injected at three different concentrations. Detection limits for these compounds, calculated on the basis of 15-g (wet weight) oyster tissue sample sizes with 0.2% by volume of the extract injected into the GC-ECD, is 0.25 ng g^{-1} dry weight.

Quality Assurance/Quality Control (QA/QC). As part of the National Status and Trends Program, this laboratory has participated in several quality assurance activities to ensure that the data produced are reproducible and accurate. The program has included several laboratory intercalibration exercises, which involved repeated, routine analyses of homogenated bivalve tissue supplied by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). Complete system blanks and spiked blanks were also analyzed with each sample set as part of the laboratory QA/QC program.

Data Analysis. One-way analysis of variance (ANOVA), at the $a = 0.05$ level, was performed on the total DDT concentrations, i.e., the sum of *o,p'*-DDT + *p,p'*-DDT + *o,p'*-DDD + *p,p'*-DDD + *o,p'*-DDE + *p,p'*-DDE, in oysters. All data were log transformed prior to statistical analysis. For summary and statistical purposes, the reported mean total DDT concentrations include contributions equal to the analytical detection limits for those analytes that were below the limit of quantitation.

Results and Discussion

DDT and its metabolites were analyzed in more than 479 oyster samples collected from 70 different sites during

Table I. DDT and Metabolite Concentrations[a] and Distribution Frequencies in the Gulf of Mexico Oysters, 1986–1988

	concn, ng/g			% distribution				
	median	mean ± 1 SD	range	0.00–<0.25	0.25–<1.00	1.00–<10.0	10.0–<100	100⁺, ng g⁻¹
				1986 (n = 147)				
o,p'-DDE	<0.25	1.6 ± 7.3	<0.25–64	61	23	14	2	
p,p'-DDE	11	17 ± 17	1.6–130			43	46	1
o,p'-DDD	2.1	5.8 ± 1.3	<0.25–120	11	11	65	12	1
p,p'-DDD	8.6	18 ± 28	<0.25–160	9	2	46	40	3
o,p'-DDT	<0.25	1.1 ± 2.6	<0.25–22	70	6	23	1	
p,p'-DDT	0.64	1.8 ± 4.1	<0.25–39	32	30	34	4	
total DDTs	27	45 ± 58	3.7–400					
				1987 (n = 143)				
o,p'-DDE	<0.25	1.3 ± 7.8	<0.25–86	76	15	8	1	
p,p'-DDE	13	29 ± 100	0.57–1200		5	38	55	2
o,p'-DDD	1.2	10 ± 81	<0.25–970	27	16	50	6	1
p,p'-DDD	8.0	25 ± 110	<0.25–1300	2	5	53	37	3
o,p'-DDT	<0.25	0.68 ± 1.8	<0.25–19	83	3	13	1	
p,p'-DDT	<0.25	1.5 ± 3.0	<0.25–26	64	8	26	2	
total DDTs	26	68 ± 300	3.0–3600					
				1988 (n = 132)				
o,p'-DDE	0.27	3.7 ± 13	<0.25–100	49	20	27	4	
p,p'-DDE	15	26 ± 40	0.42–375		4	34	59	3
o,p'-DDD	2.6	7.9 ± 21	<0.25–190	15	8	61	14	2
p,p'-DDD	7.8	27 ± 85	<0.25–860	2	5	52	38	3
o,p'-DDT	0.58	1.7 ± 2.5	<0.25–17	41	19	37	3	
p,p'-DDT	<0.25	2.1 ± 3.2	<0.25–18	57	4	35	4	
total DDTs	32	68 ± 150	2.4–1400					
				1988 (n = 189)				
o,p'-DDE	<0.25	6.4 ± 29	<0.25–250	53	20	21	4	2
p,p'-DDE	15	31 ± 42	0.42–370		3	31	60	6
o,p'-DDD	2.6	9.8 ± 27	<0.25–220	15	7	60	15	3
p,p'-DDD	7.8	29 ± 75	<0.25–860	2	4	49	40	5
o,p'-DDT	0.49	2.2 ± 3.4	<0.25–20	39	19	36	6	
p,p'-DDT	<0.25	2.5 ± 5.1	<0.25–42	56	4	35	5	
total DDTs	32	80 ± 150	2.4–1400					

[a] Concentrations on a dry weight basis.

the first 3 years of the NS&T program for the Gulf of Mexico. Average and median concentrations as well as range and distribution frequency for each analyte during 1986, 1987, and 1988 are presented in Table I. DDT and/or its derivatives were detected in every oyster sample analyzed over the first 3 years of this program with concentrations ranging over 2–3 orders of magnitude. In 1986, total DDT concentrations ranged from 3.7 to 400 ng g^{-1} with a mean value of 45 ± 58 ng g^{-1}. During 1987, the extremely high concentrations measured at site 39 (Choctawhatchee Bay, Shirk Point; 1300 ± 1900 ng g^{-1}) yielded an overall average value (68 ± 300 ng g^{-1}, range 3.0–3600 ng g^{-1}) for the Gulf of Mexico higher than the concentration reported for the previous year; however, the difference in the median concentrations was negligible (27 and 26 ng g^{-1} for 1986 and 1987, respectively). During 1988, the overall average concentration for the original sites was 68 ± 150 ng g^{-1} (range 2.4–1400 ng g^{-1}) with a slightly higher median concentration (32 ng g^{-1}) than in the previous 2 years. The addition of sites closer to contamination centers did not greatly affect the data. Although the overall average total DDT concentration (80 ± 150 ng g^{-1}) is higher when the data from these sites are included, particularly the concentration from site 66 (Mobile Bay, Hollingers Island Channel; 640 ± 30 ng g^{-1}), the median concentration is not different.

Geographical Distribution. Total DDT means for each site (±1 standard deviation) measured during 1986, 1987, and 1988 are presented in Table II. Sites are shown in geographical order from the U.S.–Mexico border to the southernmost Florida site. After the first 3 years of the NS&T program, the geographical distribution of average total DDT concentrations in oysters from the Gulf of Mexico has been well established. A comparison of the mean total DDT concentrations for the 1986–1988 period is presented in Figure 2. The key for this figure is based on the overall arithmetic mean of total DDT ($\bar{X}$ = 72 ng g^{-1}) for all sites during this study. The localized contamination of the Gulf of Mexico coastal environments by DDT and its derivatives is evident from the distribution of sites with high, intermediate, or low average concentrations. Concentrations higher than twice the overall mean for the Gulf of Mexico oysters were encountered in samples from the Brazos River and Galveston Bay, in Texas; Mississippi River, in Louisiana; Mobile Bay, in Alabama; and Choctawhatchee and St Andrew Bays, in Florida. It is interesting to note the concentration distribution at and around the Mississippi River mouth. One of the highest average total DDT concentrations measured in the Gulf of Mexico was encountered in samples from a site located near the Mississippi River mouth (site 64). To both sides of the Mississippi River, there is a gradual decrease in contaminant levels that reaches mean concentrations lower than half the overall average for all Gulf of Mexico sites. Therefore, it appears that the Mississippi River is an important source of DDT and derivatives to the Gulf of Mexico environment, possibly due to DDT contained in agricultural runoff and transported downstream. With a few exceptions, the average total DDT concentrations were consistently low in oyster samples from the southern Texas, Louisiana coast to the west of the Mississippi River, and southernmost Florida.

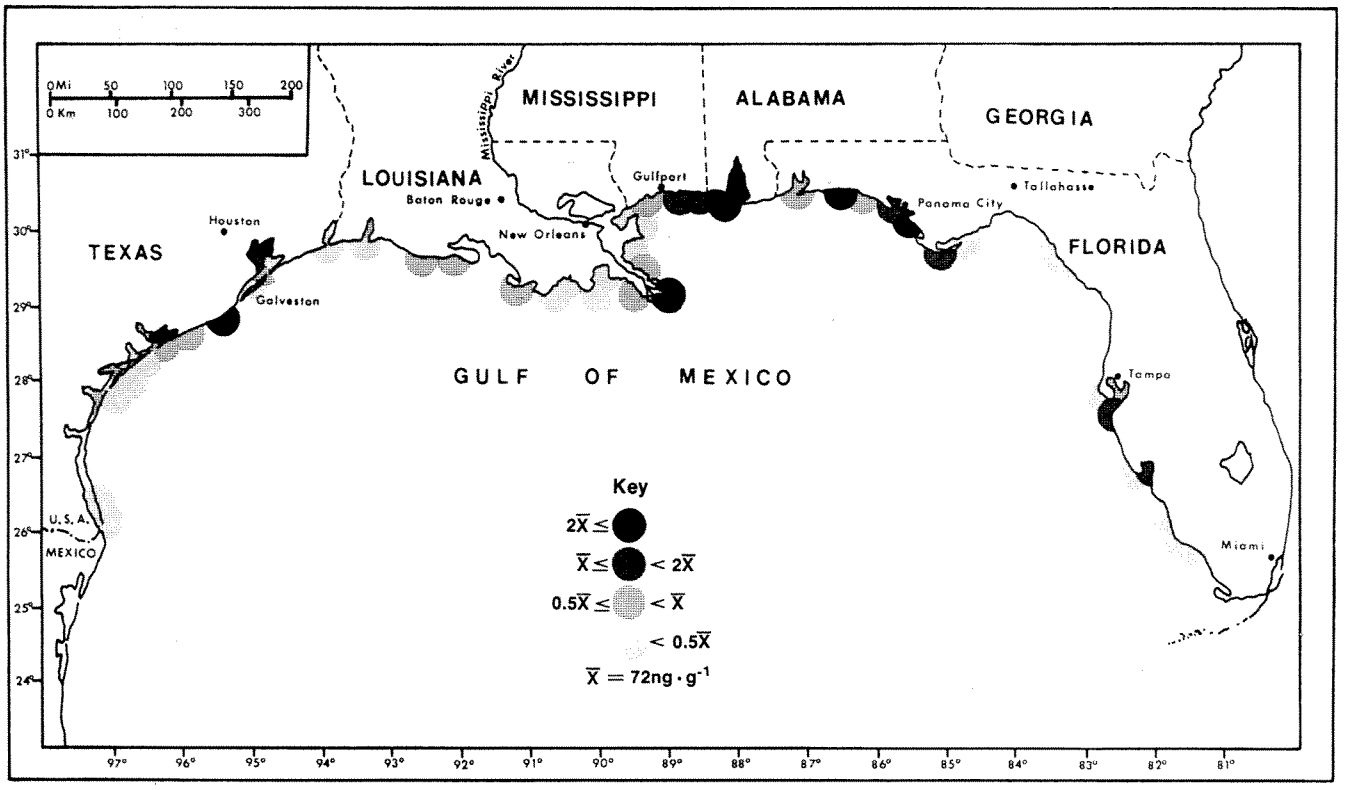

Figure 2. Geographical distribution of total DDT concentrations, 1986–1988.

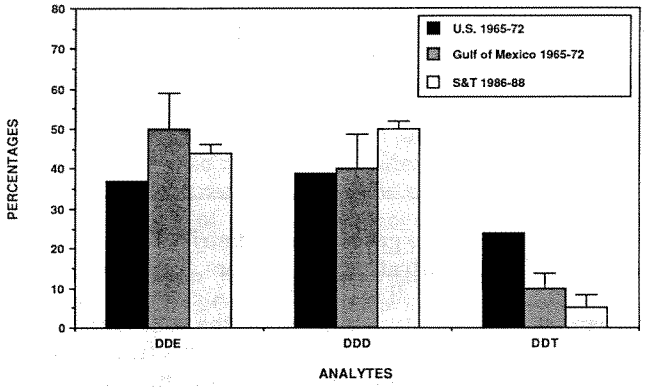

Figure 3. Average fractional composition of DDT and its derivatives in oyster samples from the U.S. coastal environments.

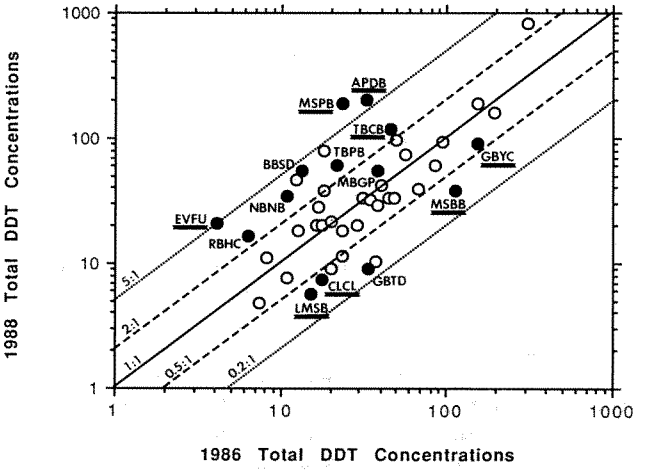

Figure 4. Oyster total DDT concentrations (in ng g^{-1}) in 1986 versus 1988. Closed circles indicate the sites with statistically significant changes in concentrations between 1986 and 1988. Dashed and dotted lines represent 2- and 5-fold changes in concentrations, respectively. Underlined sites presented monotonic changes in concentration with time.

Fractional Composition. It is generally accepted that increasing percentages of DDE and/or DDD, which are found only as impurities in commercial DDT formulations, in the total amount of DDT compounds found in organisms reflect decreasing exposures to new inputs of DDT. Technical DDT generally contains 75% *p,p'*-DDT, 15% *o,p'*-DDT, <0.5% *p,p'*-DDD, <0.5% *o,p'*-DDD, 5% *p,p'*-DDE, <0.5% *o,p'*-DDE, and <5% unidentified compounds (*32*). Isomers of the DDT accounted for a small fraction (5.2 ± 3.0%) of the total DDT burden detected in oysters during this study (Figure 3). Isomers of the DDD and DDE contributed with 50 ± 2.1 and 44 ± 2.3% of the total amount, respectively. These percentages are different from those given by Butler (*27*) for bivalve samples analyzed from 1965 to 1971, particularly for DDT. Butler reported a mean residue composition of 37% DDE, 39% DDD, and 24% for a data set of ~7000 mollusk samples, mostly *Crassostrea virginica*, *Crassostrea gigas*, and *Mercenaria mercenaria*, collected from estuaries and coastal areas of the United States. The mean residue composition for the Gulf of Mexico sites, which included exclusively *C. virginica* oysters, was similar to what was found during the first 3 years of the NS&T program (50 ± 8.9% DDE, 40 ± 8.8% DDD, and 10 ± 3.6% DDT). Approximately 80% of the total DDT load measured in oyster samples corresponded to the sum of the *p,p'* isomers. This percentage of *p,p'* isomers is similar to the percentages found in technical-grade DDT (*32*). This suggests that the *p,p'* and *o,p'* isomers are converted or degraded at similar rates in the marine environment, which disagree with the contention that *o,p'* metabolites are less persistent than their *p,p'* analogues (*33*).

Temporal Trends. With only a 3-year data base, it is presumptuous to explain the concentration tendency of any contaminant in the environment. In the following paragraphs, the present status of DDT and its metabolites in Gulf of Mexico oysters will be outlined. Scatter plots of the average total DDT concentrations encountered at

Table II. Total DDT Mean Concentrations in Oyster Samples from NS&T Program Sites, 1986–1988[a]

location				mean ± 1 SD			
site	general	specific	state	1986	1987	1988	overall
1 LMSB	Laguna Madre	South Bay	TX	15 ± 2.6	11 ± 3.2	5.7 ± 2.1	11 ± 4.7
2 CCNB	Corpus Christi	Nueces Bay	TX	31 ± 12	38 ± 14	33 ± 8.0	34 ± 10
52 LMPI	Laguna Madre	Port Isabel	TX	–	–	23 ± 4.9	23 ± 4.9
53 CCBH	Corpus Christi	Boat Harbor	TX	–	–	43 ± 22	43 ± 22
3 CCIC	Corpus Christi	Ingleside Cove	TX	24 ± 2.0	ns	18 ± 4.4	21 ± 4.2
54 ABHI	Aransas Bay	Harbor Island	TX	–	–	15 ± 1.2	15 ± 1.2
4 ABLR	Aransas Bay	Long Reef	TX	13 ± 0.63	15 ± 5.5	18 ± 6.1	15 ± 4.7
5 CBCR	Copano Bay	Copano Reef	TX	41 ± 11	30 ± 8.4	42 ± 10	38 ± 10
6 MBAR	Mesquite Bay	Ayres Reef	TX	17 ± 7.7	11 ± 5.5	28 ± 3.6	19 ± 9.1
7 SAPP	San Antonio Bay	Panther Pt. Reef	TX	13 ± 3.3	15 ± 2.3	ns	14 ± 2.9
8 SAMP	San Antonio Bay	Mosquito Point	TX	27 ± 5.4	32 ± 9.0	ns	29 ± 7.2
9 ESSP	Espiritu Santo	South Past Reef	TX	11 ± 1.6	15 ± 5.0	ns	13 ± 4.2
10 ESBD	Espiritu Santo	Bill Days Reef	TX	ns	ns	41 ± 5.3	41 ± 5.3
11 MBLR	Matagorda Bay	Lavaca River	TX	51 ± 18	27 ± 15	ns	39 ± 20
12 MBGP	Matagorda Bay	Galliniper Point	TX	39 ± 3.7	120 ± 130	55 ± 7.9	71 ± 77
56 MBCB	Matagorda Bay	Carancahua Bay	TX	–	–	40 ± 20	40 ± 20
13 MBTP	Matagorda Bay	Tres Palacios Bay	TX	94 ± 82	87 ± 58	95 ± 24	92 ± 52
55 MBDI	Matagorda Bay	Dog Island	TX	–	–	86 ± 12	86 ± 12
14 MBEM	Matagorda Bay	East Matagorda	TX	34 ± 19	43 ± 32	32 ± 6.3	39 ± 19
57 BRFS	Brazos River	Freeport Surfside	TX	–	–	190 ± 44	190 ± 44
15 GBYC	Galveston Bay	Yacht Club	TX	150 ± 15	120 ± 39	90 ± 26	129 ± 37
59 GBSC	Galveston Bay	Ship Channel	TX	–	–	230 ± 32	230 ± 32
58 GBOB	Galveston Bay	Offats Bayou	TX	–	–	70 ± 34	70 ± 34
16 GBTD	Galveston Bay	Todd's Dump	TX	34 ± 9.4	52 ± 15	7.5 ± 2.1	31 ± 22
17 GBHR	Galveston Bay	Hanna Reef	TX	11 ± 1.7	21 ± 9.6	7.7 ± 3.9	13 ± 8.1
18 GBCR	Galveston Bay	Confederate Reef	TX	16 ± 3.6	19 ± 4.7	20 ± 4.7	19 ± 4.2
19 SLBB	Sabine Lake	Blue Buck Point	TX	20 ± 8.5	19 ± 10	22 ± 21	20 ± 13
20 CLSJ	Calcasieu Lake	St. John's Island	LA	29 ± 6.7	19 ± 6.7	20 ± 4.2	22 ± 6.9
60 CLLC	Calcasieu Lake	Lake Charles	LA	–	–	58 ± 10	58 ± 10
21 JHJH	Joseph Harbor Bayou	Joseph Harbor Bay	LA	45 ± 15	39 ± 17	33 ± 6.0	39 ± 13
22 VBSP	Vermillion Bay	Southwest Pass	LA	56 ± 4.9	70 ± 26	74 ± 12	67 ± 17
23 ECSP	East Cote Blanche	South Point	LA	ns	ns	ns	deleted
24 ABOB	Atchafalaya Bay	Oyster Bayou	LA	49 ± 4.6	56 ± 26	95 ± 42	67 ± 33
25 CLCL	Caillou Lake	Caillou Lake	LA	18 ± 1.9	12 ± 5.0	7.2 ± 0.77	12 ± 5.2
26 TBLB	Terrebonne Bay	Lake Barre	LA	8.2 ± 6.2	9.5 ± 2.7	11 ± 8.9	9.6 ± 5.7
27 TBLF	Terrebone Bay	Lake Felicity	LA	7.4 ± 0.92	6.2 ± 3.6	4.7 ± 2.0	6.1 ± 2.4
61 BBTB	Barataria Bay	Turtle Bay	LA	–	–	7.0 ± 4.4	7.0 ± 4.4
28 BBSD	Barataria Bay	Bayou St. Denis	LA	14 ± 2.2	6.8 ± 3.2	54 ± 18	25 ± 24
29 BBMB	Barataria Bay	Middle Bank	LA	18 ± 12	12 ± 4.3	20 ± 5.7	16 ± 7.8
65 MRTP	Mississippi River	Tiger Pass	LA	–	–	70 ± 34	70 ± 34
64 MRPL	Mississippi River	Pass a Loutre	LA	–	–	240 ± 46	240 ± 46
30 BSBG	Breton Sound	Bay Garderne	LA	24 ± 23	4.3 ± 1.1	12 ± 1.7	13 ± 14
31 BSSI	Breton Sound	Sable Island	LA	73 ± 34	21 ± 9.5	61 ± 28	52 ± 32
32 LBMP	Lake Borgne	Malheureux Point	LA	20 ± 8.9	6.5 ± 3.2	9.0 ± 9.6	12 ± 9.3
62 LBNO	Lake Borgne	New Orleans	LA	–	–	6.9 ± 1.9	6.9 ± 1.9
33 MSPC	Mississippi Sound	Pass Christian	MS	18 ± 3.8	42 ± 27	76 ± 74	45 ± 47
34 MSBB	Mississippi Sound	Biloxi Bay	MS	110 ± 35	78 ± 93	38 ± 11	77 ± 59
35 MSPB	Mississippi Sound	Pascagoula Bay	MS	23 ± 7.8	33 ± 11	190 ± 29	82 ± 82
36 MBCP	Mobile Bay	Cedar Point Reef	AL	150 ± 58	160 ± 100	190 ± 53	160 ± 66
66 MBHI	Mobile Bay	Hollingers Is. Ch.	AL	–	–	640 ± 30	640 ± 30
67 PBPH	Pensacola Bay	public harbor	AL	–	–	59 ± 9.4	59 ± 9.4
37 PBIB	Pensacola Bay	Indian Bayou	FL	68 ± 38	47 ± 29	40 ± 7.0	52 ± 27
38 CBSR	Choctawhatchee Bay	off Sant Rosa	FL	48 ± 15	38 ± 9.8	34 ± 5.1	40 ± 11
39 CBSP	Choctawhatchee Bay	Shirk Point	FL	300 ± 91	1300 ± 1900	800 ± 610	810 ± 1100
68 PCMP	Panama City	municipal pier	FL	–	–	110 ± 68	110 ± 68
40 SAWB	St. Andrew Bay	Watson Bayou	FL	190 ± 80	160 ± 15	160 ± 68	160 ± 52
41 APDB	Apalachicola Bay	Dry Bar	FL	31 ± 1.1	59 ± 50	200 ± 120	99 ± 100
42 APCP	Apalachicola Bay	Cat Point Bar	FL	38 ± 7.6	33 ± 7.8	29 ± 9.2	33 ± 8.2
69 SRWP	Suwannee River	West Pass	FL	–	–	17 ± 3.0	17 ± 3.0
43 CKBP	Cedar Key	Black Point	FL	13 ± 2.0	24 ± 10	46 ± 71	28 ± 39
44 TBPB	Tampa Bay	Papys Bayou	FL	22 ± 4.2	100 ± 100	61 ± 10	62 ± 64
70 TBOT	Tampa Bay	Old Tampa Bay	FL	–	–	26 ± 12	26 ± 12
45 TBHB	Tampa Bay	Hillsborough Bay	FL	50 ± 13	27 ± 6.1	ns	39 ± 15
46 TBCB	Tampa Bay	Cockroach Bay	FL	46 ± 16	76 ± 24	120 ± 50	80 ± 43
47 TBMK	Tampa Bay	Mullet Key Bayou	FL	27 ± 18	29 ± 4.0	10 ± 6.4	22 ± 13
48 CBBI	Charlotte Harbor	Bird Island	FL	18 ± 7.5	36 ± 34	ns	27 ± 24
71 CBFM	Charlotte Harbor	Fort Meyers	FL	–	–	110 ± 19	110 ± 19
49 NBNB	Naples Bay	Naples Bay	FL	11 ± 0.89	52 ± 28	34 ± 10	32 ± 23
50 RBHC	Rookery Bay	Henderson Creek	FL	6.3 ± 1.9	4.6 ± 0.64	19 ± 12	10 ± 8.9
51 EVFU	Everglades	Faka Union Bay	FL	4.1 ± 0.53	6.6 ± 3.7	21 ± 8.6	10 ± 9.0

[a] Concentration (ng g^{-1}) on a dry weight basis; –, not in the sampling program; ns, no sample.

each site during 1986 and 1988 are compared in Figure 4. In 1988, ~40% of the sites had concentrations equal to or greater than a 2-fold change compared to the values reported for 1986. Approximately 50% of these sites

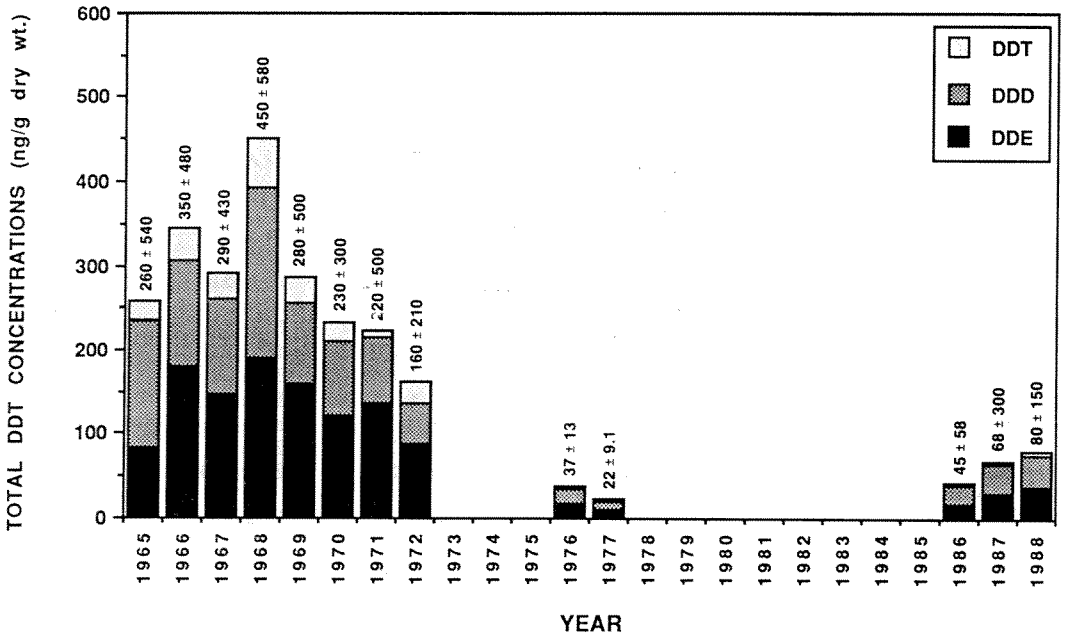

Figure 5. DDT, DDD, and DDE contributions (in ng g^{-1}) to the total DDT burden in the Gulf of Mexico oysters. Data was compiled as follows: 1965–1972 [Butler (*27*)], 1976–1977 [Farrington et al. (*29*)], and 1986–1988 (this study).

yielded mean total DDT concentrations that differed significantly from those measured during the first year of the NS&T program. A 2-fold change in the concentration observed between 1986 and 1988 at some sites was not statistically significant because of the large intrasite variability encountered. Three sites had over a 5-fold change in total DDT concentrations between 1986 and 1988. About two-thirds of the significant changes in total DDT concentrations observed by the end of the third year of the NS&T program were monotonic. At these sites, a gradual increase or decrease in total DDT concentration has occurred since 1986. The remaining sites with statistically significant concentration differences between the first and third year of the NS&T program had a concentration in 1987 that was either the lowest or the highest value measured during the first 3 years of this study (Table II). At these sites, the continuation of data collection during the next few years is needed to assess trends in total DDT concentrations.

Historical Data in the Gulf of Mexico. The only Gulf of Mexico coastal-wide data sets for DDT and its metabolites in oysters to which the present study can be compared are the works by Butler (*27*) and Farrington et al. (*29*). However, comparisons are generally complicated by the substantial changes that have been made in analytical methods in recent years and must be exercised with caution. Moreover some of the early DDT data, like Butler's, might be overestimated because of possible interferences with PCBs. For comparison purposes, 14 of Butler's sites that were sampled at least 7 years between 1965 and 1972 were recalculated on a dry weight basis by assuming a tissue water content of 85%. Farrington reported concentrations for DDT, expressed as DDE, in oysters from 10 sites sampled during 1976 and 1977. The individual contributions of DDT, DDD, and DDE to the average total DDT burden between 1965 and 1988 are shown in Figure 5. Average total DDT concentrations in oysters from the Gulf of Mexico peaked in 1968 and have been declining markedly since 1969, mainly because of the restriction applied to the use of DDT in the United States that led to its ban in 1972. Although the range of concentrations in oyster tissues encountered during the NS&T program overlaps those recalculated from Butler's data, the average concentrations were 2–10 times lower. Farrington's average concentrations for 1976 (19 ± 13 ng g^{-1}) and 1977 (11 ± 9.1 ng g^{-1}) were lower than the mean concentrations found during this study. This might, in part, be due to a methanol–KOH digestion step used during that survey, which quantitatively changed DDT to DDE and DDD to DDMU [1,1′-(2-chloroethenylidene)bis[4-chlorobenzene]]. The study only reported DDE. Assuming a contribution of DDD to the total DDT load similar to the percentage reported in this study, those total DDT concentrations can be recalculated as 37 ± 13 and 22 ± 9.1 ng g^{-1} for 1976 and 1977, respectively.

Figure 6 shows the average concentration distribution of total DDT in oysters for the 1965–1972 period. There is no evidence that any site has increased its mean concentration since Butler's study; however, a few sites have maintained their comparatively high concentrations (compare Figures 2 and 6). Schmitt et al. (*34*) suggested that heavy use of the acaricide dicofol [2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethanol] in the Southwest and other cotton-farming regions of the United States could be an important source of DDT since it might be contaminated with DDT at levels as high as 9% (*35*, *36*). It has also been suggested that DDT has been recently used in the lower Rio Grande Valley (*37*). Our data of sites near the U. S.–Mexico border, and those reported by Schmitt et al. (*34*), do not support this contention.

The average reduction observed in total DDT concentrations in Gulf of Mexico oysters between the 1965–1972 and 1986–1988 samplings is 77% (Table III). This decrease in the total DDT burden is very similar to the percent reduction calculated from the data reported for bivalves collected along the west coast of the United States as part of the NOAA's NS&T program (*38*) and the 1965–1972 survey (*27*). The observed reduction on the east coast was comparatively lower. The residues half-lifes range upward to 20 years in natural environments (*39*). An average half-life estimation of ~10 years for DDT residues within the biosphere as a whole has been reported (*40*). Therefore, if there were no new inputs of fresh DDT to the environment, the potential total DDT present in 1986–1988, i.e., 15 years after its ban, would be somewhere around 25–30% of the levels reported in the late 1960s and

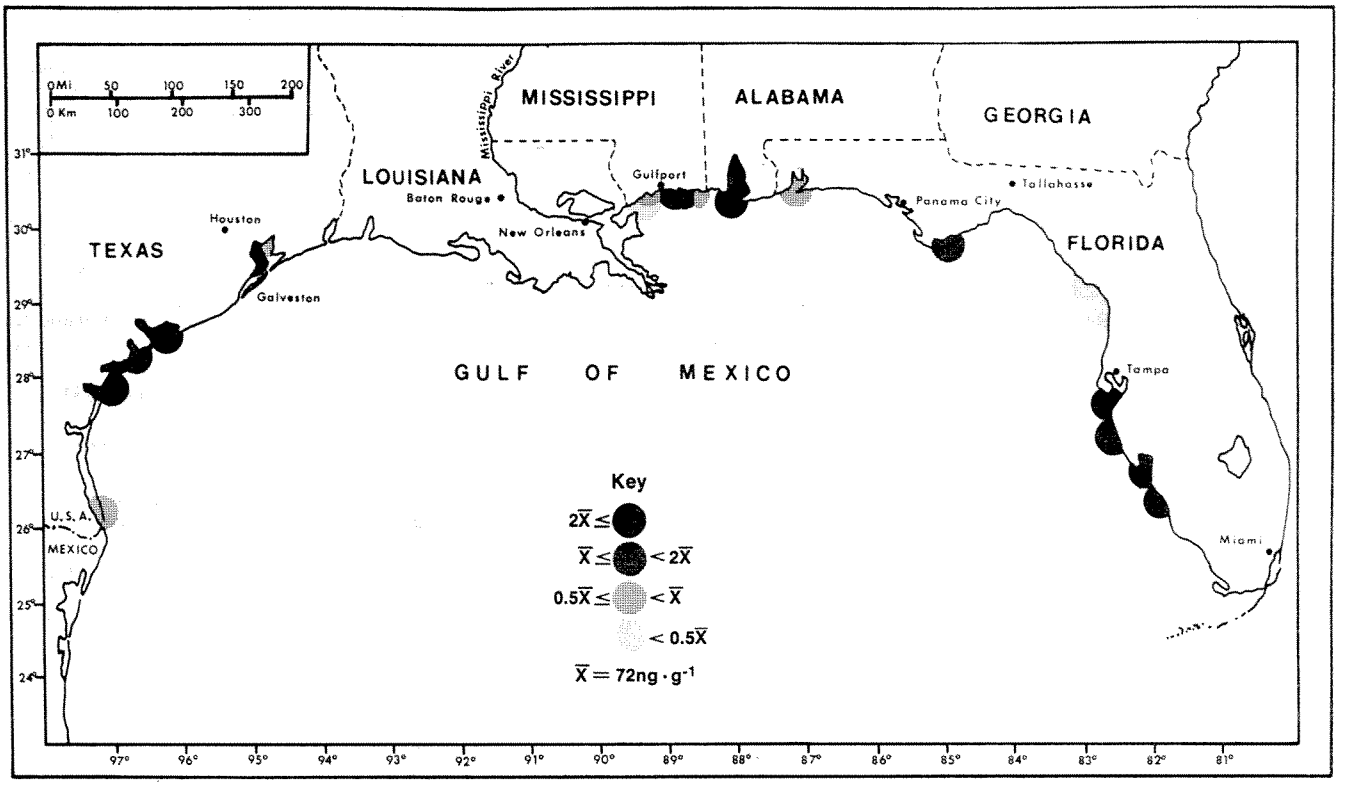

Figure 6. Geographic distribution of total DDT concentrations, 1965–1972.

Table III. Average Total DDT Concentrations[a] in Bivalves from the Gulf, West, and East Coasts of the United States during the 1965–1972 and 1986–1988 Sampling Surveys[b]

location	sample	sampling A	n	av total DDT	sampling B	n	av total DDT	ΔDDT, %	ref
gulf coast[c]	bivalve	1965–72	989	280	1986–88	479	64	−77	27, this study
west coast[d]	bivalve	1965–72	1467	670	1986–88	417	140	−79	27, 38
east coast[e]	bivalve	1965–72	5023	180	1986–88	462	89	−51	27, 38

[a] Concentrations (ng g^{-1}) on a dry weight basis. [b] Percent decrease between both sampling periods is indicated. [c] Alabama, Florida, Mississippi, and Texas. [d] California and Washington. [e] Delaware, Georgia, Maine, Marland, New Jersey, New York, North Carolina, South Carolina, and Virginia.

early 1970s. This is in good agreement with the percentages calculated for oyster samples collected along the Gulf and west coasts of the United States. The lower reduction rate in total DDT calculated for oysters from the east coast needs further evaluation. Rapaport et al. (*41*) suggested that atmospheric inputs of fresh DDT coming from Central American countries could be an important source of this pesticide and its derivatives to the northeastern and eastern regions of the United States.

Conclusions

In spite of the heavy restriction applied to the use of the DDT in the United States that led to its ban in 1972, this study demonstrates that DDT and/or its metabolites are still present, in significant concentrations, in the northern Gulf of Mexico coastal areas. The fact that DDTs were found in every sample analyzed during this study, with concentrations ranging over 2 orders of magnitude, indicates their continued availability to oysters. The Gulf of Mexico areas with the highest or lowest total DDT concentrations in oysters have been well identified after the first 3 years of the NS&T program. In contrast, the concentration trends at most of the sites could not yet be defined. Only a few sampling locations showed statistically significant monotonic increases or decreases in concentrations that could be considered as real trends with time. This is mainly because of the large intrasite variability observed in many sites compared with the relative short time period of this study. Continued sampling associated with the NS&T program will allow the observation of trends in total DDT concentrations.

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