RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Corbiculas Anodonta

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Chlorinated Pesticides and Polychorinated Biphenyls in Marine Species, Oregon/Washington Coast, 1972 ¹

Robert R. Claeys, Richard S. Caldwell, Norman H.-Cutshall, and Robert Holton

ABSTRACT

Concentrations of chlorinated pesticides and polychlorinated biphenyls (PCB's) were determined in three offshore marine species from the Oregon/Washington coast: pink shrimp, euphausiids, and flatfish; five species of bivalve mollusks from five estuaries along the Oregon coast; several fish species from the Coos Bay and Columbia River estuaries; and a summer run of steelhead from the Rogue River.

The compounds p,p'-DDE and PCB's were detected most frequently. Euphausiids and pink shrimp contained approximately 2 ppb (µg/kg) wet-weight DDE and 8 and 25 ppb-PCB's, respectively. Offshore flatfish contained an average of 9 ppb DDE and 29 ppb PCB's. DDE residues in estuarine mollusks approximated 0.5 ppb. PCB levels were not detectable (<3 ppb) except in collections from the mouth of the Columbia River where levels averaged 400 ppb PCB's and 17 ppb DDT. Selected Columbia River fish species contained 38 ppb DDE and 480 ppb PCB's; summer-run steelhead in the Rogue River contained 97 ppb DDE and 125 ppb PCB's.

PCB chromatograms of most euphausiids closely resembled those of Aroclor 1254. Chromatograms of shrimp and flat-fish indicated selective metabolism of two compounds in the Aroclor 1254 formulation. Biphenyls of higher chlorine content were also detected in the shrimp and flatfish.

Introduction

A global program to determine baseline levels of metals, hydrocarbons, and chlorinated hydrocarbons was initi-

ated in 1971 by the International Decade for Ocean Exploration (IDOE) Program of the National Science Foundation. Baseline data for chlorinated hydrocarbons in the North Pacific Ocean are reported here. In addition, baseline levels in mollusks were determined in several Oregon estuaries as part of the National Estuarine Monitoring Program. Several species of fish were collected from two of these estuaries along with some summer-run steelhead (Salmo gairdnērii), a type of rainbow trout, from the Rogue River. Chlorinated hydrocarbon levels obtained under the IDOE Program from the Atlantic Ocean (1) and the Gulf of Mexico (2) surveys have already been published.

Sampling and Analytical Procedures

Pink shrimp (Pandalus jordani), euphausiids (Euphausia pacifica), and several species of flatfish were collected at ocean stations from Newport, Oreg., to the Straits of Juan de Fuca during September and October 1971 (Fig. 1). An otter trawl and an Isaacs-Kidd midwater trawl were used in these collections.

Estuarine bivalves were collected quarterly from December 1971 through October 1972 in five Oregon estuaries: Columbia River, Tillamook Bay, Yaquina Bay, Umpqua River estuary, and Coos Bay (Fig. 1). Species collected were the cockle clam (Clinocardium nuttallii), Eastern softshell clam (Mya arenaria), bay mussel (Mytilus edulis), Asiatic clam (Corbicula fluminea), and a species of Anodonta. The latter two species inhabit only fresh water and were the most abundant mollusks in the Columbia River; estuarine clams were not readily available. In addition, several species of estuarine fish were collected in the Coos Bay and Columbia River estuaries during January 1973 and

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Research conducted under National Science Foundation International Decade of Ocean Exploration Grant 6X28744, National Marine Fisheries Contract N-042-14-72(N), and U.S. DHEW Public Health Service Grant ES00040.

² Environmental Health Sciences Center, Oregon State University, Corvallis, Oreg. 97331.

Marine Sciences Center, Oregon State University, Newport, Oreg.
 Department of Oceanography, Oregon State University, Corvallis, Oreg.

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August 1972, respectively; summer-run steelhead were obtained from the Rogue River in September 1970. Except for the steelhead, samples were frozen in glass jars washed with acetone. Special care was taken to avoid contamination because of the possible presence of polychlorinated biphenyls (PCB's) about ship.

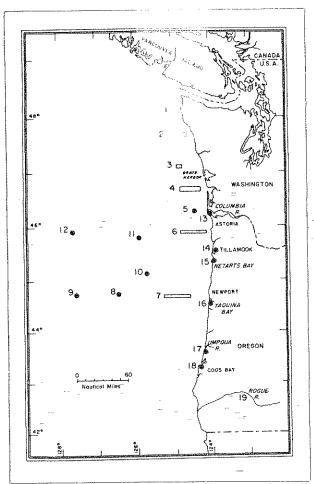


FIGURE 1. Stations on Oregon/Washington coast sampled for residues in marine species

Analytical procedures were similar to those of Porter et al. (3) except for hexane-acetonitrile partitioning; for that, analysts followed the method of Giuffrida et al. (4). Briefly, the shrimp, euphausiids, and small fish were ground whole in a meat grinder and a subsample not exceeding 3 g lipid or 100 g tissue was taken for analysis. Steelhead were analyzed individually by taking a cross section posterior to the anal opening. Mollusks were prepared and extracted as described by Butler (5). They were ground with a desiccant mixture of 10 percent QUSO (precipitated silica) and 90 percent anhydrous sodium sulfate. The sample and desiccant were mixed at an exact ratio of 1:3 by weight before taking a 120-g subsample. Fish and shrimp were extracted in a blendor with 2:1 hexane:acetone (v/v) and mollusks were extracted by Soxhlet with 1:1 hexane:acetone. A 25- 50-g sample was extracted, the solvent evaporated, and the residue weighed for an approximate lipid content.

Approximately 90 percent of the lipid was separated from the organochlorines by chromatographic column elution (4). The extract was evaporated under a stream of air and the lipid residue was mixed with florisil and loaded on a dry-packed florisil column. Pesticides were then eluted with 9:1 acetonitrile:water and partitioned into hexane after aqueous dilution. Additional cleanup was obtained on a second florisil column. PCB's, DDT, BHC, chlordane, mirex, and toxaphene compounds were eluted from the second column with 5 percent benzene in hexane (v/v). Dieldrin, endrin, heptachlor epoxide, and methoxychlor were eluted with hexane containing 10 percent ethyl ether and 0.25 percent acetone (v/v).

Major PCB isomers were separated from pesticides by a modification of the procedure of Armour and Burke (6) by substituting a 1 percent water deactivated silicic acid column. The 4-10 chloro PCB compounds were eluted with hexane and the 1-3 chloro PCB's and pesticide compounds were eluted with 5 percent aqueous methanol. Pesticides were partitioned into hexane after aqueous dilution of the methanol.

Compounds were normally separated and quantitated by gas-liquid chromatography on 122-cm-by-3-mm-ID pyrex columns filled with a 2:1 mixture of 7 percent QF-1 and 7 percent DC-11 liquid phases on high-performance chromosorb W, 100/120 mesh, or with 7 percent DC-11. Columns were operated at 195° C with 20 ml/min N₂ flow. The flow rate employed was 1.5 times the optimum rate for maximum PCB resolution. Both electron-capture and microcoulometric-halide detectors were employed. Sensitivity of the microcoulometric detector was 1-3 ng dieldrin or DDE.

Base hydrolysis was used to confirm the presence of DDD and DDT in selected samples by conversion to DDE and DDMU, respectively (7). PCB's remain stable although the α and γ BHC isomers are destroyed during this procedure. A 1:1 fuming HNO₃:concentrated sulfuric acid nitration test (8) was used to confirm the presence of chlordane and toxaphene; these are the only compounds which are not nitrated.

Special precautions were employed to improve analysis of low pesticide concentrations. Glassware was baked at 250°-300° C in a large oven (9) and other items such as glass wool, sodium sulfate, and florisil were baked at 450° C in a muffle furnace to reduce blank levels. In addition, blanks were analyzed before any samples were begun.

For PCB quantitation peak heights of the sample and standard were added. When peaks were missing, a zero was included in the summation. For two different reasons PCB values may be low no attempt was made to identify 8-10 chloro biphenyls; and 1-3 chloro biphenyls elute with the pesticide fraction from the silicic acid column.

Selected samples were spiked with known standards prior to extraction at a concentration of 10 higher than that previously analyzed. Mean recoveries were 75 percent for DDE, 63 percent for DDT, 83 percent for dieldrin, and 100 percent for Aroclor 1260 when silicic acid column separation of PCB's was employed (10). Recoveries from the silicic acid column were only 85 percent for DDE and DDT, thus accounting for low DDT recovery. Mean recovery of DDE for mollusks

was 92 percent without silicic acid column separation. Values reported here are uncorrected for recovery or blank levels, except for mollusks, in which case blank levels were subtracted.

Results

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Levels of chlorinated hydrocarbons in offshore species, estuarine fish, and Rogue River steelhead are given in Tables I and 2; offshore results are summarized in Table 3. Most of these data were presented in 1972 at a workshop of the International Decade of Ocean Exploration (10).

TABLE 1. Chlorinated hydrocarbon concentrations in marine species, Washington/Oregon—1972

| Species | | CONCENTRATION, μG/KG WET WEIGHT | | | | | | | |
|---|---|--|---|---|--|--|--|--|--|
| Funhauria pusi6 | | p.p'-DDE | p,p'-TDE | P,P'-DDT | TOTAL DDT | PCB' | | | |
| Euphausia pacifica Pandalus jordani Flatfish senus and species unknown) Blanks | Samples analyzed Samples with residues Mean Range Samples analyzed Samples with residues Mean Range Samples analyzed Samples with residues Mean Range Samples with residues Mean Range Samples with residues Mean Range Samples analyzed Samples with residues Mean Range | 14 14 2.2 0.2-5.8 13 1.9 0.9-3.7 13 13 8.5 3.4-18 11 11 0.06 0.02-0.13 | 14 5 0.2 0-0.6 13 8 0.3 0.2-1.0 13 12 1.0 0.7-1.7 11 5 0.03 0-0.12 | 14 5 0.6 0-4.0 13 8 0.5 0.2-3.0 13 12 1.0 0.6-2.0 11 4 0.03 0-0.10 | 14 14 3.0 0.2-5.9 13 13 2.7 1.1-5.0 13 10.5 4-19.7 9 7 0.12 0-0.25 | 11 11 7.5 - 1-22 13 13 25 11-69 10 29 16-12 9 7 <2 0-4 | | | |

TABLE 2. Chlorinated hydrocarbons in selected marine species collected off Oregon/Washington coast, September 1971

| SAMPLING LOCATION: STATION LATITUDE, LONGITUDE | LOCATION; | | Concentration, $\mu G/K G$ wer weight | | | | | | | | |
|--|---------------------|----------|---------------------------------------|---|----------|---------|--|------|--|--|--|
| | p,p'-DDE | p,p'-TDE | 1 | TOTAL DDT | DIELDRIN | AROCLOR | AROCLOR | | | | |
| | | Eur | hausia pacij | | | | 1254 | 1260 | | | |
| 7 | 44° 39′ 124° 31′ | 1.0 | 0,6 | 0.9 | | | | 1 | | | |
| 7 | 44° 43′ 124° 41′ | 5.8 | 210 | 0.9 | 3 | | 5 | | | | |
| 7 | 44° 39' 124° 52' | 4.5 | | | 6 | | 5 | | | | |
| 7 | 44° 41′ 125° 09′ | 1.1 | | | 5 | | 6 | | | | |
| 7 | 44° 39' 125° 14' | | | | 1 | | 8 | 3 | | | |
| 8 | 44° 43′ | 3.3 | | | 3 | | | . 3 | | | |
| 8 | 126° 29′ 44° 43′ | 2.6 | | - | 3 | | 22 | | | | |
| 9 | 126° 29′ 44° 43′ | 0.8 | | | 1 | ł | 8 | | | | |
| | 127° 35′ 45° 10′ | 1.0 | | | 1 | Ì | 25 | 5 | | | |
| 10 | 125° 39′ | 1.1 | | | 1 | | 4 | 3 | | | |
| 11 | 45° 46′ 125° 49′ | 2.3 | 0.1 | 0.5 | 3 | | - | | | | |
| 12 | 45° 56′ 127° 40′ | 3.3 | 0.4 1 | 0.5 1 | 4 | | | 13 | | | |
| 5 | 46° 21′ 124° 27′ | 1.8 | 1 | | | | At the second se | 1 | | | |
| 4 | 46° 31′ 124° 30′ | 0.2 = | | *************************************** | 2 | | 4 | • | | | |
| ontinued next | | | 1 | | 0.2 | | NA | | | | |

TABLE 2 (cont'd.). Chlorinated hydrocarbons in selected marine species collected off Oregon/Washington coast, September 1971

| Sampling | LOCATION: | CONCENTRATION, μG/KG WET WEIGHT | | | | | | | | |
|----------|------------------------|---------------------------------|---------------|----------|-----------|---|-----------------|-------------|--|--|
| STATION | LATITUDE, LONGITUDE | p,p'-DDE | p,p'-TDE | p,p'-DDT | TOTAL DDT | Dieldrin | AROCLOR 1254 | AROCLO | | |
| 4 | 46° 41′ 124° 46′ | 2,1 2 | 0.6 2 | 3 2 | 7 | 5 2 | NA | | | |
| 3 | 47° 11' 124° 48' | 1.3 1 | 0,6 1 | 4 1 | 6 | 4 3 | NA | | | |
| | | Pa | ndalus jordan | i i | | | l | L | | |
| 7 | 44° 39′ 124° 35′ | 2.4 | 0.7 | 0.3 | 3 | | 9 | 10 | | |
| 7 | 44° 43′ 124° 41′ | 3.7 | 0.2 | 0.3 | 4 | | 11 | | | |
| 6 | 45° 55′ 124° 14′ | 1.1 | | | 1 | | 12 | | | |
| 6 | 45° 55′ 124° 28′ | 1.2 | | | 1 | | 36 | 8 | | |
| 6 | 45° 56′ 124° 41′ | 2.0 | | | 2 | | 9 | | | |
| 5 | 46° 21′ 124° 27′ | 0.9 | 0,5 | 0.3 | 2 | | 35 | 10 | | |
| 4 | 46° 37′ 124° 26′ | 2.5 | 0.3 | 0.2 | 3 | | _33 | | | |
| 4 | 46° 39′ 124° 39′ | 1.4 | | | 1 | _ | 14 | | | |
| 4 | 46° 41′ 124° 37′ | - 1.8 | . 0,4 | 0.6 | 3 | | 16 | e. | | |
| 3 | 47° 06′ 124° 41′ | 1.9 | 1.0 | - | 3 | | 19 | 50 | | |
| 3 | 47° 06′ 124° 47′ | 1,0 | 0.5 | 0.2 | 2 | | 15 | | | |
| 3 | 47° 11' 124° 48' | 2.0 2 | | 3 2 | 5 | | 44 | | | |
| 2 | 47° 39' 125° 05' | 3.0 | 0.3 1 | 1.1 1 | 4 | | 20 | | | |
| | | s | AND SHRIMP | | | *************************************** | l | | | |
| 6 | 45° 55′ 124° 14′ | <1.3 | | | 1 | | ND | | | |
| 2 | 47° 39' 124° 36' | <0.3 | | | | | 7 | | | |
| 2 | 47° 40' 124° 54' | 1.1 | 0.3 | 0.3 | 2 | | 28 | | | |
| 1 ~ | 48° 06′ 124° 51′ | | | - | | ~ | - 6 | | | |
| | | SER | GESTID SHRIMI | P | | | | | | |
| 7 | 44° 43′ 124° 41′ | 25 | | 4,1 | 29 | | 17 | | | |
| | | GAL | ATHEA SHRIMI | P | | I | | | | |
| 4 | 46° 41′ 124° 37′ | 1.4 | | | 5 | | 5 | | | |
| | | | Flatfish | | | | <u> </u> | | | |
| 6 | 45° 54′ 124° 02′ | 6.4 | 0.7 | 1.1 | 8 | | ND | 12 | | |
| 6 | 45° 55′ 124° 14′ | 10.4 | 1.0 | 1.1 | 13 | | 52 | | | |
| 6 | 45° 56′ 124° 12′ | 10 2 | <3 2 | <5° | 18 | | NA | | | |
| 6 | 45° 55′ 124° 28′ | 12.6 | 0.9 | 0.8 | 14 | | 24 | | | |
| 6 | 45° 56' 124° 41' | 12.7 | 1.7 1 | 1.8 1 | 25 | *************************************** | 28 | | | |
| 4 | 46° 37′ 124° 14′ | 11.0 | 1.81 | 2.0 1 | 15 | | 85 | 36 | | |
| 4 | 46° 37′ 124° 26′ | 3.4 | 1.0 | 1.2 | 6 | | 25 | | | |
| 2 | 47° 28′ 124° 41′ | 6.7 | 1.0 | 1.5 | 9 | | 28 | | | |
| | 47° 39′ | | | | | | ŀ | | | |

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TABLE 2 (cont'd.). Chlorinated hydrocarbons in selected marine species collected off Oregon/Washington coast, September 1971

| Sampling Station | LOCATION: | | | CONCENT | RATION, μ G/KG | WET WEIGHT | | |
|---------------------|------------------------|----------|---------------|-----------|--------------------|---|-----------------|----------------|
| | Latitude, Longitude | p,p'-DDE | p,p'-TDE | p,p'-DDT | TOTAL DDT | DIELDRIN | Aroclor 1254 | Aroclo 1260 |
| 2 | 47° 39′ 124° 36′ | 5.7 | NA | ÑΑ | 6 | | 12 | |
| 2 | 47° 40′ 124° 54′ | 10.0 | 0.6 | 0.7 | 17 | | 18 | |
| 2 | 47° 41′ 124° 46′ | 5.7 | 0.9 | 0.7 | 7 | | 16 | |
| 2 | 47° 39′ 125° 05′ | 17.4 | 0.8 | 0.9 | 19 | | 30 | |
| 2 | 47° 39′ 125° 05′ | 16.6 | 0.8 | 0.9 | 18 | | 18 | |
| 2 | 47° 39′ 125° 05′ | 20.0 | NA | NA | 20 | American Property of the Control of | 21 | |
| 1 | 48° 06′ 124° 51′ | 4.3 | 0.8 | 0,9 | 6 | المعران | 16 | |
| | | | SALPA | l | Ł., | <u> </u> | 1 | |
| 9 | 44° 43′ 127° 35′ | 0.1 | | | - | - | 20 _ | |
| | | Clupe | a harengus pa | llasii | | , | · , | |
| 4 | 46° 37′ 124° 14′ | . 19- | 4.0 | 1.6 | 25 | | <u>.</u> 146 | |
| | * | | SMALL FISH | de manual | 1 | | | |
| 1 | 48° 12′ 124° 56′ | 107 | 2 1,2 | 6 1.2 | 115 | 3 1.2 | NA | |

NOTE: NA = not analyzed.

ND = no data because of interference with analytical process.

Blank spaces imply residues below detectable levels.

Representative Euphausia pacifica sample contained 1.8 percent lipid; Pandalus jordani, 2.0 percent; sand shrimp, 2.4 percent.

Alcoholic base hydrolysis.

² Microcoulometric detector confirmation.

TABLE 3. Chlorinated hydrocarbons in estuarine fish and Rogue River steelhead, 1970-73

| • | | - | | | | | |
|--|------------|----------------|---------------|----------------|-----------|--------------|---|
| Species | | | Concentr | ATION, µG/KG W | ET WEIGHT | | |
| Jrecies | p,p'-DDE | p,p'-TDE | p,p'-DDT | TOTAL DDT | Dieldrin | Aroclor 1254 | Aroclor 126 |
| | Coos Ba | y Estuary, Jan | UARY 1973, ST | ATION 18 | I | | ······································· |
| Striped Seaperch (Embiotoca lateralis) | 5 - | | | 5 | | 23 1 | - |
| and Sole (Psettichthys melanostictus) | 7 | | | 7 | | 263 | |
| Staghorn Sculpin (Leptocottus armatus) | 3 | | | 3 | | 14 1 | 1 |
| Starry Flounder (Platichthys stellatus) | 6 | | | 6 | | | 27 1 |
| Blank | 0.02 | | | 0.02 | NA | 2 | |
| Percent recovery of sample | | | | | | | |
| spiked at 17 ppb | | | 87 | | 81 | | |
| | COLUMBIA R | iver Estuary, | August 1972, | STATION 13 2 | · | <u> </u> | * |
| Starry Flounder (Platichthys stellatus) | 18 | 8 | 8 | 34 | 310 | | |
| Fom Cod (Microgadus proximus) | | | | | 90 | | |
| Peamouth Chub (Mylochilus causinus) | 81 | 62 | | 143 | 1160 | | |
| Finescale Sucker (Catostomus syncheilus) | 14 | 28 | 11 | 53 | 350 | | |
| Blank | <1 | <1 | <1 | | <1 | | |
| | South Ro | GUE RIVER, SEP | TEMBER 1970, | STATION 19 | L | <u> </u> | |
| Steelhead (Salmo gairdnerii) 3 | | | l | | | | T |
| 2 6 | 73 | | | 73 | 28 | 100 | |
| 9 | 110 | | | 110 | 15 | 150 | |
| 1,6 5 | 140 | | | 140 | 9 | NA | |
| 8,10 5 | 62 | | | 62 | 29 | NA | 1 |
| 5,7 5 | 72 | | | 72 | | NA | |
| 3,4 6 | 126 | | 1 | 126 | 24 | NA | ļ |

NOTE: NA = not analyzed.

Representative starry flounder sample contained 2.5 percent lipid; representative steelhead contained 10.6 percent lipid, Blank spaces imply residues below detectable levels.

¹ Microcoulometric confirmation.

** Arcolor 1254 concentrations not reported for species from station 13 because of interference with analytical process. 3 South Rogue River column 1 shows Oregon State University identification numbers for samples not identified by species. 4 Species also contained 6 μ g/kg chlordane and 6 μ g/kg thiodan. 5 Sample too small for PCB analysis.

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Offshore collections showed little geographical differences. DDE was frequently the only DDT-related compound present, averaging about 2 ppb in cuphausiids and pink shrimp and 9 ppb in flatfish. PCB levels were slightly higher, averaging 8, 25, and 29 ppb for cuphausiids, pink shrimp, and flatfish, respectively.

Figure 2 compares a typical shrimp chromatogram with those of Aroclor 1254 and 1260. Although most euphausiid PCB chromatograms resembled Aroclor 1254, peaks 21 and 23 were low or absent in pink shrimp and flatfish. Peak number 34 was also absent but peak 37 was usually present. Tentative indentification has been previously reported (11). Peaks 21 and 23 are both five chlorobiphenyls; peaks 34 and 37 are seven chlorobiphenyls.

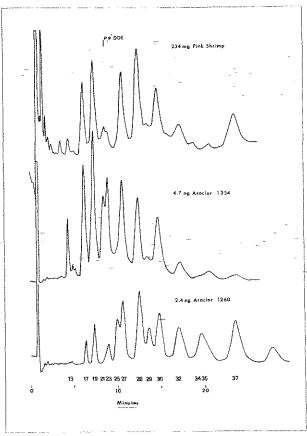


FIGURE 2. Typical chromatograms of the PCB fraction, pink shrimp extract

Dieldrin may have been present in the offshore species: but because of poor lipid separation, many peaks were present in the eluant containing dieldrin, making positive identification and quantitation difficult. In about one-half the pink shrimp and euphausiid collections and nearly all flatfish samples an apparent dieldrin peak was present. A second chromatographic column, 3 percent diethylene glycol succinate, was used for further confirmation.

Where dieldrin was indicated, levels were 0.2-0.5 ppb except for two euphausiid samples which contained about 5 ppb. In these latter two samples microcoulometric chloride detection positively confirmed dieldrin. These samples, collected 25 miles west of Grays Harbor (sampling stations 3 and 4), also contained higher levels of DDT and DDD. Dieldrin was also positively confirmed in a small unidentified fish collected near the Straits of Juan de Fuca (station 1). Dieldrin blank levels ranged from 0.004 to 0.33 ppb ($\bar{x} = 0.11$ ppb). Thus the apparent dieldrin peak in many samples may represent blank levels.

Fish collected from Coos Bay showed relatively low levels of DDE and PCB's (Table 3). PCB chromatograms resembled those found in the pink shrimp, i.e., Aroclor 1254 with two peaks missing; starry flounder chromatograms resembled those of Aroclor 1260.

Columbia River fish contained much higher levels of chlorinated hydrocarbons (Table 3), particularly PCB's (90-1160 ppb), than those found in Coos Bay fish. Starry flounder was the only species collected from both estuaries. Columbia River samples had six times the level of SDDT and 11 times the level of PCB's than had Coos Bay specimens. Interfering peaks prevented determination of dieldrin levels in these samples.

Summer-run steelhead from the Rogue River contained highest levels of DDE (97 ppb) and dieldrin (21 ppb) of all species sampled. In addition, 6 ppb chlordane and thiodan were found in several samples. PCB levels in Rogue River fish were lower than in Columbia River fish.

Results for mollusks are summarized in Table 4. The only chlorinated hydrocarbon pesticide found consistently throughout the sampling area was p,p'-DDE and, occasionally, p,p'-TDE and p,p'-DDT. Concentrations of DDT and related compounds were very low except in the Columbia River estuary. There were no significant seasonal variations. The Coos Bay Mya population had higher DDT residues (1.6-3.0 ppb) than had other clam populations from estuaries with small coastal mountain watersheds, i.e., Umpqua, Tillamook, and Yaquina. Only a single species, Clinocardium nuttallii, was analyzed from Netarts Bay; no chlorinated hydrocarbon compounds were detected.

Levels of DDT compounds in mollusks from the Columbia River were in marked contrast to those in mollusks from the other Oregon estuaries. Unfortunately, neither Clinocardium nor Mya was available from this system so comparisons must be made using different species. Except for a single sample of Mytilus edulis taken from the south jetty during the winter period, only Anodonta sp. and Corbicula fluminea were collected at this location. Levels of SDDT in Anodonta ranged from 14.9 ppb during the spring to 2 ppb in the fall. In contrast, SDDT in Corbicula ranged from

The only other pesticide detected in mollusks during the sampling period was dieldrin, which was present in all three Columbia River species analyzed during the winter and spring but was not detected in the summer and fall collections. Concentrations in mollusk tissues never exceeded 4 ppb.

During the first three sampling periods PCB's were found only in tissues of Columbia River bivalves. The PCB's found are believed to be a mixture of Aroclor 1254 and Aroclor 1260. Corbicula samples had consistently higher levels of PCB's than had Anodonta samples. In the former species concentrations ranged from 390 to 1,170 ppb. The highest level was found in the spring sampling period; levels did not exceed 570 ppb during the three remaining seasons. Levels of PCB's in Anodonta ranged from 160 ppb to levels

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TABLE 4. Chlorinated hydrocarbons in Oregon estuarine mollusks, 1972

| Species | DATE | | Concentration, µG/K | G WET WEIGHT | |
|---|--------------------------|----------------|------------------------|--|-------------|
| | | P.P'-DDE | p_*p' -TDE | p,p'-DDT | PCB' |
| | | COLUMBIA RIVER | | -4 | |
| Corbicula fluminea | 2/24 | 21 | 20 | 12 | 600 |
| | 4/14 | ND | ND | ND | 570 1170 |
| | 7/28 | 35 | 28 | 15 | 390 |
| | 10/5 | 30 | 17_ | 10 | 420 |
| Anodonta _ | ^{'''} 4/14 | 7 . | 4 | 3 | |
| | 7/28 | 7 - | 2 | 1 | 160 |
| | 10/4 - | 2 | NS . | NS | . 35 NS |
| Mytilüs edulis | -2/24 | 'NS . | NS | NS - | - |
| | | Coos Bay | | 1 NS1 | 44 |
| Mya arenaria | 1/25 | T | | ************************************** | |
| | 4/17 | 0.6 0.7 | 0.8 | 2 | NS |
| | 7/12 | 0.7 | NS 0.7 | 1.6 ' | NS |
| | 9/30 | ND | NS | 3 | NS |
| Clinocardium nuttallii | 1/25 | | | NS | 26 |
| | 4/17 | NS NS | NS | NS | NS |
| | 7/12 | 0.3 | NS NS | NS | NS |
| | 9/30 | ND | NS NS | 0,4 NS | NS |
| | | TILLAMOOK | | [183 | NS NS |
| Mya arenaria | 1/14 | T NS T | | | |
| • | 4/13 | - NS | . NS | NS | . NS |
| - | 7/9 | 0.2 | - NS - NS | NS | NS |
| | ·· 10/5 | 0.6 | NS | 0.3 | NS. |
| Clinocardium nuttallii | 1/14 | | | NS | NS |
| ere . | 4/13 | NS 0.5 | - NS | NS | NS" |
| | 7/9 | 0.1 | NS | - 0,4 | NS |
| | 10/5 | 0.6 | NS NS | NS NS | NS |
| | | Umpqua | | 183 | NS |
| Mya arenaria | _ 1/13 | 7 | | | |
| | 1/13 | 0.6 | <0.7 | <0.5 | NS |
| | 4/17 | 1.0 | NS 0.5 ¹ | NS | NS |
| | 7/11 | 0.2 | 0.3 | 0.4 1 | NS |
| | 10/2 | 1.2 | NS | NS NS | NS |
| Aytilus edulis | 1/26 | 1 | İ | ŀ | NS |
| | 5/19 | 0.7 | NS | NS | NS |
| | 7/12 | 0.8 | NS 0.3 | NS | NS |
| | 10/2 | 1.8 | NS | NS NS | NS |
| | | YAQUINA | | 149 | NS |
| Aya arenaria | 1/24 | 0.2 | N.C | | |
| | 4/15 | 0.5 | NS NS | NS | NS |
| | 7/8 | 0.2 | NS | NS NC | NS |
| | 9/25 | 0.6 | NS | NS NS | NS |
| linocardium nuttallii | 1/1 | NS | 1 | | 5 |
| | 4/15 | 0.2 | NS 0.5 | NS | NS |
| - | 7/8 | 0.2 | NS NS | NS NS | NS |
| | 9/25 | 0.3 | NS | NS NS | NS |
| lanks 2,3 | Winter | 0.2 | | E . | 7 |
| | Spring | 0.2 | 0.3 | 0.5 | 19 |
| *************************************** | Summer | 0.2 | 0.2 0.2 | 0.4 | 9 |
| | Fall | 0.1 | 0.2 | 0.4 | 5 |
| | ed for sea water blanks. | | 0.2 | 0.4 | 1 |

ND = no data because of interference with analytical process.

NS = residues not significant (less than twice the blank values).

¹ Confirmed by base hydrolysis. ² Values assume 30-g sample weight.

3 Average of two blanks.

lower than those determined for blank samples. Like Corbicula, Anodonta displayed the highest PCB level in the spring. During the fall sampling period, low levels (5-7 ppb) of PCB's were detected in the two bivalve species from Yaquina Bay, and 26 ppb PCB's were found in the Coos Bay Mya population.

Discussion

Relative concentrations of DDT and PCB compounds differed in the three offshore species. Residues of SDDT were 3 ppb in both euphausiids and pink shrimp, but PCB levels differed between the two species by a factor of three: 7.5 versus 25 ppb, respectively (Table 3). Levels of DDT in flatfish were three times higher than in euphausiids and pink shrimp, but PCB levels were similar to those in the pink shrimp. Considering that all three species have nearly the same lipid content, approximately 2 percent, other factors probably account for these differences. Both euphausiids and pink shrimp feed on zooplankton and smaller animals. Euphausiids are found in the water column, however, and pink shrimp are found near the ocean floor. Another possible explanation for the difference between these levels is that the two species were collected from different geographic locations. Most euphausiids were collected west of Newport (station 7); pink shrimp were collected farther north at stations 2 and 5.

DDT levels reported by Giam et al. (2) for the Gulf of Mexico are considerably higher. DDT levels for Gulf shrimp (family Panaeidae) ranged from 33 to 165 ppb; PCB chromatograms lacked sufficient resemblance to an Aroclor formulation for quantitation. DDT levels in Gulf fish were also much higher than those from the study reported here, but PCB levels were comparable.

Atlantic Ocean levels (1) are similar to those reported from the present study of the Northeast Pacific. Icelandic shrimp (*Pandalus borealis*) contained 1 and 18 ppb DDT and PCB compounds, respectively.

In 1968 Stout (12) reported pesticide residues in fish and shellfish in the Northeast Pacific. Residues in hake collected along the Oregon/Washington coast ranged from 115 to 285 ppb total DDT; DDE represented only 26-36 percent of the total DDT residue. Some PCB interference may have accounted for higher DDD and DDT residues. In the authors' 1972 collections, DDE often represented the major portion of the total DDT residue; Columbia River collections, which showed signs of recent DDT contamination, were the exception.

Little is known about biological effects of PCB's on the marine environment. Duke et al. (13) exposed shrimp (Penaeus duorarum) to 5 ppb Aroclor 1254 in sea water for 20 days. Shrimp that died after 10 days had only 1,600 ppb PCB's; those living after 20 days had 3,300 ppb PCB's. Thus mortality probably was not

caused by PCB poisoning. If 1,600 ppb is taken as a toxic residue level for shrimp, then pink shrimp (*Pandalus jordani*) in the Northeast Pacific contain only 1/60 the toxic residue level. Similar studies for DDE were not located.

DDE and PCB levels in the Coos Bay fish were slightly less than those found in the offshore flatfish collections (5 vs. 9 ppb DDE and 22 vs. 29 ppb PCB's, respectively).

Traces of chlordane and thiodan found in the steelhead may have originated from agricultural use in Medford, Oreg., a fruit-growing area. Only minor quantities of these chemicals are presently being applied in this area. Dieldrin found in those collections may have originated in the Rogue River, although dieldrin was also found in a few offshore collections.

PCB chromatograms of shrimp samples indicate selected metabolism of some isomers. All shrimp species had very low peaks for isomers 21 and 23 although-euphausiids contained the expected ratio of isomers. The lower quantities of isomers 21 and 23 in flatfish may be a result of their feeding on pink shrimp. The larger fish, herring, salpa, and steelhead, had chromatograms closely resembling Aroclor 1254. PCB chromatograms of common murres collected in this area were very similar to the shrimp chromatogram (11). It is significant that three of the four fish collected in the Coos Bay estuary had PCB patterns closely resembling Aroclor 1254. The pattern of the fourth, a starry flounder, resembled Aroclor 1260.

Except for the Columbia River collections, organochlorine residues reported here for Oregon estuarine mollusks are consistently lower than those reported for mollusks from many other coastal States. Coos Bay mollusks had higher SDDT residues than had mollusks from the small coastal drainage estuaries, but even these did not exceed 5 ppb. In contrast, a very high percentage of mollusks sampled in other States contained between 11 and 100 ppb SDDT; significant numbers contained even more than 100 ppb (5).

Residues found in Columbia River Corbicula (53-78 ppb) more closely paralleled those reported in other States, but Anodonta collected in the same area contained less than 15 ppb SDDT. In general, a higher level of DDT tissue residues would be anticipated in Columbia River mollusks considering the enormous area of agricultural land drained by this river system. However, high levels of SDDT found in Corbicula may also be a result of the extraordinary ability of this species to accumulate organochlorine compounds.

Like DDT, PCB's accumulated far more heavily in *Corbicula* than in the other mollusks examined. The higher levels of PCB's in the Columbia River fish suggest that PCB contamination of the Columbia River greatly exceeded that of adjacent coastal waters.

Acknowledgment

Authors gratefully acknowledge the National Science Foundation IDOE Program for financial support of the offshore investigation and the National Marine Fisheries Service for financial support of the mollusk study.

LITERATURE CITED

- (1) Harvey, George R., and H. P. Miklas. 1972. Baseline studies of pollutants in the marine environment. International decade of oceanography workshop, Brookhaven National Laboratory, May 24-26, 1972. Pp. 469-492.
- (2) Giam, C. S., A. R. Hanks, R. C. Richardson, W. M. Sackett, and M. K. Wong. 1972. DDT, DDE, and polychlorinated biphenyls in biota from the Gulf of Mexico and Caribbean Sea—1971. Pestic. Monit. J. 6(3):139-143.
- (3) Porter, Mildred L., S. J. V. Young, and J. A. Burke. 1970. A method for the analysis of fish, animal, and poultry tissue for chlorinated polychaete pesticide residues. J. Ass. Offic. Anal. Chem. 53(6):1300-1303.
- (4) Giuffrida, Laura, D. C. Bostwick, and N.-F. Ives. 1966. Rapid cleanup techniques for chlorinated pesticide residues in milk, fats, and oils. J. Ass. Offic. Anal. Chem. 49(3):634-638.
- (5) Butler, Philip A. 1973. Organochlorine residues in estuarine mollusks, 1965-72. National Pesticide Monitoring Program. Pestic. Mont. J. 6(4):238-362.

- (6) Armour, Judith A., and J. A. Burke. 1970. Method for separating polychlorinated biphenyls from DDT and its analogs. J. Ass. Offic. Anal. Chem. 53(4): 761-768.
- (7) Klein, A. K., and J. O. Watts. 1964. Separation and measurement of perthane, DDD (TDE) and DDT in leafy vegetables by electron capture gas chromatography. J. Ass. Offic. Anal. Chem. 47(2):311-316.
- (8) Kawano, Y. A., A. Bevenue, H. Beckman, and F. Erro. 1969. Studies on the effect of sulfuric-fuming nitric acid treatment on the analytical characteristics of toxaphene. J. Ass. Offic. Anal. Chem. 52(1):167-172.
- (9) Lamberton, J. G., and R. R. Claeys. 1972. A large inexpensive oven to decontaminate glassware for environmental pesticide analysis. J. Ass. Offic. Anal. Chem. 55(4):898-899.
- (10) Claeys, R. R. 1972. Baseline studies of pollutants in the marine environment. International decade of oceanography workshop, Brookhaven National Laboratory, May 24-26, 1972. Pp. 499-514.
- (11) Scott, J. M., J. A. Wiens, and R. R. Claeys. Organochlorine levels associated with a common murre dieoff in Oregon. J. Wildl. Mgmt. (In press).
- -(12) Stout, Virginia F. 1968. Pesticide levels in fish of the Northeast Pacific. Bull. Environ. Contam. Toxicol. 3(4):240-246.
- (13) Duke, T. W., J. I. Lowe, and A. J. Wilson, Jr. 1970. A polychlorinated biphenyl (Aroclor 1254) in the water, sediment, and biota of Escambia Bay, Florida. Bull. Environ. Contam. Toxicol. 5(2):171-180.