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# PESTICIDE RESEARCH AT THE FISHERY-OCEANOGRAPHY CENTER

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Chemicals that are used today differ strikingly from those used before World War II. Pesticides in use then, with a few exceptions like lead arsenate and paris green, were not persistent. They consisted of organics that were found in nature, for example pyrethrins, nicotine sulfate, or rotenone. Compared to the post war use of pesticides they were not used in great quantities.

Within 20 years of the end of World War II there were 8,000 manufacturing firms in the U. S. mixing about 500 chemical compounds into more than 60,000 formulations registered for use as pesticides. The U. S. chemical industry was producing about 800 million pounds of pesticides a year and several pesticides had achieved almost universal distribution in the environment.

The first of a large group of synthetic chlorinated hydrocarbon chemicals, DDT, became available for public use in 1945 and has since become the best known and most widely used of post-war pesticides. It is also the most persistent and widespread of these chemicals.

Late in 1969, the then U.S. Bureau of Commercial Fisheries initiated a survey of chlorinated hydrocarbon pesticide residues in marine fishes found in the coastal waters of the U.S. The Fishery-Oceanography Center in La Jolla was assigned the task of collecting fish samples off southern California and Baja California. For this survey only fish livers were analyzed. Liver is easily sampled and it tends to concentrate the residues, therefore, it was felt that this organ would be a good indicator of the degree of pesticide contamination among fishes in any area.

In January 1970, samples of various species of fish were taken along the Baja California coast plus a few samples from Cortes Bank, which is about 100 miles offshore from San Diego, and one sample from Farnsworth Bank, which is on the west side of Catalina Island. In May, additional samples were taken at Cortes Bank, Farnsworth Bank, Santa Monica Bay, and along the coast between San Diego and Oceanside (Fig. 1; sample #1 taken off Manzanillo, Mexico, and sample #37 taken off Cape Mendocino, California, not shown). All of these samples were sent to the National Marine Fisheries Service (NMFS) Pesticide Laboratory in Gulf Breeze, Florida, for analysis. The samples showed that residues of DDT and its metabolites in fish livers increased from very low values in the south to very high values in Santa Monica Bay (Table 1). Off southern Baja California, DDT residues averaged about 140 parts per billion (ppb) for 9 samples, which included a total of 170 fish. Values for the 9 samples ranged from 38–430 ppb. In the Sebastian Viscaino Bay area, central Baja California, 3 samples totaling 29 fish averaged 1.2 parts per million (ppm) and ranged from 0.23–2.1 ppm. Fifteen samples, totaling 179 fish taken along the coast between San Diego and Oceanside at Cortes Bank and at Farnsworth Bank, averaged 13 ppm and ranged from 0.94 for ocean whitefish at Cortes Bank to 30 ppm for rockfish, *Sebastodes rosaceous* taken at Cortes Bank. In Santa Monica Bay, 8 samples, 65 fish, averaged 370 ppm and ranged from 63 ppm for Dover sole to over 1,000 ppm for one species of rockfish, *Sebastodes constellatus*.

Later the fillets of some of these fish were sent to the NMFS Laboratory in Seattle, for analyses. Analyses of the fillets (Table 2) showed that for 7 samples, Farnsworth Bank, San Diego, and Oceanside, in which total pesticide residues in the liver averaged from 7.3–18 ppm, the values for fillets ranged from 0.23–0.78 ppm. In five samples from Santa Monica Bay in which the liver residues ranged from 63–1,030 ppm, fillets ranged from 12–57 ppm. In the above 12 liver samples DDE averaged 87%, (82–96%) of the total pesticide residues, DDD 6% and DDT 7%. In 8

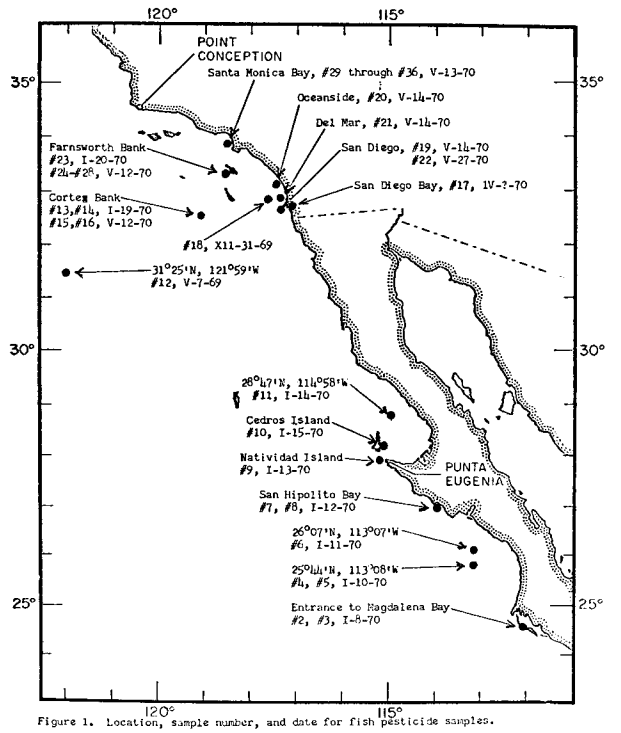

Figure 1. Location, sample number, and date for fish pesticide samples.

**FIGURE 1. Location, sample number, and date for fish pesticide samples.**

of the fillet samples, excluding the 4 containing less than 0.3 ppm total of residue, DDE averaged 87% (81–95%), DDD 5%, DDT 8%. One sample of fat from the body cavity of a Santa Monica Bay *S. constellatus* contained 2,600 ppm of DDT and its metabolites, of which 85% was DDE, 7% DDD and 8% DDT.

These extremely high residues in fish from the Santa Monica Bay area apparently resulted from the large amounts of pesticides discharged into the ocean at Whites Point by the sewers of the County Sanitation Districts of Los Angeles County (Carry and Redner, 1970). In March 1970, an estimated 800 pounds of DDT was being dumped into this sewer system each day. Investigators from the County Sanitation Districts determined that the source of most of this pesticide was the Montrose Chemical Company of Torrance, California. This company is the sole manufacturer of DDT in the United States, and reportedly produced two-thirds of the world's supply. On March 30, 1970, samples of sewage taken by County Sanitation District personnel upstream from the Montrose Chemical Company's sewer connection contained 34 ppb of DDT in a flow of 25.3 million gallons per day or 7.2 pounds of DDT per day. Samples taken downstream contained 2950 ppb in a flow of 26.6 MGD or 654 pounds of DDT per day. The situation has since been corrected. In April 1970, the company began hauling by truck what was termed a "caustic liquor waste" to landfills for disposal.

In contrast to the roughly estimated 146 tons of DDT per year that were being dumped into the Los Angeles County sewer system, it has been estimated that the Mississippi River contributes about 10 tons of pesticides a year to the Gulf of Mexico, and that the easterly tradewinds transport an estimated one-half ton of DDT across the north Atlantic annually (Butler, 1969).

**TABLE 1**

**Residues of DDT and its metabolites, DDD and DDE, in the livers of fish taken off the Pacific Coast of the United States and Mexico (1969–1970)**

| Sample Number | Species | Number of Fish in Sample | Residues in parts per million | | | |
|---|---|---|---|---|---|---|
| | | | DDE | DDD | DDT | Total |
| | SOUTH OF POINT EUGENIA | | | | | |
| 1 | Yellowfin tuna (*Thunnus albacares*) | 11 | .047 | .091 | .026 | .164 |
| 2 | San bass (*Paralabrax nebulifer*) | 10 | .038 | -- | -- | .038 |
| 3 | Ocean whitefish (*Caulolatilus princeps*) | 10 | .22 | -- | -- | .22 |
| 4 | Pacific mackerel (*Scomber japonicus*) | 19 | .040 | -- | .009 | .049 |
| 5 | Bonito (*Sarda chiliensis*) | 10 | .050 | .012 | .038 | .100 |
| 6 | Hake (*Merluccius productus*) | 90 | .36 | .018 | .048 | .426 |
| 7 | Sand bass (*Paralabrax nebulifer*) | 10 | .15 | -- | -- | .15 |
| 8 | Ocean whitefish (*Caulolatilus princeps*) | 10 | .088 | -- | -- | .088 |
| | SEBASTIAN VISCAINO BAY | | | | | |
| 9 | Bonito (*Sarda chiliensis*) | 6 | 1.1 | .054 | .13 | 1.284 |
| 10 | Ocean whitefish (*Caulolatilus princeps*) | 10 | .14 | .031 | .056 | .227 |
| 11 | Lizzardfish (*Synodus sp.*) | 13 | 1.6 | .18 | .35 | 2.13 |
| | CORTEZ BANK AREA | | | | | |
| 12 | Jack mackerel (*Trachurus symmetricus*) | 2 | .092 | .019 | -- | .111 |
| 13 | Ocean whitefish (*Caulolatilus princeps*) | 2 | .78 | .060 | .099 | .939 |
| 14 | Treefish (*Sebastodes serricepts*) | 10 | 1.6 | .080 | .16 | 1.84 |
| 15 | Rosy rockfish (*Sebastodes rosaceus*) | 7 | 27. | 1.2 | 1.6 | 29.8 |
| 16 | Olive rockfish (*Sebastodes serranoides*) | 5 | 21. | 1.0 | 2.6 | 24.6 |
| | SOUTHERN CALIFORNIA COAST | | | | | |
| 17 | Sardine (*Sardinops caeruleus*) | 32 | .96 | -- | -- | .96 |
| 18 | Hake (*Merluccius productus*) | 52 | 4.5 | .71 | 1.4 | 6.61 |
| 19 | English sole (*Parophrys vetulus*) | 14 | 12. | 1.1 | .83 | 13.93 |
| 20 | White croaker (*Genyonemus lineatus*) | 16 | 16. | .28 | .35 | 16.63 |
| 21 | Ling cod (*Ophiodon elongatus*) | 1 | 15. | .90 | 1.9 | 17.80 |
| 22 | Jack mackerel (*Trachurus symmetricus*) | 10 | 2.5 | .16 | .41 | 3.07 |
| | FARNSWORTH BANK (STA. CATALINA IS.) | | | | | |
| 23 | Rockfish (*Sebastodes sps.*) | 11 | 21. | 1.4 | .23 | 22.63 |
| 24 | Sculpin (*Scorpaena guttata*) | 10 | 7.0 | .55 | .58 | 8.13 |
| 25 | Blue rockfish (*Sebastodes mystinus*) | 5 | 9.4 | .79 | 1.3 | 11.49 |
| 26 | Rosy rockfish (*Sebastodes rosaceus*) | 16 | 8.5 | .54 | 1.0 | 10.04 |
| 27 | Treefish (*Sebastodes serriceps*) | 7 | 6.4 | .31 | .56 | 7.27 |
| 28 | Starry rockfish (*Sebastodes constellatus*) | 13 | 16. | .71 | 1.4 | 18.11 |
| | SANTA MONICA BAY | | | | | |
| 29 | Bocaccio (*Sebastodes paucispinis*) | 9 | 510. | 33. | 48. | 591. |
| 30 | Sablefish (*Anoplopoma fimbria*) | 10 | 90. | 6.0 | 7.1 | 103.1 |
| 31 | Vermilion rockfish (*Sebastodes miniatus*) | 10 | 141. | 9.0 | 12. | 162. |
| 32 | Starry rockfish (*Sebastodes constellatus*) | 5 | 900. | 56. | 70. | 1026. |
| 33 | Dover sole (*Microstomus pacificus*) | 13 | 54. | 4.1 | 4.9 | 63. |
| 34 | Spiny dogfish (*Squalus acanthias*) | 5 | 200. | 15. | 13. | 228. |
| 35 | Spiny dogfish (Large female with embryos) | 1 | 406. | 24. | 43. | 473. |
| 36 | Spiny dogfish (embryos from #35) | 12 | 300. | 20. | 32. | 352. |
| | CAPE MENDOCINO AREA (RUSSIAN TRAWLER) | | | | | |
| 37 | Hake (*Merluccius productus*) | 13 | 1.4 | .29 | .43 | 2.12 |

Our own program in pesticide research at the Fishery-Oceanography Center has just started, so we do not have any results of our own to present at this point. We expect our research to be along two main lines: 1) the effect of pesticides on the reproductive metabolism of fish and the survival of eggs and larvae, and 2) an investigation of residues in plankton, current and historical, using the extensive collections of the California Cooperative Oceanic Fisheries Investigations (CalCOFI).

With respect to the reproductive metabolism of fish, it has been demonstrated that DDT in fish eggs can cause heavy mortality among the fry. Concentrations on the order of 3 ppm caused mortality in lake trout fry (Burdick *et al.*, 1964). In a few of the samples of fish collected in our original survey, we found females that were nearly ripe. One sample of *Sebastodes rosaceous* that contained 10 ppm DDT and metabolites in the liver had 3.6 ppm in the ovaries. One sample of *Sebastodes serriceps* contained 7.3 ppm in the liver and 4.3 ppm in the ovaries. More than 80% of the total was DDE rather than DDT in both samples, and DDE appears to be less toxic than DDT.

The rockfish taken in Santa Monica Bay that had very high pesticide residues in the liver were species that spawn earlier in the year and had no ovarian development at the time of capture.

It is possible that some fish in California coastal waters contain such high residues of pesticide that they cannot reproduce effectively. We are going to explore this problem in the laboratory.

We are also designing experiments to describe the uptake by various tissues of adult marine fish under chronic sub-lethal exposure to pesticides.

In the plankton project, we are still experimenting with analyzing material preserved in formalin and trying to determine if we should concentrate our efforts on only certain constituents of the plankton samples. Samples of plankton have been collected regularly each year by vessels of CalCOFI agencies since 1949. Most of these samples have been sorted into fish eggs and larvae, and to a lesser degree some of the other constituents have been removed. This means that the formalin has been changed one or more times for each sample and possibly some of the pesticide residue may have been discarded with the old formalin. We are presently investigating some of the possible problems associated with using such preserved material.

There are also extensive collections of small fishes taken by dip netting and plankton net over the past 20 years on the CalCOFI cruises that might be valuable in determining the historical trend of pesticide accumulation in the ocean off California.

We have run a series of frozen plankton samples that were collected earlier this year. These were taken along CalCOFI line 87, which starts in Santa Monica Bay and runs to the southwest. We took samples out to about 400 miles along this line. Pesticide residues were higher for the two inshore stations and tended to decrease offshore except for one high value in the shallows off San Nicolas Island. Only the San Nicolas Island station and the two inshore stations contained DDE in excess of 1 part per million dry weight. Two-thirds of the samples contained only traces or no detectable DDD, and the same held true for three-fourths of the samples with respect to DDT. At these low pesticide levels there is great difficulty in interpreting the chromatograms owing to the large number of other small peaks, most of which may be polychlorinated biphenyls.

All of the samples had prominent peaks at the retention time of DDMU, a metabolite of DDT, but the PCB's also have peaks at that point. In fact the peak can be obtained by soaking some plastics in hexane, and can be introduced into samples as a processing, preservation or experimental artifact, although it appears to occur "naturally" in many samples.

The constituents of the plankton samples were primarily crustaceans, ctenophores, and salps. Most of

**TABLE 2**

**DDT residues in the flesh of fish from Southern California**

| Sample Number | Species | Length (mm) | Oil (percent) | Moisture (percent) | Residues in fillets (Parts per million) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | DDE | DDD | DDT | Total |
| | CORTEZ BANK | | | | | | | |
| None | *Sebastodes* sp. | no data | 0.9 | 80.0 | .123 | -- | -- | .123 |
| | FARNSWORTH BANK | | | | | | | |
| 24 | *Scorpaena guttata* | 194–262 | 0.9 | 77.8 | .258 | -- | trace | .258 |
| 25 | *Sebastodes mystinus* | 166–219 | 1.8 | 79.6 | .436 | trace | .058 | .494 |
| 26 | *Sebastodes rosaceus* | 137–180 | 0.7 | 80.0 | .283 | trace | trace | .283 |
| 27 | *Sebastodes serriceps* | 139–215 | 0.9 | 80.8 | .229 | -- | -- | .229 |
| 28 | *Sebastodes constellatus* | 142–194 | 0.9 | 80.2 | .283 | -- | -- | .283 |
| | SOUTHERN CALIFORNIA COAST | | | | | | | |
| 19 | *Parophrys vetulus* | 160–269 | 0.8 | 82.0 | .653 | .051 | .077 | .781 |
| 20 | *Genyonemus lineatus* | 181–255 | 0.7 | 79.0 | .583 | trace | .029 | .612 |
| | SANTA MONICA BAY | | | | | | | |
| 29 | *Sebastodes paucispinis* | 226–670 | 1.4 | 78.5 | 9.38 | 1.02 | 1.24 | 11.6 |
| 30 | *Anoplopoma fimbria* | 390–460 | 6.0 | 78.9 | 19.02 | 2.36 | 2.05 | 23.4 |
| 31 | *Sebastodes miniatus* | 205–304 | 2.2 | 79.1 | 14.9 | trace | 1.25 | 16.0 |
| 32 | *Sebastodes constellatus* | 165–248 | 1.8 | 76.4 | 50.5 | 3.14 | 3.64 | 57.2 |
| 33 | *Microstomus pacificus* | 180–205 | 3.6 | 79.9 | 11.55 | 0.82 | 0.93 | 13.3 |

the larger jellies were discarded before the samples were frozen. Inclusion of fish larvae or small fishes in the sample increased the pesticide residues noticeably. Myctophids weighing 0.3–0.5 g contained more than 100 times (on a dry weight basis) as much pesticide residue as the plankton samples from which they were removed. At the present stage of our plankton investigations, it appears that the best plankton constituents upon which to base a study of the historical trend in pesticide accumulation may be the myctophid fishes that have been taken in the plankton nets and by dipnetting on CalCOFI cruises since 1949.

*Question:* What kind of errors do you get in your DDT measurements or your other constituents of these in the high pressure stations? How extensively do you separate these?

*MacGregor:* We are getting pretty good separation with things like DDE.

*Question:* PCB's don't interfere?

*MacGregor:* They interfere, yes, especially when everything is there in very small quantities. We have a lot of interference with DDT.

*Question:* Have you done any mass spectrometry work?

*MacGregor:* No, but Dr. McClure is working—trying to use thin layer chromatography in conjunction with this and see if we can separate them out that way.

*Question:* Using one column or two?

*MacGregor:* Just one now.

*Question:* What concentrations are necessary in the fish flesh of DDT before you become concerned?

*MacGregor:* U.S. Food and Drug says 5 ppm.

*Question:* Has anyone worked the same species of fish from north of Pt. Conception?

*MacGregor:* We got one sample of hake from a Russian trawler that was sort of low.

*Question: Pearcy*—I am curious to know if this is a hot spot? You have the data from there south. How about north?

*MacGregor:* I think it is, around Los Angeles. How far north do you want to go? I know they got salmon off Alaska that they couldn't detect any residues in.

*Question: McGowan*—One sample of 20–30 fish and within that sample of fish DDT concentration varied by a factor of 10? On individuals?

*MacGregor:* We don't run individuals. Each sample was the same species. We would take all the livers in those species and blend them together.

*Question:* But you gave a range of numbers.

*MacGregor:* That was for different samples and different species of fish. Generally pelagic fish seem to be low as far as livers are concerned. Bottomfish tend to be higher.

*Question: McGowan*—Do you know if there is much variability among individuals within the species?

*MacGregor:* Not if you get them all from the same location. We had two samples of Pacific mackerel from the same school and it was just about the same.

*Question:* In samples of fish flesh, you said that DDE, or at least the residue, was from 12–57 ppm in the tissue. How is this information used from a consumer's standpoint? Obviously they shouldn't be consumed if they have that high concentration.

*MacGregor:* We didn't.

*Question: Fitch*—Most of the rockfish you are working on range in age with maturity up to 20 years or more, the ones that you mentioned anyway, and if this is accumulative you are bound to get great differences in individuals depending on the age of the individual.

*MacGregor:* If we take a simplistic view of this, what we think happens is—of course, each fish doesn't take in DDT, it is taking in a combination of different things, but DDT apparently breaks down to DDE, which is sort of an end point and that is stored in the fatty tissue and DDT also breaks down to DDD, which in turn breaks down to DDMU and eventually is excreted. So it apparently goes two ways—stores one and not the other.

*Question: Schmitt*—Are you passing out this information to FDA?

*MacGregor:* Actually FDA are just interested in stuff that goes into Interstate Commerce. They are sampling fish all along the coast themselves.

## LITERATURE CITED

Burdick, G. E., E. J. Harris, H. J. Dean, T. M. Walker, Jack Skea and David Colby. 1964. The accumulation of DDT in lake trout and the effect on reproduction. *Trans. Amer. Fish. Soc.*, 93(2):127–136.

Butler, Phillip A. 1969. Pesticides in the sea. The Encyclopedia of Marine Resources. Van Nostrand Reinhold Company, pp. 513–516.

Carry, Charles W. and John A. Redner. 1970. Pesticides and heavy metals, Progress Report, December 1970. County Sanitation Districts of Los Angeles County, 51 p.