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Persistence and Metabolism of TDE in California Clear Lake Fish

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Clear Lake is a naturally occurring lake located in northern California in the inner coastal range of mountains. It is shallow (mean depth of 8 meters), has a surface area of approximately 42,000 acres and shows no thermal stratification. On three occasions in 1949, 1954, and 1957 a total of over 120,000 lbs. of TDE [1,1,-dichloro-2,2-bis-(chlorophenyl)-ethane] was applied to control the substantial population of Clear Lake gnats (Chaoboras astictopus). A second and indirect source of additional contamination is the possible run off from numerous neighboring orchards (pears, almond, and walnut) and grape vineyards into creeks and streams feeding Clear Lake itself. In spite of the approximately 500,000 lbs of DDT applied agriculturally during 1949-1964, the observed residue levels in the lake proper does not indicate that this route of contamination was of any major proportions (RUDD and HERMAN 1972, and HERMAN et al. 1969). Additionally, these authors reported residue levels of TDE and isomers in the top 5 inches of sediment ranged from 0.05 ppm to 1.0 ppm. This TDE in the bottom sediments of the lake infers that bottom feeding species would probably suffer from greater exposure to such high levels of TDE.

The mortality rate and reproductive failure of the Western Grebe (Aechmophorus occidentalis) have been directly attributed to the three TDE applications (CRAIG and RUDD 1974, RUDD and HERMAN 1972, HUNT and BISCHOFF 1960, LINN and STANLEY 1969, and HERMAN et al. 1969). As a direct result of the problems with the Western Grebe, analyses of various species of fish were undertaken. Results of these samples, collected in 1958, showed TDE residue levels ranging from 5.0 to 221 ppm with a mean of 85.7 ppm (HUNT and BISCHOFF 1960). In fish collected in 1965, a mean residue level of 9.6 ppm TDE

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in white catfish was documented (LINN and STANLEY 1969). These results indicated that a dramatic decrease in TDE fish residue levels had occurred since 1958 (from a mean of 85.7 ppm to 9.6 ppm). Such findings are not completely surprising since the last application of TDE to the lake took place in 1957.

The California Department of Fish and Game has since issued commercial fishing permits for the harvesting of carp, blackfish and hitch from the lake. These fish are "purse seined" and the commercially harvestable species are tranferred to holding ponds and pens where they are maintained until the "muddy taste" has left the meat. Such fish are then shipped to and sold live in various ethnic communities on the west coast, notably San Francisco. During a routine pesticide surveillance program on food commodities, in 1976, FDA obtained for analysis twelve samples of whole fish representing eight different commercial and game species.

In this paper, we present data on the persistence and metabolism of TDE in these fish samples long after the final treatment of the lake with TDE in 1957.

EXPERIMENTAL

Composites were prepared from the edible portion of the fish, including the skin (except catfish). The head, tail, bones, scales, viscera, etc., were discarded. Using a commercial food chopper and meat grinder the "fillets" from each fish in the sample were composited. Each sample was then reground until homogeneous.

Samples were extracted and the extracts worked up using the methods described in PAM I 211.13f(2) and 211.14(d) (MCMAHON and SAWYER 1977). Basically these procedures entail an extraction with CH_3CN, and "flooding out" of the pesticides from the extract with excess H_2O into petroleum ether. The petroleum ether extract is then dried with anhydrous Na_2SO_4 and transferred to the florisil column which is developed with 6% and 15% ethyl ether/ petroleum ether. These florisil eluates are then examined by electron capture gas chromatography.

Gas chromatographic identification and quantitation of eluates were carried out using a constant current ^{63}Ni electron capture detector and

Dohrmann microcoulometric detector using stationary phases OV101 and OV210 on Chromosorb WHP 80/100 mesh. Gas chromatography - mass spectrometry (GCMS) results were obtained on a Finnigan Model 3300 with Data System 6000 using methane as carrier gas and reagent gas in the chemical ionization mode.

RESULTS AND DISCUSSION

A pathway for the metabolism of DDT in rats and other mammalian species has been the subject of considerable scientific investigation over the last two decades. Collectively these data have led to the construction of a map summarizing the overall metabolic profile of DDT (Figure 1). The twelve fish samples of Clear Lake provided an opportunity to further evaluate the details of this sequence and to extend our knowledge of the metabolism of other compounds to fish species.

TABLE 1
Residue Analysis of Fish Samples by Electron Capture Gas Chromatography

	Residue Levels (ppm)						
	pp'TDE	op'TDE	(DDMU) pp'TDEE	pp'DDE	DDMS	DDNU	DDNS
European Carp	5.73 6.0	2.58 2.06	1.86 1.6	0.73 0.56	* 1.56	- 0.05	- 0.03
Sacramento Blackfish	0.44	0.40	0.20	trace	*	-	-
European Carp	4.09 5.1	1.74 1.70	1.08 1.5	0.45 0.57	* 1.16	- trace	- trace
Sacramento Blackfish	0.32	0.34	0.14	trace	*	-	-
Hitch	1.0	0.72	0.59	trace	*	-	-
European Carp	0.95	0.91	0.43	trace	*	-	-
Sacramento Blackfish	0.28	0.30	0.22	trace	*	-	-
White Crappie	0.52	0.50	0.24	trace	*	-	-
Catfish	0.35	0.03	0.17	0.08	*	-	-
Yellow Catfish	0.25	0.03	0.11	0.04	*	-	-
Common Catfish	0.40	0.03	0.20	0.09	*	-	-

*Chromatograms indicate the presence of DDMS. The residue was not confirmed or quantitated since no standard was available when these samples were analyzed.

- Not Determined.

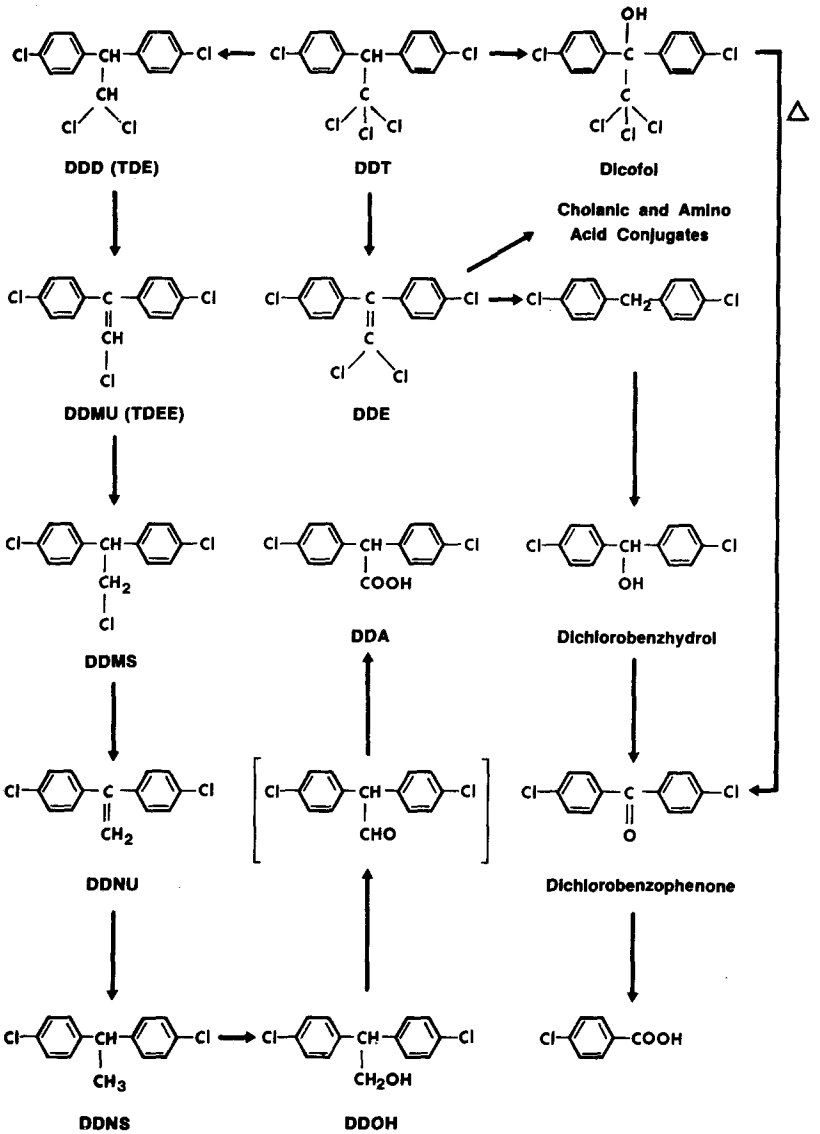

FIGURE 1. DDT Metabolic Pathway

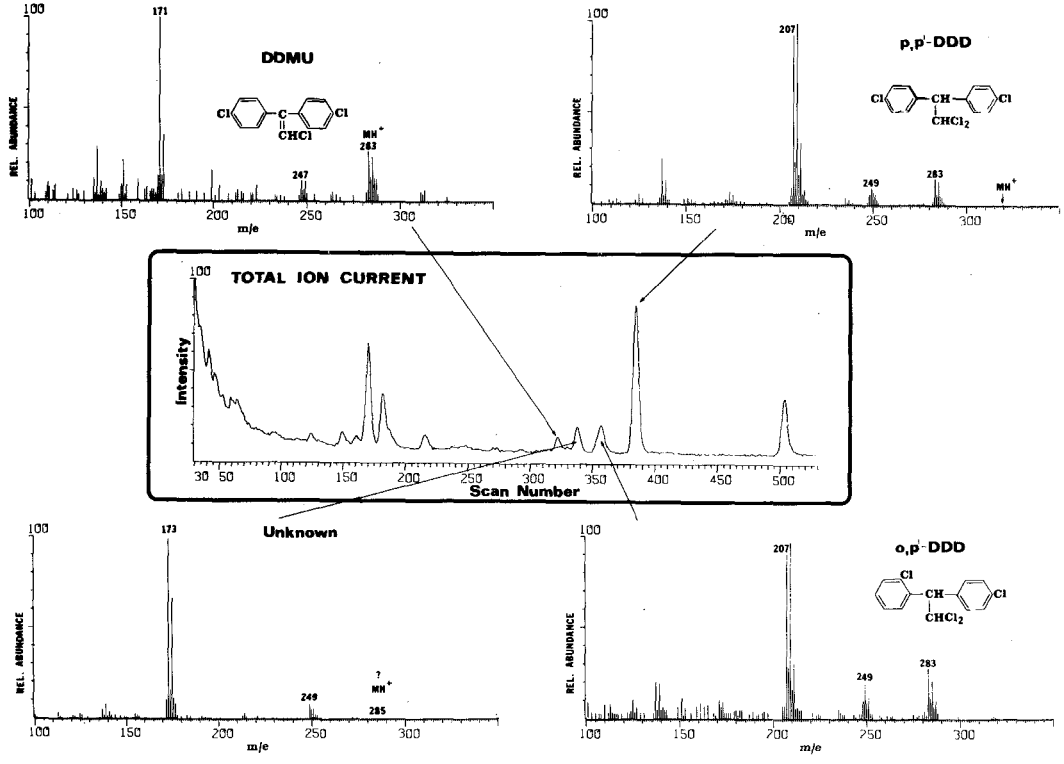

FIGURE 2. GCMS Residue Analysis of Fresh Carp - Unknown Identified as DDMS.

Results of the fish samples analyzed by gas chromatography and structurally confirmed by GCMS are presented in Table 1. During the original screening analyses of the fish extracts, a significant amount of an unidentified halogen containing compound was encountered (Figure 2). Structural investigation by GCMS of this compound revealed that it was DDMS. Confirmation was provided by comparison with a reference standard. Two samples were then rerun and quantitated for DDMS, DDNU, and DDNS by electron capture detection. Detailed discussions of these and related GCMS data will be published separately.

The presence of TDE and its metabolites, DDMS, DDNU, and DDNS are significant for two reasons. In the first place, the persistence of the parent TDE after 19 years in the lake is clearly demonstrated. Secondly, the identification of its metabolites in fish parallels that observed in other mamallian species. The high levels of TDE observed in the carp samples are further evidence that bottom feeding species suffer greater exposure to TDE because of high sediment concentrations of the pesticide.

It is regrettable that due to the surveillance nature of this survey, no provisions were made for saving the non-edible portions of the fish or for determining the age of the individual fish. Hence no correlations can be drawn concerning age and residue level or a comparison of residue levels in the non-edible portions. However, it should be noted that the two samples of carp which had the highest residue levels of TDE, consisted of large fish (three to four pounds) while those carp with the lower levels were much smaller (less than two pounds).

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