

PERSISTENCE OF TOXAPHENE IN TREATED LAKES

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Abstract—The persistence of toxaphene (chlorinated camphene) in eight Wisconsin lakes treated for rough fish control has been investigated. Lakes treated with 0.1 ppm of toxaphene 3-9 yr prior to sampling had the following distribution of toxaphene: water 1-4 $\mu\text{g/l}$, sediments 0.2-1 ppm, and aquatic plants 0.05-0.4 ppm. The results suggest that the components of toxaphene are degraded at different rates and that the components have different toxicity for fish.

INTRODUCTION

THE USE of toxaphene (chlorinated camphene) as a substitute for rotenone for the control of rough fish populations in lakes has become a frequent and accepted fish management practice in several states. For example, the state of Wisconsin has treated over 30 lakes with toxaphene in the past 10 yr. The use of toxaphene for this purpose has not been without some problems. The principal problem is that some lakes cannot be restocked with fish for several years due to the persistence of toxaphene. This paper reports on a study of the persistence of toxaphene in treated lakes.

Previous studies on the use and persistence of toxaphene in lakes

Toxaphene (chlorinated camphene—octachloro camphene) is a mixture of polychlor bicyclic terpenes with chlorinated camphene predominating. It has an empirical formula of approximately $\text{C}_{10}\text{H}_{18}\text{Cl}_8$ and contains 67-69 per cent chlorine. Toxaphene has the greatest toxicity to fish of any chlorinated hydrocarbon, except endrin now marketed as an insecticide (HENDERSON *et al.* 1959). Although highly toxic to fish, toxaphene has a somewhat lower acute toxicity to humans than endrin, dieldrin, aldrin and rotenone. HOOPER and FUKANO (1960) and JOHNSON (1965) have summarized the previous studies on the use of toxaphene in fish management programs. These references should be consulted for additional sources and details on previous studies.

The concentrations of toxaphene normally used in treating various lakes have varied from 2 to 100 $\mu\text{g/l}$. Concentrations between 2 and 7 $\mu\text{g/l}$ appear to affect only small fish (FUKANO and HOOPER, 1958), while concentrations above this amount may result in complete eradication of all fish. The Wisconsin Conservation Department normally uses 5 $\mu\text{g/l}$ of toxaphene for the epilimnion only when they wish to reduce the numbers of small fish in a lake. A concentration of 0.1 mg/l is normally used to effect complete kill of all fish (WISCONSIN CONSERVATION DEPARTMENT, 1965).

HOOPER and FUKANO (1960) show that lakes treated with toxaphene for complete kill normally require 2-12 months before detoxification of the toxaphene to concentrations which allow restocking of the lake. However, certain lakes have remained

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toxic for a period approaching 4 yr before restocking could be accomplished (HOOPER and FUKANO, 1960). As a result of the variable persistence of toxaphene, some state departments of conservation do not use toxaphene in fish management programs. ROSE (1957), HOOPER and GRZENDA (1957), HEMPHILL (1954), HOOPER and FUKANO (1960), KALLMAN *et al.* (1962), STRINGER and MCMYNN (1958), and TANNER and HAYES (1955) have reported that the following influence the persistence of toxaphene: concentration applied, sunlight, temperature, oxygen, alkalinity, hardness, turbidity, presence of bacteria, and pH. No quantitative relationships have been found between these factors and the persistence of toxaphene in treated lakes. Since, at the initiation of this study, all reports of persistence of toxaphene in lakes were based on the time necessary (via bioassay procedures) until restocking could be accomplished, it was felt that a study on the distribution of toxaphene in treated lakes using gas chromatographic procedures might give some clues to the mechanism of detoxification of toxaphene. For example, ROSE (1957) found that detoxification was more rapid when lake sediments were stirred into the water, and therefore it is possible that detoxification was the result of sorption of toxaphene on particulate matter. COHEN *et al.* (1960) found that toxaphene was effectively adsorbed from dilute aqueous solutions by activated carbon. Therefore, it is possible that sorption reactions may play a dominant role in the aqueous environmental chemistry of toxaphene. Subsequent to the initiation of this study, TERRIERE *et al.* (1966) have reported the results of a study of the persistence and distribution of toxaphene in two Oregon lakes. The results obtained by these investigators will be compared to the results of this study in the discussion section of this paper.

EXPERIMENTAL PROCEDURES

Analysis of toxaphene

The amount of toxaphene present in the samples was determined by gas chromatography using electron capture detector on a Perkin-Elmer Model 801 gas chromatograph. All-glass injection ports and columns were used. Nitrogen was used as a carrier gas at a flow rate of approximately 100 ml/min. The column oven and detector were maintained at 200° C. The column consisted of a 2 m × 2 mm glass column packed with silicon oil on Anachrom ABS. Also a 1 m × 2 mm glass column packed with 1.5 per cent SE-30 silicon gum rubber on Chromasorb W, HMDS was used. Toxaphene's gas chromatograms consist of a broad peak with several smaller peaks superimposed upon it ("finger print"). The concentration of toxaphene was determined by mechanical integration of the total area of the broad and smaller peaks.

The procedure used for extraction, clean up and concentration of samples was similar to that described in the Pesticide Analytical Manual (FOOD AND DRUG ADMINISTRATION, 1964). JOHNSON (1965) has presented the details of the procedure. In general, water samples were extracted with hexane and cleaned up on Florsil, Celite, and magnesium oxide columns. The aquatic plant samples were washed with water, blotted dry on filter paper, weighed, and blended in a Waring blender, extracted with acetonitrile and then cleaned up as described above. The lake sediment samples were dried at room temperature, ground to a powder, and extracted in a soxhlet extractor with 10 per cent acetone in hexane. Care was taken to purify all reagents used in this study to minimize interferences. The toxaphene used for standards was technical

grade, 100 per cent obtained from City Chemical Corporation, New York, U.S.A. These analytical procedures gave approximately 90 per cent recovery of toxaphene added to Lake Mendota water and sediment.

Sample collection

The samples of water and lake sediments were taken near the center of each lake. Surface samples were obtained by holding a 10 l. carboy about $\frac{1}{2}$ m below the surface. Deeper water samples were obtained with a Van Dorn bottle. Lake sediment was collected with a Peterson dredge. Aquatic weeds were collected where they could be found, usually near the shore. All samples were refrigerated upon arrival at the laboratory approximately 6 hr after sampling.

The water samples were filtered through Whatman GF/A glass filters. The toxaphene that passed through the filter was termed dissolved with that retained called suspended matter. The suspended matter was air dried at 26° C and analysed separately. The net plankton were obtained by towing a 20-mesh plankton net near the surface behind a boat near the center of the lake.

RESULTS

On 13 July 1965 eight Wisconsin lakes having previously been treated with toxaphene were sampled. Single grab samples were taken of the water and lake sediment. No attempt was made in this study to evaluate the distribution of toxaphene in the lakes or the changes in concentrations at various times during the year.

TABLE 1. CHEMICAL AND PHYSICAL CHARACTERISTICS OF LAKES SAMPLED

Lake	County	pH	Temperature (°C)	Specific conduct- ance (μ mhos at 25° C)	Dis- solved oxygen (mg/l)	Secchi depth (m)	Sus- pended solids (mg/l)	Sampling point depth (m)	Surface area (acres)
Emily	Dodge	8.9	23.7	340	9.8	0.3	64	3.5	271
Little Green (west end)	Green Lake	8.7	23.7	250	8.5	0.8	10	6	481
Big Twin (surface)	Green Lake	9.2	23.8	360	9.0	2.0	7	5	77
Comstock (surface)	Marquette	8.7	25.0	250	9.3	2.5	8	8	60
(6.5 m depth)		8.0	10.3	320	0	—	92	—	
Round	Waushara	9.4	24.6	150	10.0	2.0	7	5	76
Kusel	Waushara	8.4	24.4	240	8.7	1.5	8	7	79
Wilson	Waushara	8.4	24.7	220	9.2	1.5	7	4	79
Marl	Waushara	8.8	24.8	200	12.1	3.5	7	5.5	49

The characteristics of the lakes at the time of sampling are presented in TABLE 1. All of the lakes' samples are classified as hard water, alkaline, shallow, eutrophic lakes with large amounts of plankton and higher plants in near-shore areas. The only lake of the group that had a well-developed thermocline at the time of sampling was Comstock Lake.

The amount of toxaphene found in the samples from each of these lakes is presented in TABLE 2. Examination of TABLE 2 shows that the water samples from these lakes had an apparent nonfilterable toxaphene of 1 to 4 $\mu\text{g/l}$ with the exception of Comstock Lake surface water, which has a factor of 10 higher in concentration. The filterable matter (suspended matter) in all lakes varied from 9 to 500 ppb of toxaphene, with the deep waters in Comstock Lake showing the highest concentrations. The concentrations in the aquatic plants ranged from 50 to 400 ppb toxaphene, while the lake sediments ranged from 20 to 1000 ppb, with Comstock Lake again the highest. The high concentrations in Comstock Lake are explicable in terms of the fact that it was

TABLE 2. AMOUNTS OF TOXAPHENE IN LAKES STUDIED
(concentrations given in ppm*)

Lake	Water (nonfilter- able)	Sus- pended matter	Aquatic plants	Lake sedi- ments	Net plankton	Date	Treatment Amount (ppm)
Emily	0.004	0.02	0.4	0.2	—	1959	0.1
Little Green	0.001	0.04	—	0.02	15	1956	0.1
Big Twin	0.002	0.02	0.04	0.8	—	1963	0.1 and 0.05
Comstock (surface)	0.02	0.1	0.05	1	—	29 June 1965	0.1
(6.5 m depth)	0.004	0.5	—	—	—	—	—
Round	0.002	0.2	0.08	0.6	—	1964 and 1965	0.005 (each)
Kusel	0.003	0.2	0.07	0.4	—	1960	0.1
Wilson	0.004	0.08	0.05	0.5	—	1964	2.5–3.5 ppb
						18 May 1965	5 ppb epilim- nion only
Marl	0.003	0.009	0.08	1	—	1960	0.1

* These concentrations are the average of the results obtained with the DC-200 and SE-30 column.

treated 14 days prior to sampling with 0.1 mg/l. It is interesting to note that the concentrations of nonfilterable toxaphene decreased with increased time since treatment. Of particular interest is the fact that Little Green Lake, treated 9 yr prior to sampling, still had measurable amounts of toxaphene in all types of samples. The net plankton from this lake had a concentration of 15 ppm toxaphene. Unfortunately, net plankton were not collected from the other lakes. It is apparent from these data that toxaphene is concentrated in the aquatic organisms and lake sediments, and that it may persist for long periods of time.

DISCUSSION

TERRIERE *et al.* (1966) reported on a three year study of the persistence and distribution of toxaphene used in two Oregon lakes. Miller Lake, deep and oligotrophic, was treated with toxaphene in 1958 at an estimated rate of 44 $\mu\text{g/l}$. Davis Lake, shallow and eutrophic, was treated in 1961 with 88 $\mu\text{g/l}$ of toxaphene. Gas chromatographic analyses of the toxaphene was accomplished with microcoulometric detection.

Davis Lake was restocked with fish within a year after treatment, while Miller Lake remained toxic to fish for at least 5 yr after treatment. TERRIERE *et al.* (1966) reported that 1 yr after treatment Davis Lake in 1962 contained toxaphene in the following

amounts: water 0.6 $\mu\text{g/l}$, aquatic plants 0.4 ppm, aquatic invertebrates 1.4 ppm, fish (trout and salmon) 2–5 ppm, and bottom muds 0.6 ppm. In 1963, the concentration in the water had decreased to 0.4 $\mu\text{g/l}$, aquatic plants 0.2 ppm, and aquatic invertebrates 0.5 ppm. The concentrations in fish had increased to 3–7 ppm and bottom muds to 0.8 ppm. In Miller Lake in 1963, 5 yr after treatment, the following concentrations were found: water 1.2 $\mu\text{g/l}$, aquatic plants 2.7 ppm, aquatic invertebrates 3 ppm, and bottom muds 4 ppm. Rainbow trout placed in this lake in 1964 accumulated 10 to 12 ppm toxaphene in 14 days.

The lakes sampled in the present study are similar to Davis Lake in that they were all shallow, eutrophic lakes that rapidly detoxified. It is apparent from both of these studies that detoxification is accomplished at least in part by sorption reactions rather than degradation. However, it should be pointed out that Davis Lake had less than 1 $\mu\text{g/l}$ in the water 1 yr after treatment, while the Wisconsin lakes had 1–4 $\mu\text{g/l}$ for periods ranging up to 9 yr after treatment. Since these concentrations are approximately the same as those used for treating lakes for the kill of small fish, it is possible that a significant part of the toxaphene measured by gas chromatographic techniques is not highly toxic to small fish. It should be pointed out that the lakes studied in this investigation all show excellent fishing after restocking.

There is some evidence for modification of the toxaphene based on the shape of the "finger print" pattern in the gas chromatograms obtained from the lake samples as compared to the standard used in this investigation. TERRIERE *et al.* (1966) noted similar changes in the toxaphene extracted from fish.

Based on the results of the current study, it is plausible to propose that the components of toxaphene may be degraded at varying rates. Evidently, one or more of the more toxic components is degraded at a greater rate than the bulk of the toxaphene resulting in a relatively large residue of low toxicity. Support for this proposal is provided by studies by TERRIERE and INGALSBE (1953) in which they reported a difference in the relative persistence of toxaphene versus other pesticides in soils as measured by chemical and bioassay procedures.

The concentrations of toxaphene reported in the current investigation could have been in error due to several factors. The most important source of error was the standard used for calibration of the gas chromatograph. Various formulations of toxaphene showed slightly different gas chromatograms. The concentrations presented in this report assumed that the toxaphene applied to the lakes was identical to that used in the standard. It is highly probable that this is not the case, and therefore the concentrations listed in this report are merely indicative of approximate levels of toxaphene in the lakes.

The toxaphene found in the lakes is believed to be derived solely from the treatment of the lake by Wisconsin Department of Conservation personnel. There is no reason to suspect that toxaphene is being washed into these lakes in agricultural runoff.

This study has shown that toxaphene may persist in a lake for several years after its application in fish eradication programs. It is apparent that much additional study is necessary before the chemistry of toxaphene in natural waters is understood.

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