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DDT, DDD, and DDE in Abiotic Media and Near-Shore Marine Biota from Sand Island, Midway Atoll, North Pacific Ocean

B. K. Hope,[1] S. Scatolini[2]

[1] Oregon Department of Environmental Quality, 811 SW Sixth Avenue, Portland, OR 97204-1390, USA
[2] California Department of Transportation, District 11, MS 46, Post Office Box 85406, San Diego, CA 92186-5406, USA

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Midway Atoll is located in the North Pacific Ocean 1,320 kilometers northwest of Pearl Harbor, Hawaii, at approximately 177° 22' W longitude, 28° 11' N latitude. The atoll consists of two main islands, Sand and Eastern, surrounded by a fringing coral reef. Although heavily modified by human activity, the islands provide breeding and feeding habitat for more than one million migratory seabirds; a total of 45 migratory bird species have been recorded at the atoll. The atoll came under the control of the United States Fish and Wildlife Service in May 1996. As a result of its historical use in industrialized countries and its continued use in the rapidly industrializing countries of low-latitude tropical and subtropical Asia and Oceania, DDT has entered and is still being released into the global environment. It has been measured in seawater along the route followed by the Kuroshio current from the low-latitude rapidly industrializing regions, past the Northwestern Hawaiian Islands (including Midway Atoll), and northward into the Gulf of Alaska and the Bering Sea (Iwata et al. 1994). This suggests that Midway Atoll may be receiving ambient environmental DDT exposures from atmospheric deposition and ocean surface water circulation.

Although considerable work has been directed at DDT in higher trophic level consumers at Midway Atoll, primarily albatrosses, little has been done on abiotic media or organisms lower in the food chain (Auman et al. 1997). Thus this study measured the concentration and distribution of *o,p'*-DDT (1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane), *p,p'*-DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane), *o,p'*-DDD (1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane), *p,p'*-DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane), *o,p'*-DDE (1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorphenyl) ethylene), and *p,p'*-DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene) in marine sediment, surface water, and tissues of twelve species of near-shore marine biota, specifically: two macroalgaes (*Dictyota acutiloba*; *Giffordia breviarticulata*), a sea grass (*Halophila ovalis*), a bivalve mollusk (*Chama iostoma*), a sea urchin (*Echinometra mathaei*), a snail (*Nerita picea*), two holothurians (*Bohadschia obesus*; *Holothuria atra*), and four fishes: striped convict tang (*Acanthurus triostegus*), goatfish (*Mulloidichthys flavolineatus*), Pacific gregory (*Stegastes fasciolatus*), and blacktail wrasse (*Thalassoma ballieui*).

Correspondence to: B. K. Hope

MATERIALS AND METHODS

Samples of marine sediment were collected from locations in nearshore areas around Sand and Eastern Islands using horizontal and vertical cores. Sediment, water, and biota samples were collected subtidally. Seawater samples were also collected from locations in nearshore areas around Sand and Eastern Islands. Organisms collected for tissue analysis were selected based on trophic level, specificity of location, and availability. The goal was to collect representatives from a wide range of trophic levels, especially species that may be prey for higher trophic level consumers (Hope et al. 1997). Resulting samples were homogenized in decontaminated stainless steel bowls, placed in new, laboratory-certified clean glass jars, sealed, cooled to 4°C, and shipped to the laboratory for analysis of the *o,p'*- and *p,p'*- isomers of DDT, DDD, and DDE.

Analysis of total DDT (ΣDDT) was performed by Arthur D. Little, Inc., (ADL) Cambridge, Massachusetts. Low-level ΣDDT analysis was performed in accordance with the National Oceanic and Atmospheric Administration's Status and Trends Program Methods ST IV 141E (Lavenstein and Cantillo 1993, Sericano et al. 1990). In preparation for low level analyses for DDTs, seawater samples were extracted with methylene chloride in a separatory funnel. This extract was dried with sodium sulfate, concentrated, and an aliquot of the sample weighed. Sediment samples were spiked with surrogate compounds and then extracted with a solution of methylene chloride/acetone (1:1 ratio) using a sonication/shaking technique, then dried with sodium sulfate, followed by concentration, centrifugation, and weighing. Tissue samples were homogenized, an aliquot removed, weighed, and placed in a Teflon® jar, after which they were dried with sodium sulfate and spiked with surrogates. Samples were then serially extracted with methylene chloride, the solvent and matrix having been mixed through maceration; the extract was then concentrated for cleanup and fractionation. Total extractable (lipid) weight was calculated as part of the cleanup process. Sediment, surface water, and tissue sample extracts were all analyzed using gas chromatograph-electron capture detector (GC-ECD) instrumentation.

Method detection limits were determined in accordance with U.S. Environmental Protection Agency criteria (40 CFR 136, Appendix B). The gas chromatograph was calibrated prior to DDT, DDD, and DDE analyses, then daily or after every 10 samples analyzed. Concentrations of all analytes were determined relative to that of the internal standard spiked just prior to analysis. Recovery of surrogates were also determined relative to the internal standard. Individual compounds were then identified by their retention time in the gas chromatograph, and the concentration of each analyte computed on the basis of sample volume or weight. A complete set of quality control (QC) samples was analyzed with each analytical batch (one batch per matrix). QC samples included procedural blanks, laboratory control samples (LCS), and standard reference materials (National Institutes of Standards and Technology SRM 1941 for marine sediment and SRM 1974 for

mussel tissue). No analytes were detected in the procedural blanks. Recoveries for LCS samples ranged from 95% to 117%; those for SRM samples approached 100%. Sample quantification limits (SQLs) were 0.0002 μg L^{-1} for seawater, 0.015 μg kg^{-1} for sediment, and 0.06 μg kg^{-1} for tissues. All data were validated to Naval Energy and Environmental Support Activity (NEESA) Level D criteria.

RESULTS AND DISCUSSION

For statistical purposes, if at least one sample in a data set (i.e., analyte in a media or species) was reported above the SQL, values in that data set reported as below the limit of quantification ("U" qualified data) were included in statistical analyses at one-half their SQL (USEPA 2002). Arithmetic mean concentrations (± 1 mean standard error (MSE)) are summarized in Table 1.

Table 1. Summary of DDT, DDD, and DDE concentrations

Media / Species	N	*o,p'*- DDT	*o,p'*- DDD	*o,p'*- DDE	*p,p'*- DDT	*p,p'*- DDD	*p,p'*- DDE
Surface water †	30	0.0002 ± 0.00004	<0.0002 ‡	<0.0002 ‡	0.0004 ± 0.00003	0.0003 ± 0.00004	0.0001 ± 0.00001
Sediment †	79	0.3 ± 0.1	0.6 ± 0.3	0.1 ± 0.03	0.8 ± 0.4	1.2 ± 0.6	1.2 ± 0.5
D. acutiloba †	8	nd §	2.8 ± 0.6	nd	nd	1.0 ± 0.1	0.6 ± 0.1
G. breviarticulata	4	0.5 ± 0.2	1.7 ± 1.2	nd	nd	2.9 ± 1.7	2.1 ± 0.7
H. ovalis	6	nd	0.9 ± 0.7	nd	nd	nd	0.6 ± 0.1
B. obesus	7	7.3 ± 4.6	20.8 ± 12.4	2.1 ± 1.3	0.2 ± 0.02	2.7 ± 1.9	22.8 ± 12.6
C. iostoma	10	0.5 ± 0.2	1.1 ± 0.2	nd	nd	0.9 ± 0.06	1.5 ± 0.2
E. mathaei	13	nd	0.3 ± 0.1	0.2 ± 0.2	nd	0.6 ± 0.4	0.9 ± 0.2
H. atra	7	nd	nd	nd	nd	nd	0.7 ± 0.1
N. picea	2	0.3 ± 0.3	0.3 ± 0.1	nd	0.6 ± 0.5	0.4 ± 0.1	1.1 ± 0.6
A. triostegus	4	0.9 ± 0.5	nd	nd	nd	5.6 ± 1.6	4.7 ± 1.4
M. flavolineatus	2	55.1 ± 54.9	nd	nd	nd	55.5 ± 54.5	165.8 ± 164.3
S. faciolatus	7	2.2 ± 1.4	3.6 ± 2.4	nd	5.5 ± 2.1	90.0 ± 83.4	116.8 ± 78.5
T. ballieui	3	nd	0.6 ± 0.4	nd	1.6 ± 1.3	2.2 ± 0.9	29.1 ± 14.2

† Units are μg L^{-1} for surface water and μg kg^{-1} (dw) for sediment and tissues.
§ No detections above the sample quantification limit (SQL).
‡ No samples above the SQL; value is SQL given detection in biota.

Data sets which did not include any samples reported above the SQL were considered to be "non-detects" and statistical analyses were not performed on them. Because DDT and its metabolites have been shown to cumulatively increase (i.e., biomagnify) in successively higher trophic levels of aquatic food chains (Leblanc 1995), an exception was made for *o,p'*-DDD and *o,p'*-DDE. Here, because of their detection in biota, their presence in surface water was assumed at one-half the SQL, or 0.0001 μg L^{-1}; no such assumption was made for sediment or biota.

Tissue and surface water concentrations are typically related through a bioconcentration factor (BCF), the ratio of chemical concentration in an organism to chemical concentration in water at equilibrium, where uptake occurs directly from water alone, or: $BCF = C_t / C_{sw}$, where: BCF = bioconcentration factor (L kg^{-1}), C_t = Mean tissue concentration (μg kg^{-1}, dry weight), C_{sw} = Mean surface water concentration (μg L^{-1}). There are numerous estimates of BCF values for DDT and its metabolites in various aquatic species in freshwater and marine ecosystems, ranging from 41 to 700,000 (cited in ATSDR 2002). BCF values measured at Midway are within range of those reported previously (Table 2). Unusual departures (e.g., (*Mulloidichthys*, *Stegastes*) may be attributable to the relatively high concentrations of DDT in nearshore waters at Midway (4×10^{-3} μg L^{-1} versus a mean of 1.2×10^{-6} μg L^{-1} measured by Iwata *et al.* (1994) in open water), differences between laboratory and field conditions, or other unknown environmental factors. In the natural environment, tissue residues are reflective of an organism's exposure to chemicals both in the water they respirate and from food they ingest, whereas in the laboratory, exposure is only through respiration.

In surface water, *p,p'*-DDT is proportionally the largest component (42.8%) of the total load, followed by *p,p'*-DDD (27.4%) and *o,p'*-DDT (20.8%). Together, DDT isomers comprised the majority (≈ 63%) of the total load. In biota, however, DDT is infrequently detected and *p,p'*-DDE is the dominant isomer, reaching ≈ 87% of total load in *Thalassoma* and 100% in *Holothuria*. Previous investigations have noted that, of DDT and its metabolites, DDE residues are usually highest and are found most frequently in environmental samples, particularly at higher trophic levels (Blus 1995). Here, as has been reported elsewhere, the majority of ΣDDT in fish is *p,p'*-DDE (Schmitt *et al.* 1990). This observed increase in DDE could be due to the presence of metabolic pathways in higher trophic level species that more readily transform DDT to DDE, coupled with DDE being a stable end product incapable of further degradation (ATSDR 2002).

Concentrations of contaminants in sediment are used as a surrogate for characterizing the exposure of fish to compounds found in water and the food they ingest, because concentrations of neutral organic compounds found in water and prey items are expected to be proportional to those found in sediment (Di Toro et al. 1991). Tissue and sediment concentrations are typically related through a

biota-sediment-accumulation factor (BSAF), calculated as: BSAF = (C_t / f_L) / (C_s / f_{OC}), where: C_t = Mean tissue concentration (μg kg^{-1}, dry weight), f_L = Lipid fraction (unitless), C_s = Mean sediment concentration (μg kg^{-1}), and f_{OC} = Organic carbon fraction, (0.01, unitless; default value). BSAF values estimated at Midway (Table 2) are within the range of those reported by others, for both freshwater and marine ecosystems (USACE 2004).

Table 2. Summary of BCF and BSAF values

Species		*o,p'*- DDT	*o,p'*- DDD	*o,p'*- DDE	*p,p'*- DDT	*p,p'*- DDD	*p,p'*- DDE
D. acutiloba	*BCF*	---[§]	14,175	---	---	3,357	5,943
	BSAF	---	3.0	---	---	0.5	0.3
G. breviarticulata		1,987	8,350	---	---	9,675	20,930
		0.8	1.0	---	---	1.0	1.0
H. ovalis		---	4,625	---	---	---	5,897
		---	1.8	---	---	---	0.7
B. obesus		31,990	103,993	10,536	390	8,919	226,744
		1.8	2.3	2.9	0.1	0.2	1.5
C. iostoma		1,993	5,548	---	---	3,026	15,090
		4.8	3.7	---	---	2.8	3.2
E. mathaei		---	1,490	1,061	---	1,868	8,426
		---	2.31	35.70	---	1.69	3.10
H. atra		---	---	---	---	---	6,927
		---	---	---	---	---	0.22
N. picea		1,485	1,263	---	1,282	1,298	10,415
		3.0	1.1	---	1.8	0.9	2.4
A. triostegus		3,821	---	---	---	18,481	46,844
		0.2	---	---	---	0.3	0.2
M. flavolineatus		240,666	---	---	---	183,490	1,651,993
		14.39	---	---	---	3.44	10.44
S. faciolatus		9,473	17,979	---	11,613	297,756	1,163,977
		0.7	0.5	---	0.5	3.1	4.4
T. ballieui		---	3,183	---	3,274	7,277	289,701
		---	0.2	---	0.6	0.4	4.4

[§] --- = No detections above the SQL.

Others have noted consistent proportional relationships between DDT concentrations and lipid content, but with concentrations also varying in response to food chain length (Bentzen et al. 1996). Regression of lipid fraction against ΣDDT tissue residue concentrations for individual samples suggests that, at Midway, ΣDDT residues increase non-linearly with increases in an organism's lipid fraction. Food web influences were further explored by organizing the twelve species into six groups (on the basis of trophic position, feeding guild, and

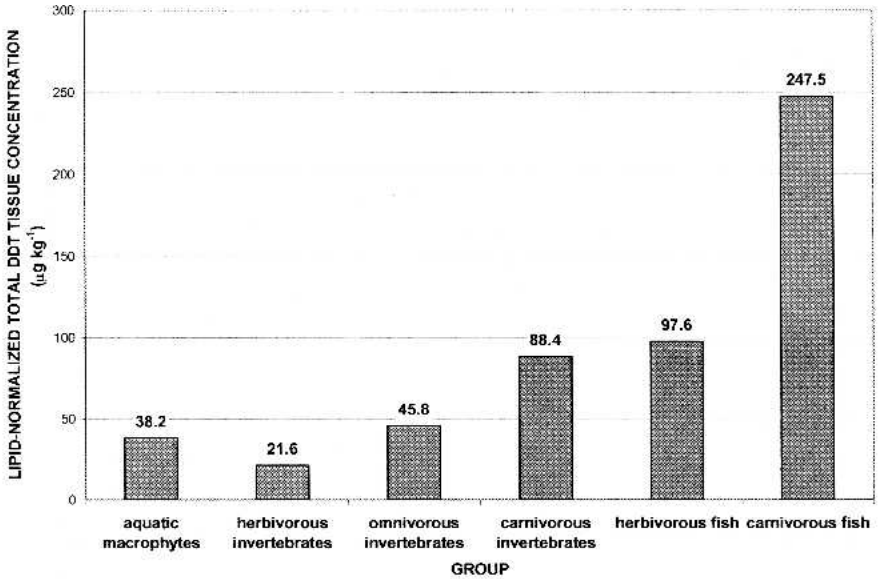

Figure 1. Relationship of trophic group to ΣDDT residues.

taxonomic classification), then calculating and comparing lipid-normalized mean ΣDDT tissue residue values for each group. The six groups were: aquatic macrophytes (*D. acutiloba*; *G. breviarticulata*, *H. ovalis*), herbivorous invertebrates (*E. mathaei*), omnivorous invertebrates (*C. iostoma*, *B. obesus*, *H. atra*), carnivorous invertebrates (*N. picea*), herbivorous fish (*A. triostegus*, *S. fasciolatus*), and carnivorous fish (*M. flavolineatus*, *T. ballieui*). As shown in Figure 1, the ΣDDT tissue residue concentration appears to increase with presumptive increases in trophic position, following normalization for increases in lipid fraction.

However, the influence of other environmental factors (e.g., variations in habitat and food preferences, foraging strategy, etc.) on DDT accumulation, while not examined in this study, cannot be discounted. Herbivores (*E. mathaei*, *A. triostegus*, *S. fasciolatus*) and omnivores (*B. obesus*, *H. atra*) may graze to some extent on algae species (*D. acutiloba*; *G. breviarticulata*) or sea grass (*H. ovalis*). *Dictyota* contains alkaloids that discourage grazing on its own tissues but may support epiphytic algae that are consumed by fish. The carnivorous fish *M. flavolineatus* preys primarily on benthic invertebrates which may include *N. picea*. *T. ballieui* preys on urchins, crabs, small fish, gastropods, damselfish eggs, and other crustaceans. It may also prey on the eggs or young of *A. triostegus*, *S. fasciolatus*, or *M. flavolineatus*. The omnivorous bivalve mollusk (*C. iostoma*) is a potential prey item for the carnivorous snail (*N. picea*). It is unlikely that either of the two holothurians serve as a food source for any of the other ten species.

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