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# TOXAPHENE

STATUS IN THE GREAT LAKES

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PRIORITY POLLUTANT STATUS REPORT, NO. 2

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# TOXAPHENE

STATUS IN THE GREAT LAKES

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by John R. Sullivan and David E. Armstrong

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University of Wisconsin Sea Grant Institute  
Priority Pollutants Status Report No. 2

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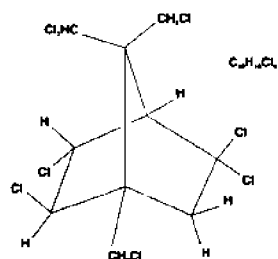
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### **Toxaphene: Status in the Great Lakes**

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Priority Pollutant Status Report No. 1 -- Dioxin: A Cause for Concern? -- is also available from the UW Sea Grant Communications Office free of charge.

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## Introduction

For more than a decade, the University of Wisconsin Sea Grant Institute has been a leader in research on contaminant problems in the Great Lakes region. Building on the expertise gained from past research on DDT and PCBs, UW Sea Grant scientists are assessing the status of a select group of the 126 compounds or classes of compounds currently targeted as "priority pollutants" by the U.S. Environmental Protection Agency -- toxaphene, chlorinated dibenzodioxins, chlorinated benzenes and chlorophenols.

Toxaphene was selected because of the special public concern generated by recent reports of its presence in Great Lakes waters, fish and waterfowl, and the lack of information and uncertainties about its sources, fate and effects.

This report is based on extensive searches of both published and unpublished data and other information about toxaphene. It includes descriptions of the chemical properties, manufacture and uses of toxaphene; the analytical methods and problems involved in detecting it; and a discussion of its toxicity, sources, distribution and environmental fate in the Great Lakes basin. For additional information, the authors recommend another recent report on toxaphene published in Toxic Contaminants In The Great Lakes (see Rice and Evans 1984).

The UW Sea Grant Institute is producing this series of reports in response to the widespread concern about the presence of hazardous substances in the Great Lakes basin and the need for objective, semitechnical information about these contaminants by public decision-makers, government agencies, environmental scientists, Great Lakes resource managers and interested citizens.

The presence of toxic substances in the Great Lakes Basin is well documented. However, understanding the environmental fate and the implications of the presence of toxic substances in the aquatic environment poses special challenges. With the passage of various environmental legislation in the 1970s, increased emphasis was focused on answering these questions for those chemicals used in large amounts in the United States. One such chemical is toxaphene, a chemically complex contact insecticide used in the U.S. since the late 1940s, most uses of which were banned in October 1982 by the U.S. Environmental Protection Agency (USEPA) shortly after the federal House of Representatives passed an amendment to ban the pesticide.

### Discovery of Toxaphene in the Great Lakes

The major impetus for the ban came from the release of data confirming the presence of toxaphene in fish sampled from all five Great Lakes, a region where toxaphene has never been heavily used (Zygadlo 1982). Toxaphene concentrations in numerous Great Lakes fish exceeded the U.S. Food and Drug Administration (USFDA) guideline of 5 mg/kg (5 parts per million), and mean concentrations were as high as those found in fish from heavily toxaphene-contaminated areas of the Cotton Belt. This led investigators to believe that atmospheric transport of toxaphene is substantial.

The presence of toxaphene in fish from the Great Lakes is of concern because toxaphene is a known animal carcinogen (Reuber 1979), is mutagenic in the Ames histidine assay (TA-100 strain *Salmonella typhimurium*) (Hooper et al. 1979), causes adverse toxicological effects in fish at ng/L (part-per-trillion) concentrations (Mehrle and Mayer 1975; Mayer et al. 1975), and has a mean acute 50-percent lethal concentration (LC<sub>50</sub>) in water for fish of 1.6 µg/L (1.6 parts per billion) (USEPA 1980).

Like other organochlorine pesticides that have been banned, toxaphene is persistent in the environment. It is relatively insoluble in water, chemically stable and bioaccumulates in the aquatic food web. Unlike most other organochlorine pesticides, however, toxaphene is a complex mixture of more than 177 chlorinated camphenes. As it is a multicomponent mixture, toxaphene is very difficult to measure in environmental matrices. The analytical detection limits used until recently were inadequate; interference from other chlorinated compounds, such as PCBs and chlordane, further complicate the analysis of toxaphene. Low analytical sensitivity and interference problems may explain why toxaphene is rarely identified and reported in environmental matrices (Cohen et al. 1982). However, recent evidence indicates that toxaphene may be a worldwide contaminant, similar to PCBs or DDT (Zell and Ballschmitter 1980).

### History of Toxaphene Usage

Toxaphene has been registered and used as a pesticide since 1947. It was the most heavily used insecticide in the U.S. from the 1960s to the mid-1970s



(Zygadlo 1982). Toxaphene was also the most common substitute for DDT after DDT was banned in 1971. Historically, the major use of toxaphene was to control the budworm-bollworm complex of insects that infest cotton crops. Its major area of use, therefore, was the Cotton Belt area of the U.S. South.

The amounts and distribution of toxaphene use are known only approximately. In 1976, about 70 percent of the total toxaphene usage of 38 million pounds (17.3 million kg) was applied to cotton (Eichers et al. 1978). With the registration in 1979 of synthetic pyrethroids as alternative cotton insecticides, toxaphene usage decreased sharply. In 1982, only about 2.5 million pounds (1.1 million kg) were used in the treatment of cotton (Zygadlo 1982).

Since about 1979, toxaphene has been used mostly as a herbicide to control sicklepod in soybeans. Toxaphene was also applied to several other crops, including wheat, sorghum, corn, peanuts, sunflowers, tomatoes, rice, dry beans and peas. Toxaphene is also used as a miticide for scabies control on cattle and other livestock. In 1981, the estimated total use of toxaphene was approximately 16 million pounds (7.3 million kg) (Zygadlo 1982).

Though total annual use has declined and the usage patterns have shifted, more than 75 percent of the toxaphene usage in the U.S. in the early 1980s occurred in the South. Figure 1 shows the geographic distribution and approximate quantities of toxaphene use on agricultural crops in the U.S. in 1981.

A less-known use of toxaphene was as a piscicide. Its use as a fish toxicant apparently was first recognized in 1950, when low concentrations of toxaphene killed fish in waters adjacent to dusted fields (Veith 1968). Subsequently, toxaphene was used for this purpose in several states and Canada.

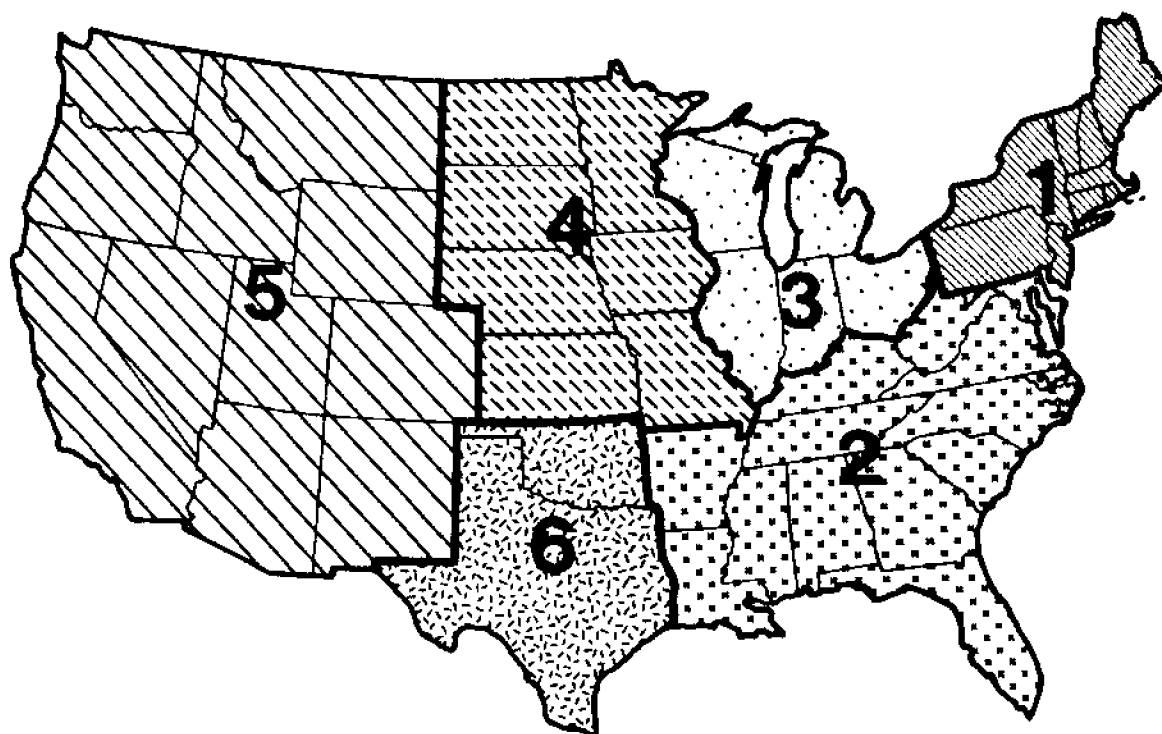
In Wisconsin, for example, toxaphene was applied to at least 80 lakes in the 1950s and 1960s (Hughes 1968). It was not only very effective as a fish toxicant but also relatively inexpensive. The principal problem encountered was its persistence in treated lakes. In some lakes treated with toxaphene, fish could not be restocked for up to nine years (Johnson et al. 1966; Terriere et al. 1966; Johnson 1966).

### **Restrictions on Use**

Though restricted only recently in the U.S. as a whole, the use of toxaphene was banned by several Eastern states in the early 1970s and by many nations between the early 1960s and early 1970s — including Egypt, Algeria, Denmark, France, Hungary, Italy, Switzerland, Sweden, Finland and the United Kingdom (Cohen et al. 1982). During 1980-81, Canada severely restricted any use of toxaphene.

Today, toxaphene can legally be used in the U.S. for scabies control on cattle and sheep, for insect control on bananas and pineapples in certain geographic areas, and for emergency insect control. The remaining stocks of toxaphene will be allowed to be sold over the next three years, after which all uses of toxaphene are expected to be banned.

**FIGURE 1: Estimated 1981 Geographic Distribution and Approximate Usage of Toxaphene on Agricultural Crops in the United States (from Zygadlo 1982)**



**Region**

- 1 North Atlantic States
- 2 South Central/Southeastern States
- 3 East North Central States
- 4 West North Central States
- 5 Western States
- 6 West South Central States

Region	Active Ingredients	
	Pounds	Kilograms
1	180,000	73,000
2	10,380,000	4,178,000
3	100,000	45,000
4	1,020,000	464,000
5	485,000	211,000
6	1,420,000	645,000

## The Chemical Properties and Manufacture of Toxaphene

Toxaphene is a chlorinated camphene product with an average elemental composition of  $C_{10}H_{10}Cl_8$  corresponding to an average molecular weight of 414 (Figure 2). It is commercially produced by reacting camphene (a bicyclic terpene) with chlorine, followed by activation with ultraviolet irradiation and certain catalysts to yield chlorinated camphene with a chlorine content of 67-69 percent (Metcalf 1966). The chemical camphene is derived from the isomerization of  $\alpha$ -pinene, a compound extracted from pine trees.

A U.S. corporation, Hercules, Inc., developed toxaphene and held the patent on it until 1971. By 1974, toxaphene was manufactured by about 186 companies in 817 registered products (USEPA 1977). It was sold in numerous forms, including technical toxaphene (100 percent), as a 90 percent solution in xylene, and as a 40 percent crop dust base.

It was marketed to formulators who blended, distributed and sold the finished products. Toxaphene was sold under many tradenames -- Strobane-T, Alltox, Chlor-Chem T-590, Motox, NCI-C00259, Synthetic Compound 3956, Phenacide, Phenatox, Geniphene, Phephene, Toxakil, Toxadust, Extonox and Facio-Terpene, among others (Lewis and Tatken 1978).

Physically, toxaphene is a yellow-amber, waxy solid with a pleasant, piney odor. It will dehydrochlorinate in the presence of alkali and dechlorinate after prolonged exposure to sunlight at temperatures around  $155^{\circ}C$  (Merck Index 1976). Toxaphene is relatively water soluble, in the range of 0.5-3 mg/L (Paris et al. 1977; Brooks 1974), as compared to DDT (1.7-5  $\mu g/L$ )

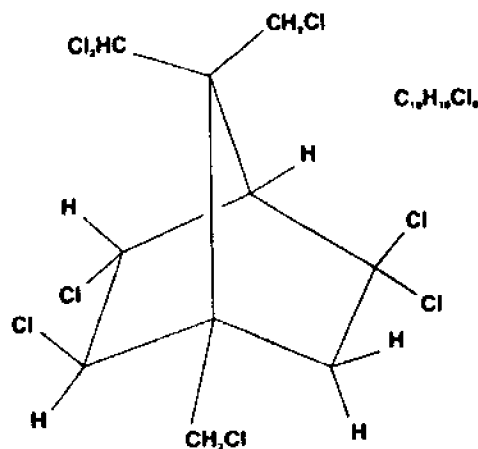


FIGURE 2: Structure of the Average Elemental Composition of Toxaphene

and PCBs (0.01-4,000 µg/L), but it possesses a low water solubility compared to most other organic compounds. The octanol/water partition coefficient -- an indication of the tendency for a compound to bioconcentrate in an organism -- has been reported in the range of  $10^{3.5}$  to  $10^{6.4}$  (Paris et al. 1977; ISHOW 1979). This value is relatively high, so toxaphene would be expected to bioconcentrate in organisms.

Reported vapor pressures are in the range of 0.2 to  $10^{-6.5}$  mmHg (Brooks 1974; Bidleman and Christensen 1979; Korte et al. 1979). Such a wide range of reported vapor pressures makes it difficult to surmise the volatility of toxaphene, but values in the range of  $10^{-6}$  to  $10^{-7}$  seem more consistent with other chlorinated hydrocarbons (Rice and Evans 1984).

A better understanding of its relative volatility can be obtained from the evaporation rates from soils and gas chromatographic retention times of different environmental pollutants. Using these data, a volatility order of p,p'DDT < toxaphene < Aroclor 1254 < cis- and transchlordane < Aroclor 1016 is obtained, although some overlap exists among components of Aroclor 1254 and toxaphene (Bidleman and Christensen 1979). Other properties of toxaphene are given in Table 1.

Many of the individual components of toxaphene have been identified. While the average elemental composition is  $C_{10}H_{10}Cl_8$ , individual toxaphene components may contain anywhere from six to 10 chlorines on the parent molecule (Casida et al. 1973). Research aimed at identifying these components has revealed toxaphene to be a mixture of polychloroboranes or their isomers:

$$Cl_6 = 3, Cl_7 = 29, Cl_8 = 64, Cl_9 = 31, Cl_{10} = 7, \text{ and } Cl_{11} = 1$$

TABLE 1  
Physical Properties of Toxaphene

Properties	Value	Source
Melting Point	70-95°C	Brooks 1974
	65-90°C	Merck Index 1976
Aqueous Solubility	3 mg/kg (at room temperature)	Brooks 1974
	0.5 mg/kg	Paris et al. 1977
Vapor Pressure at 25°C	0.2-0.4 mmHg	Brooks 1974
	$10^{-6}$ mmHg	Korte et al. 1979
	$10^{-6.5}$ mmHg	Bidleman and Christensen 1979
Octanol/water partition coefficient	$3.3 \pm 2.5 \times 10^3$	Paris et al. 1977
	$10^{6.4}$	Cohen et al. 1982

and polychlorobornenes or their isomers:

$$Cl_6 = 15, Cl_7 = 13, Cl_8 = 12, Cl_9 = 2$$

(Holmstead et al. 1974). Much of the research to identify the components of toxaphene was focused on the component(s) demonstrating the greatest toxicity to various organisms. As with other complex synthetic organic compounds like PCBs, its toxicity is related to the structure of the component (Saleh and Casida 1979; Chandurkar et al. 1978).

Analytically, toxaphene is a very difficult group of compounds to measure. Because it is a multicomponent mixture with a complex chemical composition, several basic analytical problems are apparent: the multicomponent nature of the pesticide decreases the analytical sensitivity for the total toxaphene mixture as compared to other chlorinated pesticides containing one or two components, and interference from other xenobiotics common in many environmental samples further complicates the analysis. These analytical problems may explain the relatively few reports of toxaphene in many environmental surveys.

### Analytical Methodology

The analytical methodology for identifying, quantifying and confirming toxaphene in environmental samples has undergone substantial evolution in the last 15 years. Early methods involved the use of packed column gas chromatography-electron capture detection (GC-ECD). A typical gas chromatogram is shown in Figure 3. Investigators described the gas chromatogram as a broad peak with several superimposed smaller peaks (Johnson et al. 1966). Quantification was accomplished by mechanically integrating the total area of the sample's chromatogram and comparing it to standards analyzed at different concentrations.

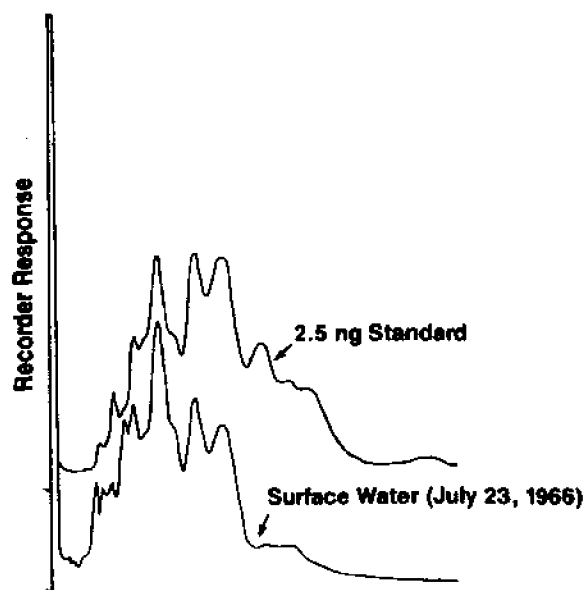


FIGURE 3: Toxaphene Chromatogram of a Water Extract (from Hughes 1968)

Much of the initial research was directed toward lakes treated with toxaphene as a piscicide. Consequently, confirmation of a toxaphene identification was seldom undertaken. In some cases, confirmation was performed with a spectrophotometric method, which is applicable only to relatively high toxaphene concentrations (Veith 1968).

Today, most research is aimed at determining low-level toxaphene contamination in different environmental compartments. This required advances in analytical procedures, including the use of size exclusion, adsorption and capillary column gas chromatography. These analytical procedures decreased the interference and low sensitivity problems previously associated with toxaphene analysis. With these procedures, toxaphene can be resolved into about 75 major, distinct, sharp peaks (see Figure 4, Part C) (Ribick et al. 1982). Confirmation of toxaphene identification is essential, and this is usually accomplished by mass spectrometry.

### **Sample Preparation**

Figure 5 illustrates a sample preparation scheme commonly used today for multiresidue analysis of fish tissue. Prior to analysis, the fish sample is combined with sodium sulfate and ground to the consistency of powder. The sample is then extracted with an organic solvent, and the extract is concentrated by rotary evaporation and subjected to gel permeation chromatography to separate the fish lipids from PCBs, toxaphene and other chlorinated pesticides. The sample is then subjected to Florisil column chromatography to remove interferences and separate common pesticides and contaminants into groups. The eluate is further fractionated by chromatography on silica gel.

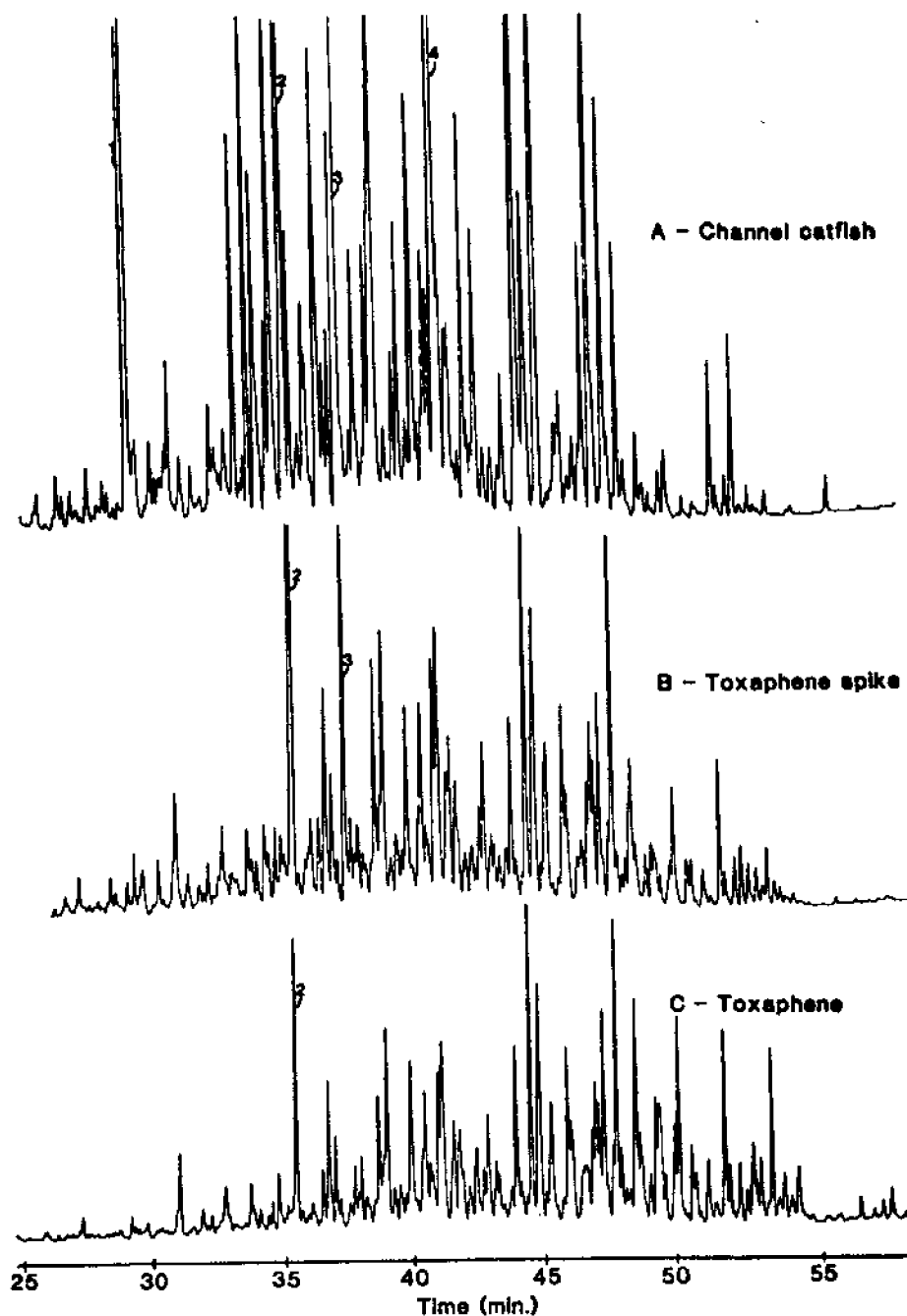
The separation of toxaphene from PCBs is particularly important, because the more analytically sensitive PCBs can mask the less sensitive analysis for toxaphene. By combining this sample preparation scheme with analysis by capillary column GC-ECD, toxaphene can be separated from most other ubiquitous environmental contaminants. This analytical scheme enables accurate measurements of toxaphene in spiked fish samples, with results reported within one percent of a spiked value (Ribick et al. 1982).

Figure 4 shows typical gas chromatograms of toxaphene samples and standards obtained with this method. For comparison, chromatograms of an extract from a Lake Michigan lake trout and a toxaphene standard are shown in Figure 6. Some toxaphene components coelute with chlordane, another ubiquitous multicomponent insecticide, and quantification is best accomplished by selecting toxaphene peaks that elute after trans-nonachlor (see Figure 4), which is added as an internal standard (Ribick et al. 1982).

### **Confirmation**

Since certain components of toxaphene are degraded differently by biological and chemical processes in the environment, confirmation of an identification of toxaphene is necessary. Most confirmations use electron impact mass spectrometry (EIMS) (Stalling and Huckins 1976). The major limitation of EIMS for toxaphene confirmation is its lack of sensitivity for the individual

**FIGURE 4: WCOT Column Chromatogram of Toxaphene-Containing Fraction of Two Samples and Technical Toxaphene Standard (from Ribick et al. 1982)**



Chromatogram A is from a channel catfish from the Arroyo Colorado; chromatogram B is a 4.0  $\mu$ g/g spike of brook trout; chromatogram C is a toxaphene standard. The numbered peaks are (1) dacthal, (2)trans-nonachlor, (3) p,p'-DDE, and (4) p,p'-DDD + cis-nonachlor.

Conditions: 55 M x 0.32 mm i.d. fused-silica SE-54 column, temperature programmed with a 10-minute hold at 140°C to 250°C at 2°C/min.; H<sub>2</sub> carrier gas; 10 percent argon in methane makeup gas for ECD.



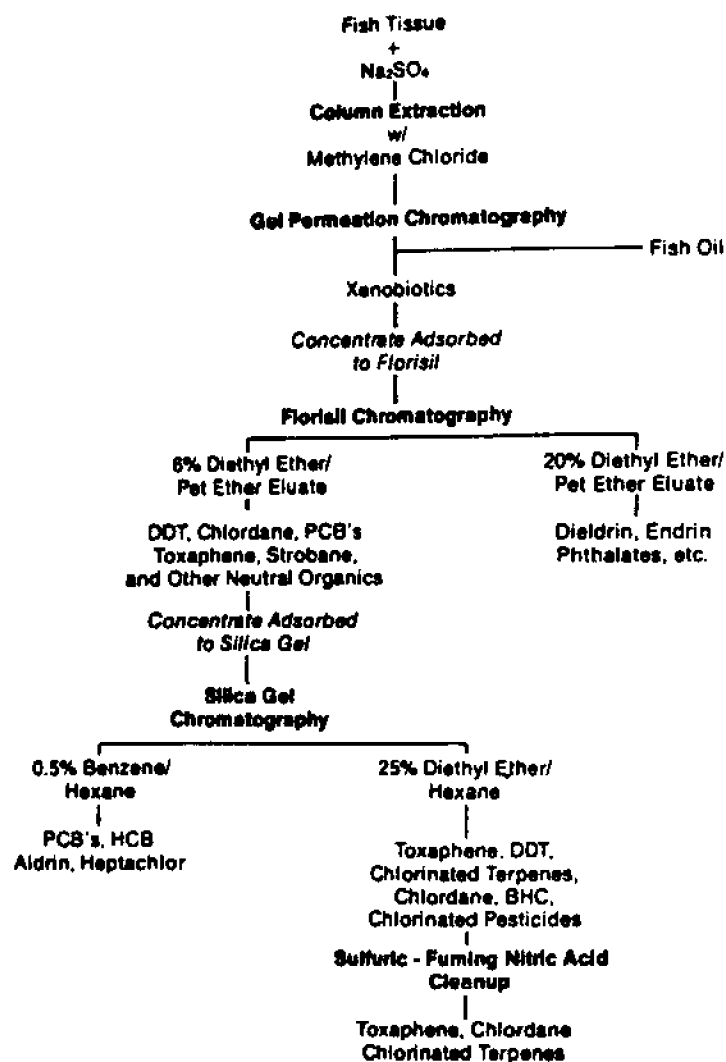
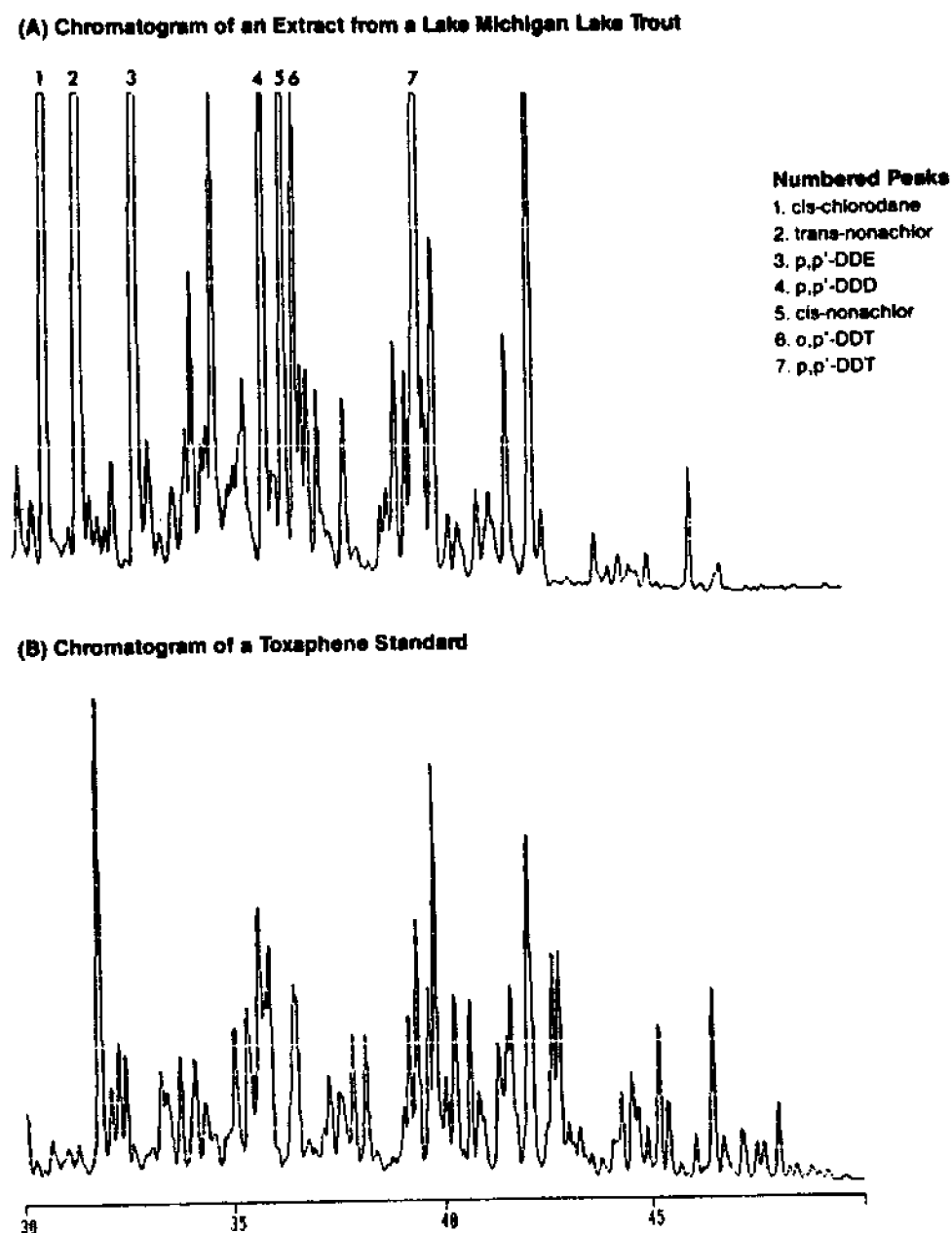


FIGURE 5: Sample Preparation Flow Scheme of the Procedure Used for Toxaphene and Other Residue Analysis in Fish Tissue (from Ribick et al. 1982)

components of the compound. However, the use of select ion monitoring increases the sensitivity of the EIMS method. Due to fragmentation of the molecules by EIMS, fragment ions must be used in characterization, so the method is not useful in determining the molecular weight of a particular toxaphene component (Ribick et al. 1982).

A superior confirmation technique appears to be chemical ionization -- negative ion mass spectrometry (NIMS). This method is more sensitive than EIMS because fragmentation of the molecules is not as severe (Bidleman and Christensen 1979). Through the increased sensitivity and selectivity achieved with NIMS, the study of individual toxaphene components in the environment is now becoming possible.

FIGURE 6: Comparison of a Chromatogram from a Lake Michigan Lake Trout (A) with One from a Toxaphene Standard (B) (from Ribick et al. 1982)



The analytical method is described in Ribick et al. 1982. The chromatograms were obtained using a 30 m x 0.25 mm i.d. SE-30 fused silica column, temperature programmed with a 10-minute hold at 140°C to 240°C at 2°C/min. (Chromatograms provided by M.A. Ribick and D.L. Stalling, Columbia National Fisheries Research Laboratory, U.S. Fish and Wildlife Service, Columbia, Mo.)

Due to the complexity of toxaphene chromatograms and the different rates of component degradation or fractionation in the environment, a computer analysis method for establishing similarities in residue profiles has recently been developed (Wold and Sjostrom 1977). This series of computer programs, collectively known as SIMCA, applies the technique of principal component pattern recognition. This technique has been used successfully to establish similarities and differences among toxaphene residues for many samples from different geographic regions (Stalling et al. 1982). This technique is also used for differentiating toxaphene from strobane, a pesticide very similar to toxaphene.

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## Environmental Fate of Toxaphene

The environmental fate of a compound is an important factor that should be considered prior to its use. If a pesticide is found to be persistent in the environment, bioaccumulated or extremely toxic to nontarget organisms, its use can be restricted or prohibited. Until recently, however, such information was generally not obtained before chemical compounds could be used and released into the environment.

Toxaphene is an example of a pesticide that was used for many years while its environmental fate was not fully known. In fact, even today the environmental fate of toxaphene is not fully understood (Sanborn et al. 1976).

Because toxaphene is a multicomponent mixture, assessing its fate is much more complex than for compounds that consist of a few chemical components. Such factors as differential degradation, metabolism and volatilization of the individual toxaphene components add to this complexity.

### Transport Routes

Like other pesticides, most of the toxaphene in the environment was introduced through its application to field crops as an insecticide or herbicide. After application, several transport routes and/or degradative pathways may dissipate the compound. Some is degraded or remains in the soil or vegetation. The remainder may be transported away from the treated area by volatilization to the atmosphere and/or runoff directly to adjacent terrestrial or aquatic environments. Leaching to groundwater appears to be negligible (Cohen et al. 1982).

Studies on the persistence of toxaphene in soil indicate that its half-life -- defined as the time required for half the original amount present to dissipate -- ranges from two months to 11 years (Seiber et al. 1979; Nash and Woolson 1967; McDowell et al. 1981). The variable half-life values reported probably reflect differences in soil types, weather conditions, application rate, drift, and sampling and analytical methods. However, anaerobic microbial degradation of toxaphene in soil has been documented (Parr and Smith 1976).

Volatilization to the atmosphere probably is the most significant route of toxaphene loss from soil, water and plant canopy (Cohen et al. 1982). Though the vapor pressure of toxaphene is relatively low, its resistance to degradation probably contributes to the importance of its vaporization. However, differential volatilization of the components of toxaphene complicates both the identification and the accurate quantification of toxaphene residues.

Figure 7 shows the alteration in toxaphene chromatograms that results from volatilization. Apparently, the less-chlorinated components of toxaphene have high vapor pressures and are more easily and quickly volatilized (Cohen et al. 1982).

Toxaphene has been identified in air samples taken over the western North Atlantic Ocean. The mean concentration for 56 samples was 0.6 ng/m<sup>3</sup>, as

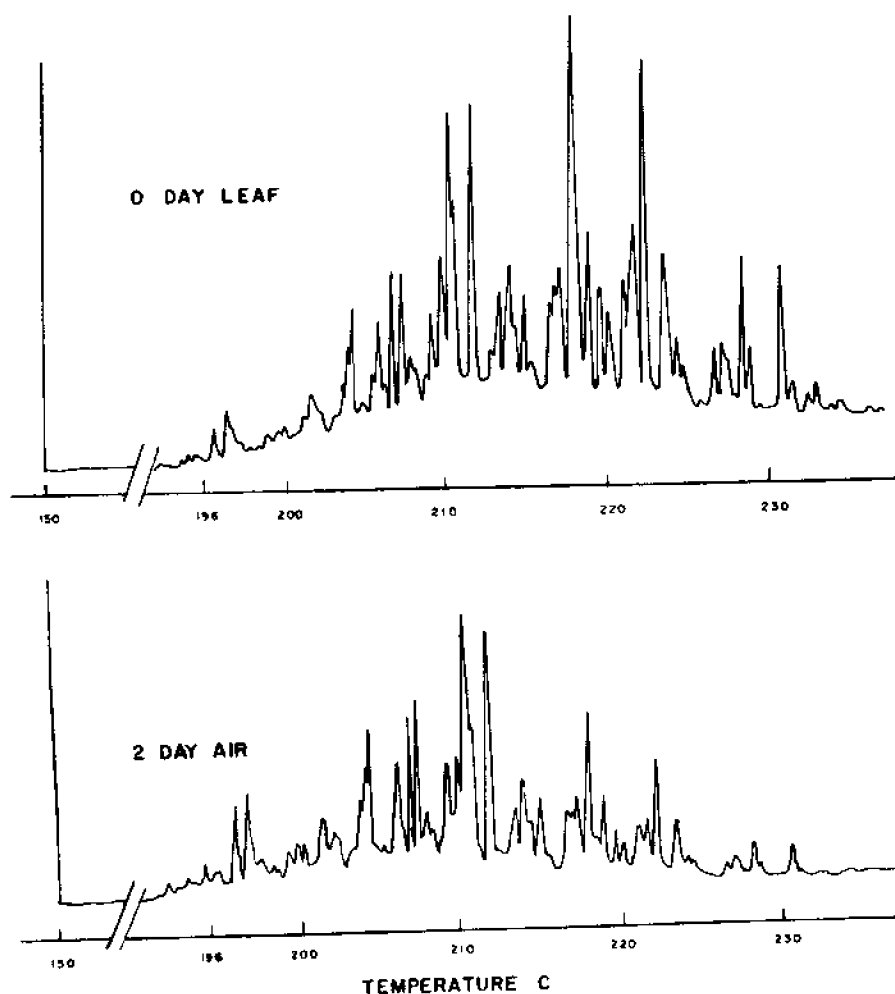


FIGURE 7: Capillary Gas Chromatograms of Toxaphene Residue in 0-Day Cotton Leaf and 2-Day Air Samples Taken from the Same Field (from Seiber et al. 1979)

compared to  $0.2 \text{ ng/m}^3$  for p,p'DDT (Bidleman and Olney 1975). The ratio of these concentrations is close to the ratio of the outdoor evaporation rates of these two pesticides (Bidleman and Olney 1975).

Also, toxaphene was identified in fish sampled from waters of the Great Lakes, Alaska, the Alps, northwestern Ireland, Caspian Sea and the North Atlantic, North Pacific and Antarctic oceans (Zell and Ballschmitter 1980; U.S. Fish and Wildlife Service 1982). The identification of toxaphene in air samples from over the ocean and in fish samples far from areas of toxaphene usage indicates that long-range transport occurs and that the major transport mechanism is most likely volatilization to the atmosphere.

The mechanism by which toxaphene is removed from the atmosphere is uncertain. Recent research indicates toxaphene is a major organochlorine in precipitation

(Bidleman and Christensen 1979). Based on the reported vapor pressure of  $10^{-6}$  mmHg (Korte et al. 1979) and a water solubility of 0.5 to 3 mg/L (Korte et al. 1979; Brooks 1974; Paris et al. 1977), toxaphene may be incorporated into rain droplets by vapor dissolution at high altitudes. Therefore, unlike PCBs and DDT -- which have higher air-water partition coefficients and are removed during precipitation by particle washout -- toxaphene may be removed by dissolution in raindrops. However, this assertion is based on vapor pressure and solubility data of uncertain accuracy.

Another route by which toxaphene is transported to streams and lakes is by direct runoff from treated fields. A linear relationship between toxaphene concentrations and sediment yield in runoff from treated fields has been observed in a Mississippi delta watershed (McDowell et al. 1981). Only a small portion of the total toxaphene concentration in the runoff was found in the water phase, indicating that toxaphene is strongly adsorbed to soil particles in the field. However, only about one percent of the total toxaphene applied to the field was accounted for in the runoff, even though a 58-day, 50 percent disappearance time was reported (McDowell et al. 1981).

### **Toxaphene in Aquatic Environments**

Once toxaphene enters an aquatic environment, several physical, chemical and biological mechanisms may contribute to dispersion of the compound. These include chemical or biological degradation, bioconcentration by living organisms, adsorption to suspended particulate matter, and/or removal from the water column by sedimentation or volatilization.

Toxaphene exhibits a variable persistence in the water column of lakes that is similar to its behavior in soil. Most of the available data is from lakes treated with toxaphene as a piscicide. These data indicate that toxaphene may persist in lake water anywhere from several months to nine years (Johnson et al. 1966; Terriere et al. 1966; Johnson 1966). Though the cause of this variable persistence is uncertain, toxaphene is less persistent in more eutrophic, shallow lakes than in deeper, less productive lakes.

Toxaphene can be chemically or biologically degraded in a number of ways, including dechlorination (elimination of a chlorine atom), dehydrochlorination (elimination of a chlorine and hydrogen atom), and reductive dechlorination (elimination of a chlorine atom and addition of a hydrogen atom) (Cohen et al. 1982). Chemical degradation by dehydrochlorination (Archer and Crosby 1966) and reductive dechlorination (Saleh and Casida 1978) has been observed in the laboratory, but under experimental conditions that are unlikely to occur in natural aquatic environments.

The major processes leading to dissipation of toxaphene in the water column are most likely adsorption to suspended matter and bioconcentration by aquatic organisms; volatilization to the atmosphere is probably minimal. Comparison of the Henry's Law constant (air-water partition coefficient) -- calculated from a vapor pressure of  $10^{-6}$  mmHg and an aqueous solubility of 1.5 mg/L with reported concentrations of 0.6 ng/m<sup>3</sup> in air (measured over the Atlantic) and of 0.6 ng/L in water of the Great Lakes -- suggests that toxaphene should not volatilize from the Great Lakes.

Table 2 gives the reported toxaphene bioconcentration factors for various freshwater species. The reported octanol-water partition coefficient of  $10^{3.5}$  to  $10^{6.4}$  is consistent with the observed tendency for bioaccumulation.

Once toxaphene reaches lake sediments through the settling of suspended particulate matter, both aerobic and anaerobic microbial degradation apparently occur (Seiber et al. 1979; Parr and Smith 1976; Clark and Matsumura 1979). However, degradation rates are probably slow, as shown by the range of a few months to several years for the half-life of toxaphene in soil. Based on available information, Figure 8 shows a simplified scheme of toxaphene transport and fate in the environment.

TABLE 2  
Bioconcentration Factors for Toxaphene

Freshwater Species	Bioconcentration Factor	Source
Brook Trout	5,000-76,000	Mayer et al. 1975
Rainbow Trout	10,000-20,000	Terriere et al. 1966
Aquatic Macrophytes	500-3,000	Terriere et al. 1966
Aquatic Invertebrates	1,000-2,000	Terriere et al. 1966
Alga	6,900	Archer and Crosby 1966
Snail	9,600	Archer and Crosby 1966
Fathead Minnow	37,000-69,000	Mayer et al. 1977
Channel Catfish	2,000-50,000	Mayer et al. 1977
Brook Trout Fry	15,000-20,000	Mayer et al. 1975

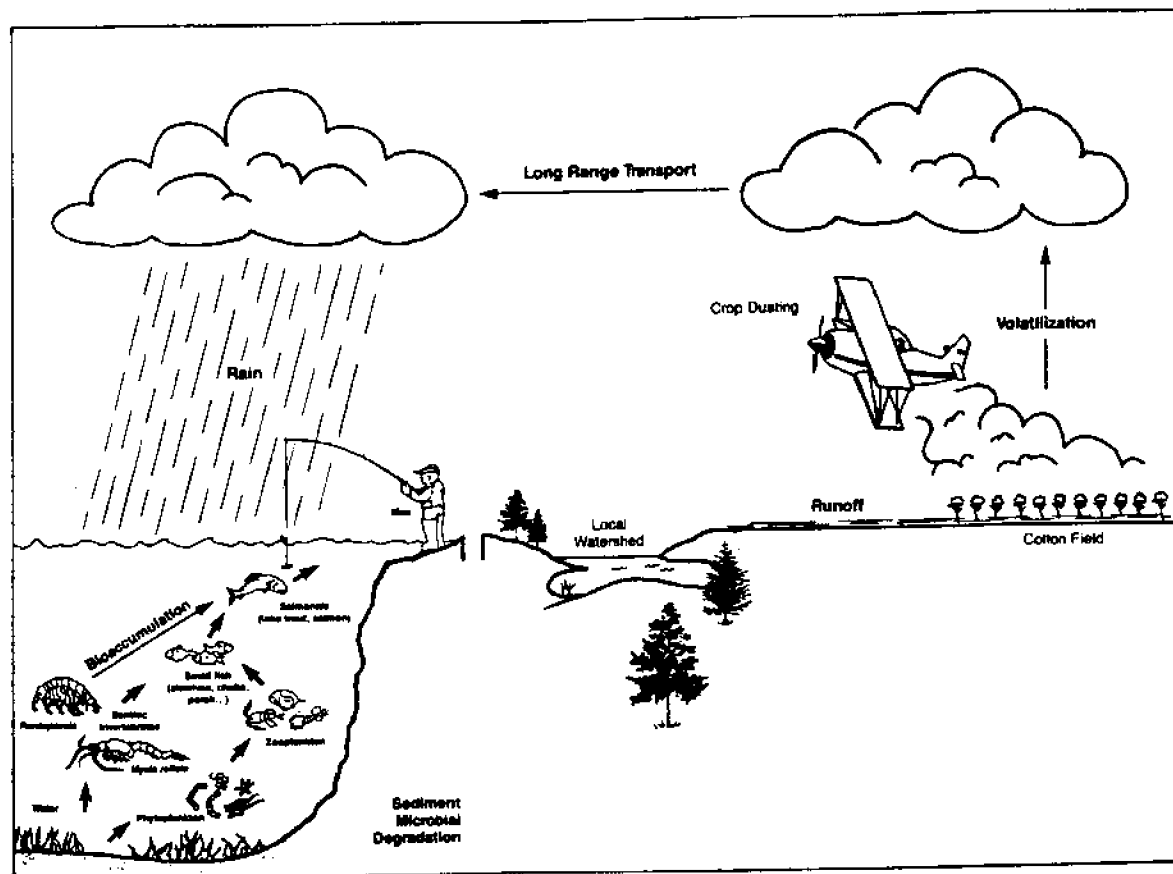


FIGURE 8: Transport and Fate of Toxaphene in the Environment



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## Toxicology of Technical Toxaphene

The acute and chronic toxicity of technical (100 percent) toxaphene to many organisms has been determined. At present environmental concentrations, toxaphene is probably a greater threat to aquatic life than to terrestrial wildlife or humans.

It is chronically toxic to fish at moderate (130–390 ng/L) concentrations and acutely toxic at higher (2–18 µg/L) concentrations (U.S. Fish and Wildlife Service 1982). In contrast, no toxic effect has been observed in monkeys, rats or dogs at dietary levels of 15, 25 and 40 mg/kg, respectively. However, toxaphene is a known animal carcinogen (USEPA 1980).

As with other multicomponent contaminants like PCBs, the toxicity is largely due to a few key components. This section discusses the identity of these toxic components, the alteration and metabolism of the technical toxaphene mixture, and the toxicity to aquatic and terrestrial life.

### Alteration, Metabolism and Component Toxicity

The composition of a major portion of the toxaphene transported through the environment is probably altered from that of the technical mixture. This alteration is due to a variety of factors, including differential volatilization and degradation. Microbiological degradation or metabolism by fish and solid-solution partitioning are possible alterations that may occur in lakes. Toxaphene residues collected from the atmosphere are similar to technical toxaphene, but those found in fish are not. The processes causing alteration and the toxicity of altered toxaphene components are key questions that remain unanswered.

Most organism exposure experiments have used technical toxaphene and so may not accurately reflect the true toxicity of environmentally altered toxaphene. However, a few components of toxaphene probably account for most of the toxic properties, so it is extremely important to determine the environmental fate and ultimate metabolic or degradation products of these toxicants. While the nature of toxaphene degradation products in aquatic systems is uncertain, the dechlorination and oxidative metabolism of toxaphene in animals has been documented (Khalifa et al. 1976; Matsumura et al. 1975).

At least four toxic components or toxic fractions of toxaphene have been isolated. The most toxic component, termed either toxic fraction A or toxicant A, is a mixture of two very similar compounds (Clark and Matsumura 1979; Nelson and Matsumura 1975; Turner et al. 1975), the structures of which are shown in Figure 9. A minor contaminant of toxic fraction A — toxicant Ac — has also been identified (Chandurkar et al. 1978).

Two other major toxic components and their structures are known: toxicant B and toxicant C (Casida et al. 1973; Palmer et al. 1975). The toxicity of these components has been established with a variety of test organisms, including mice, houseflies, fathead minnows, mosquito larvae and goldfish (Casida et al. 1973; Saleh and Casida 1979).

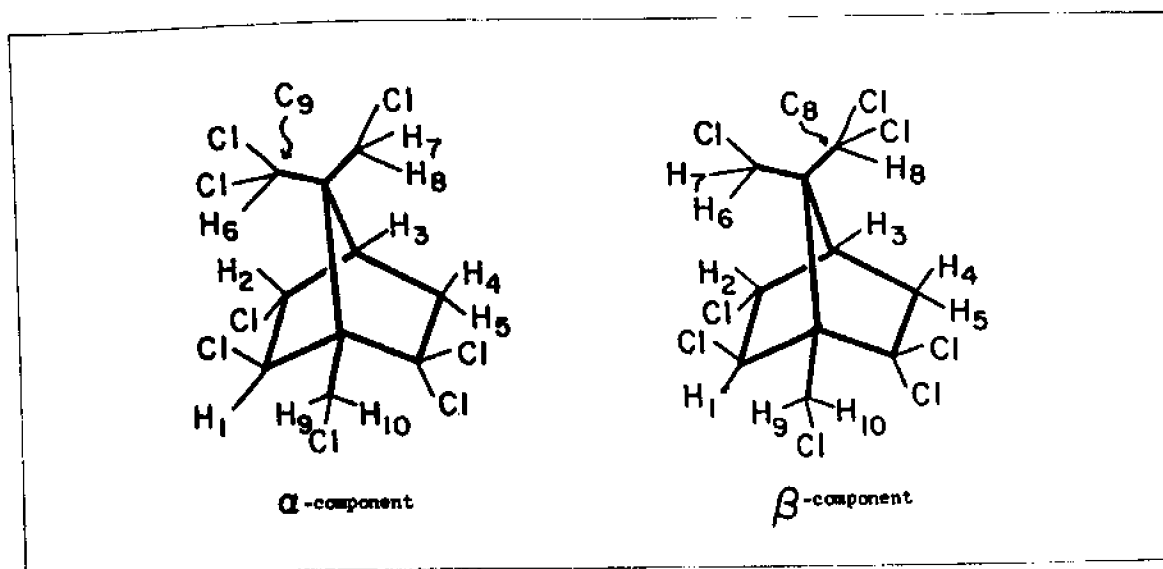


FIGURE 9: Chemical Structures of Toxic Fraction A, or Toxicant A (from Matsumura et al. 1975)

### Aquatic Toxicology

The acute toxicity of toxaphene to many aquatic species has been measured. The  $LC_{50}$  range for all freshwater animal species tested is 0.8–180  $\mu\text{g/L}$  (Table 3). A single test on a freshwater algal species, *Selenastrum capricornutum*, provided an  $EC_{50}$  of 0.38  $\mu\text{g/L}$  (USEPA 1980). ( $EC_{50}$  is the non-lethal concentration producing some effect in 50 percent of the test organisms).

TABLE 3  
Toxaphene Concentrations Acutely Toxic to Freshwater Aquatic Life

Organism	Number Tested (species)	Range of $LC_{50}$ ( $\mu\text{g/L}$ )	Most Sensitive Species	Least Sensitive Species
Fish	18	0.8–28	Channel Catfish ( <i>Ictalurus punctatus</i> )	Goldfish ( <i>Carassius auratus</i> )
Invertebrates	11	1.3–180	Midge Larvae ( <i>Chironomus plumosus</i> )	Stonefly ( <i>Claassenia sabulosa</i> )

SOURCE: Summarized from USEPA 1980.

Chronic toxicity is defined as death or damage to an organism by poisoning through prolonged exposure. The length of the test is generally determined by the life span of the organism and can last from days to years. Ideally, the chronic test period includes the organism's most sensitive life stage.

The chronic effects of toxaphene on freshwater fish include inhibited growth; reduced egg viability, growth rate and collagen levels; increased mortality during spawning; atrophy of liver cells, and proliferation of tissues of the kidney (Mayer et al. 1975; Mehrle and Mayer 1975; Hamilton et al. 1981). Known chronic toxicity in freshwater invertebrates includes fewer offspring, decreased growth and delayed emergence from the larval stage (Sanders 1980). Chronic effects to fishes have occurred at concentrations as low as 25 ng/L. Table 4 summarizes chronic toxaphene exposure values for freshwater organisms; Table 5 gives examples of specific chronic toxicities observed in fish.

### Wildlife Toxicology

Warm-blooded animals are less sensitive than aquatic organisms to acute toxaphene poisoning. In cases of acute toxicity in laboratory mammals, toxaphene, like most other chlorinated hydrocarbon insecticides, appears to act as a central nervous system stimulant (Archer and Crosby 1966). In general, birds are more sensitive than mammals to acute poisoning. Table 6 summarizes the acute oral toxicity of toxaphene to warm-blooded animals.

Toxaphene is a known animal carcinogen but is not listed as one of the 18 known human carcinogens by the International Agency for Research on Cancer. The National Cancer Institute, however, states that "chemicals found carcinogenic in animal tests are generally considered capable of causing cancer in humans." Furthermore, the potential carcinogenicity of toxaphene appears to be more important than noncarcinogenic effects in animals (Cohen et al. 1982).

TABLE 4  
Toxaphene Concentrations Chronically Toxic to Freshwater Aquatic Life

Organism	Number Tested (species)	Concentration (ng/L)	Most Sensitive Species	Least Sensitive Species
Fish	2	25-72	Fathead Minnow ( <u>Pimephales promelas</u> )	Channel Catfish ( <u>Ictalurus punctatus</u> )
Invertebrates	3	70-320	Cladoceran ( <u>Daphnia magna</u> )	Midge Larvae ( <u>Chironomus plumosus</u> )

SOURCE: Summarized from USEPA 1980; based on life cycle exposure or substantial portion of life cycle.

TABLE 5  
Sublethal Concentrations and Effects of Toxaphene to Fish

Species	Duration of Test	Concentration (ng/L)	Effect
Brook Trout	161 days	288	Growth inhibition and mortality
Fathead Minnow	30 days	97	Growth inhibition
Fathead Minnow (fry)	30 days	54	Growth inhibition
Brook Trout	161 days	68	Decreased reproduction (egg viability)
Channel Catfish (fry)	15 days	72	Impaired backbone quality

SOURCE: Summarized from USEPA 1980.

TABLE 6  
Acute Oral Toxicity of Toxaphene to Warm-Blooded Animals

Organism	Number Tested (species)	Range of LD <sub>50</sub> (mg/kg)	Most Sensitive Species	Least Sensitive Species
Avians	6	10-316	Sharp-Tailed Grouse	Lesser Sand Hill Crane
Laboratory Mammals	6	25-220	Cats and Dogs	Rat
Mule Deer	1	139-240	NA	NA
Domestic Goat	1	160	NA	NA

NA = Not Applicable.

## **Toxaphene in the Great Lakes Basin**

As early as 1972, toxaphene-like residues were reported in Great Lakes fish (Schmitt et al. 1981), yet only recently has toxaphene been documented as a ubiquitous contaminant of the Great Lakes basin (U.S. Fish and Wildlife Service 1982; Filkins et al. 1983). Apparently, both the chemical and analytical complexities associated with toxaphene analysis led to the underreporting and/or lack of analysis for this compound.

Even today, the analytical data are considered very complex and not completely understood (USEPA 1981). However, recent advances in analytical methodology are helping to better understand and more accurately and precisely report such data (Ribick et al. 1982; Stalling et al. 1982).

### **Sources of Toxaphene**

Long-range atmospheric transport appears to be the major pathway of toxaphene input to the Great Lakes basin. Depending on seasonal weather patterns, the major sources for long-range transport to the basin are most likely the Cotton Belt area of the southern U.S. and, in lesser amounts, California and/or the Dakotas.

The limited evidence available on toxaphene sources and transport support this assumption. Toxaphene concentrations of about 3 mg/kg have been found in lake trout from Siskiwit Lake, a landlocked lake on Isle Royale, a national park island in Lake Superior; the only known source of contaminant input to this lake is atmospheric (Swain 1980).

The assumption is further supported by data showing rainwater over Lake Erie to contain toxaphene concentrations of approximately 0.03  $\mu\text{g/L}$  (U.S. Fish and Wildlife Service 1982). And measurements of toxaphene in offshore waters of four of the five Great Lakes indicate that all four are contaminated at nearly equal concentrations, again suggesting a diffuse (i.e., atmospheric) source rather than local point sources (Filkins et al. 1983).

Toxaphene was never manufactured in the Great Lakes basin, and usage data indicate that, basinwide, only small amounts were applied for pesticidal use (Zygadlo 1982). A recent select summary of data on priority pollutants in the discharges of major Great Lakes industries -- pulp and paper mills, petroleum refineries, iron and steel mills, and organic chemical and plastic/synthetic materials manufacturers -- did not reveal any toxaphene discharges at levels exceeding 10  $\mu\text{g/L}$  (Nunno et al. 1983). While this is a relatively high concentration and it is possible that unreported discharges of toxaphene at lower concentrations are significant, it is unlikely that industrial discharge of toxaphene into the Great Lakes is substantial.

Formulators and distributors of toxaphene products are located in Minnesota and Ohio, but discharges from these types of sources are probably minimal as well. When all available usage and discharge data for toxaphene in the basin are considered, the contribution from these sources, though not quantifiable, is probably small.

### Other Possible Sources

Other possible sources for the toxaphene-like residues in the Great Lakes have been suggested. One is strobane, an insecticide very similar to toxaphene first marketed by the B.F. Goodrich Chemical Company in 1951. However, the use of strobane as an insecticide was small compared to use of toxaphene, and strobane was classified as being of little commercial interest in 1971 -- five years before its use was banned by the USEPA, and 11 years before toxaphene use was restricted (Martin 1971; Ware 1978). Therefore, strobane is probably not a significant source of the toxaphene-like residues in the Great Lakes.

Another potential source of such residues to the Great Lakes are local pulp and paper mills that use chlorine as a bleaching or disinfecting agent. Because toxaphene itself is ultimately derived from natural extractives found in pine trees, softwood pulp mills with bleach plants or final effluent chlorination could contain low concentrations of chlorinated camphene-like compounds. However, the degree of chlorination of technical toxaphene -- five to 10 chlorine atoms per molecule -- probably would not be achieved in a pulp mill bleach plant or final effluent chlorination.

Other potential sources of chlorinated camphene-like compounds are industries that use pine oil (i.e., the textile industry) and chlorinate it at some point in the plant before discharge. However, such industrial sources of toxaphene-like residues would probably have only a local effect, creating contaminant "hotspots" rather than the diffuse contamination found in the Great Lakes. To date, no localized contamination of Great Lakes fish by toxaphene-like residues has been reported.

### Toxaphene Concentrations in Great Lakes Water and Fish

The database on toxaphene concentrations in the Great Lakes is limited, but data has been obtained on both water and fish samples. In 1981, measurements of the offshore waters of Lakes Ontario, Erie, Michigan and Superior revealed that each lake had nearly equal concentrations of toxaphene, averaging 0.6 ng/L (Table 7). These concentrations are in the same range as those reported for

TABLE 7  
Open Lake Water Column Concentrations of Toxaphene

Lake	Number of Samples	Mean Toxaphene Concentration (ng/L)
Ontario	4	0.6
Erie	3	0.7
St. Clair	1	0.3
Michigan	4	0.6
Superior	4	0.5

SOURCE: Filkins et al. 1983.

PCBs (0.5–2 ng/L) in open waters of the Great Lakes (Eisenreich et al. 1983; Swackhamer 1985). Lake Huron was not measured. One sample from Lake St. Clair near Detroit contained 0.3 ng/L of toxaphene.

Measurements of Great Lakes lake trout in 1977 and 1979 indicate toxaphene concentrations in the 1.9–10.7 mg/kg range, averaging 6.3 mg/kg (Table 8). The relatively uniform concentrations in lake trout are consistent with the uniformity of the toxaphene concentrations found in the water column of each lake.

Toxaphene concentrations in bloater chubs and lake whitefish follow the same pattern as those for lake trout (Figure 10), except they are lower (Table 9). The bloater chub and lake trout data are comparable because the fish tested for both species were in the same age range. The lower concentrations in chubs are to be expected because they occupy a lower trophic level in the lake food chain.

TABLE 8  
Toxaphene Residues in Lake Trout from Three Great Lakes

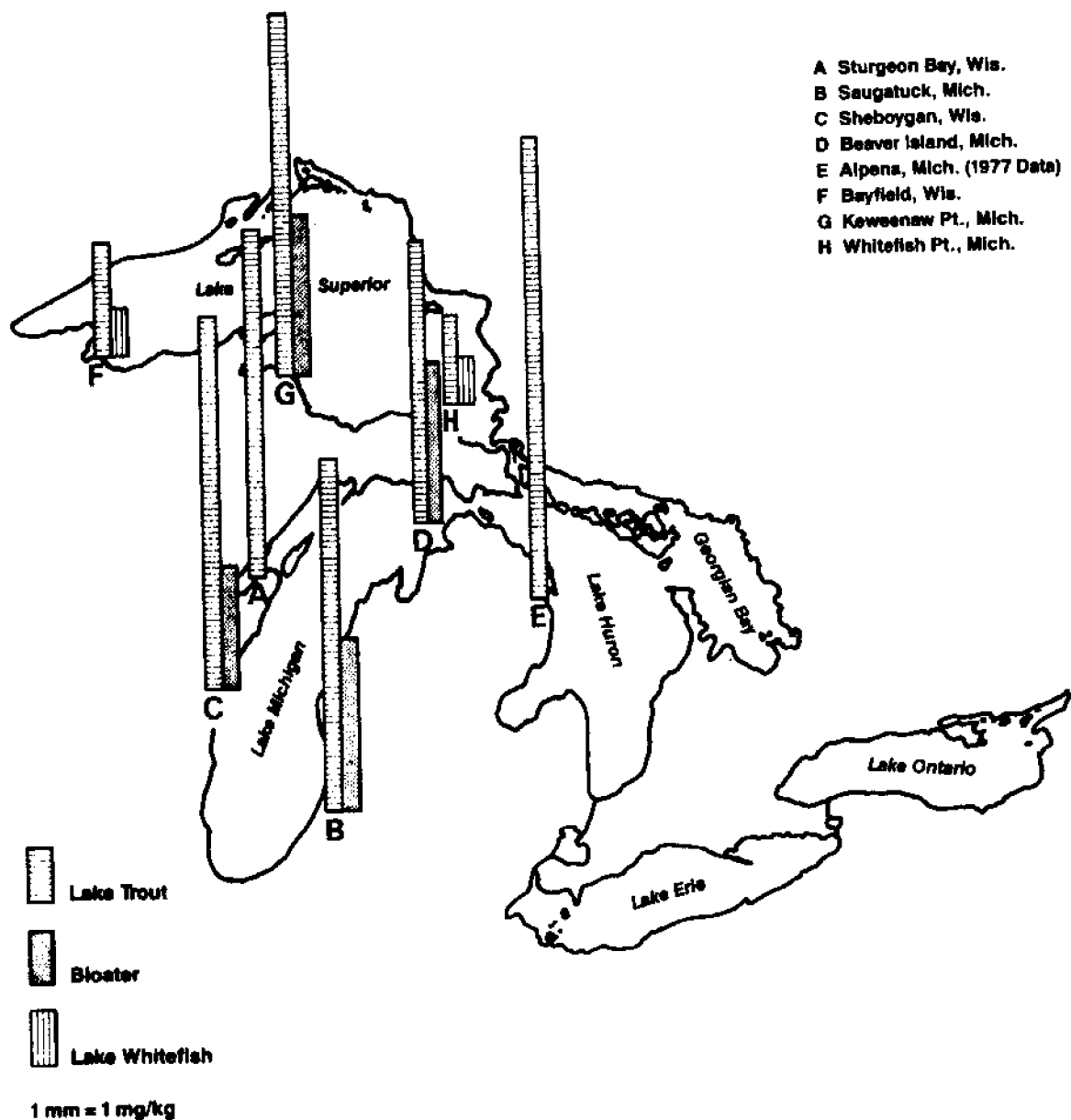
Lake	Location	Year	Mean Length (mm)	Toxaphene Concentration (mg/kg wet weight)
Michigan	Sheboygan, Wis.	1977	698	7.8
Michigan	Sheboygan, Wis.	1979	612	7.1
Michigan <sup>1</sup>	Sturgeon Bay, Wis.	1978	717	10.7*
Michigan <sup>1</sup>	Sturgeon Bay, Wis.	1979	688	6.7*
Michigan <sup>1</sup>	Charlevoix, Mich.	1977	697	6.7*
Michigan <sup>1</sup>	Charlevoix, Mich.	1978	671	8.4*
Michigan	Beaver Island, Mich.	1977	653	8.1
Michigan	Beaver Island, Mich.	1979	610	5.5
Michigan	Saugatuck, Mich.	1977	627	7.0
Michigan <sup>1</sup>	Saugatuck, Mich.	1977	653	7.0*
Michigan <sup>1</sup>	Saugatuck, Mich.	1978	701	7.6*
Michigan	Saugatuck, Mich.	1979	701	6.8
Michigan <sup>1</sup>	Saugatuck, Mich.	1979	694	6.8*
Huron	Alpena, Mich.	1977	594	9.0
Superior	Bayfield, Wis.	1977	627	5.2
Superior	Bayfield, Wis.	1979	630	2.2
Superior	Keweenaw Pt., Mich.	1977	559	3.0
Superior	Keweenaw Pt., Mich.	1979	605	7.3
Superior	Whitefish Pt., Mich.	1977	607	3.1
Superior	Whitefish Pt., Mich.	1979	561	1.9

<sup>1</sup>Average of duplicate analyses.

\*20 fish per sample; all others five fish per sample.

SOURCE: U.S. Fish and Wildlife Service 1982.

FIGURE 10: Average Toxaphene Concentrations in Fish, 1979



The concentrations of toxaphene in other species of carnivorous fish are also lower than in lake trout (Table 10). This is consistent with the lake trout's high lipid content, which is often used as an indication of an animal's tendency to accumulate contaminants. However, other factors -- such as age, size, ecological niche, forage base and efficiency of conversion of food to body weight -- probably also contribute to these differences.



**TABLE 9**  
**Toxaphene Concentrations in Bloater Chub and Lake Whitefish**  
**from Lakes Superior and Michigan**  
**(5 fish/sample)**

Lake	Location	Species	Year	Mean Length (mm)	Toxaphene Concentration (mg/kg wet wt.)
Michigan	Sheboygan, Wis.	Bloater	1977	257	3.5
Michigan	Sheboygan, Wis.	Bloater	1977	254	3.3
Michigan	Sheboygan, Wis.	Bloater	1979	284	2.7
Michigan	Sheboygan, Wis.	Bloater	1979	269	2.3
Michigan	Beaver Island, Mich.	Bloater	1977	287	6.4
Michigan	Beaver Island, Mich.	Bloater	1979	307	3.3
Michigan	Beaver Island, Mich.	Bloater	1979	282	3.1
Michigan	Saugatuck, Mich.	Bloater	1977	290	3.7
Michigan	Saugatuck, Mich.	Bloater	1977	287	0.6
Michigan	Saugatuck, Mich.	Bloater	1979	287	3.4
Michigan	Saugatuck, Mich.	Bloater	1979	297	3.4
Superior	Bayfield, Wis.	Whitefish	1977	516	2.3
Superior	Bayfield, Wis.	Whitefish	1979	335	0.9
Superior	Bayfield, Wis.	Whitefish	1979	328	0.6
Superior	Keweenaw Pt., Mich.	Bloater	1977	264	2.8
Superior	Keweenaw Pt., Mich.	Bloater	1977	262	2.9
Superior	Keweenaw Pt., Mich.	Bloater	1979	277	3.6
Superior	Keweenaw Pt., Mich.	Bloater	1979	295	2.8
Superior	Whitefish Pt., Mich.	Whitefish	1977	488	1.4
Superior	Whitefish Pt., Mich.	Whitefish	1977	503	2.1
Superior	Whitefish Pt., Mich.	Whitefish	1979	566	1.2
Superior	Whitefish Pt., Mich.	Whitefish	1979	495	0.7

SOURCE: U.S. Fish and Wildlife Service 1982.

#### Contamination Criteria for Water, Fish and Humans

To protect freshwater aquatic life, the USEPA has established a water quality criterion of an average toxaphene concentration of 0.013 µg/L over 24 hours, with the concentration not to exceed 1.6 µg/L at any time. The U.S.-Canadian International Joint Commission has recommended a maximum water concentration of 0.008 µg/L for the protection of aquatic life. Based on known water column concentrations and the proposed criteria, it appears that aquatic life in the Great Lakes is not threatened. However, the U.S. Fish and Wildlife Service has suggested that toxaphene is a contributing factor in the agency's failure to reestablish a self-sustaining lake trout population in Lake Michigan (Jantzen 1982). Laboratory tests with brook trout show that toxaphene body burdens in the range of 2-5 mg/kg have resulted in reduced egg viability (Mayer et al. 1975).

TABLE 10  
Toxaphene Concentrations in Various Fish  
from Lakes Huron, Ontario and Erie, 1979

Lake	Location	Fish Species	Mean Length (mm)	Toxaphene Concentration (mg/kg wet wt.)
Huron	Saginaw Bay/Bayport, Mich.	Common Carp	470	0.31
Huron	Saginaw Bay/Bayport, Mich.	Common Carp	434	3.70
Huron	Saginaw Bay/Bayport, Mich.	Yellow Perch	180	0.20
Huron	Alpena, Mich.	White Sucker	325	ND
Huron	Alpena, Mich.	White Sucker	345	0.30
Huron	Alpena, Mich.	Yellow Perch	236	1.50
Huron*	Tawas River/Tawas, Mich.	Coho Salmon	719	1.50
Erie	Port Colbourne, Canada	Common Carp	447	ND
Erie	Port Colbourne, Canada	Common Carp	384	ND
Erie	Port Colbourne, Canada	Walleye	378	0.50
Erie*	Detroit River/Detroit, Mich.	Coho Salmon	654	0.4
Erie**	Erie, Pa.	Red Horse	399	0.17
Erie**	Erie, Pa.	Yellow Perch	218	0.34
Ontario	Port Ontario, N.Y.	Rock Bass	221	0.20
Ontario	Port Ontario, N.Y.	Yellow Perch	208	ND
Ontario	Port Ontario, N.Y.	Yellow Perch	208	0.30
Ontario	Putneyville, N.Y.	Coho Salmon*	773	0.77
Ontario	Roosevelt Beach, N.Y.	Brown Trout	442	1.40
Ontario	Roosevelt Beach, N.Y.	Rock Bass	196	ND
Ontario	Roosevelt Beach, N.Y.	Rock Bass	198	0.60

\*Apparent toxaphene (1980 sample).

\*\*1980 sample.

ND = Not Detected.

SOURCES: Clark et al. 1984 and National Pesticide Monitoring Program Data (Great Lakes Region) from the Columbia National Fisheries Research Laboratory.

In an attempt to protect human health from the potentially carcinogenic effects of toxaphene exposure through the ingestion of contaminated water and aquatic organisms, the USEPA has recommended water quality criteria based on ambient water column concentrations. The toxaphene levels at which an increased risk of cancer may result over a human lifetime are estimated at risk increments of  $10^{-5}$ ,  $10^{-6}$  and  $10^{-7}$ . The corresponding recommended criteria for toxaphene concentrations in water are 7.3, 0.73 and 0.07 ng/L, respectively.

According to these criteria and the present water column concentrations of toxaphene (0.3-0.7 ng/L) in the Great Lakes, the expected increase in human cancer deaths due to consumption of toxaphene-contaminated water and aquatic organisms is approximately one per million ( $10^{-6}$ ), assuming a daily ingestion of 2 liters of water and 6.5 grams of fish.

### **Maximum and Acceptable Daily Human Exposure**

In 1976, the USEPA estimated the maximum safe daily dose (MSDD) of toxaphene for humans at 3.4  $\mu\text{g/kg}$  of body weight. The MSDD was based on extrapolation of test data that revealed minimal or no effects in rats fed a comparable amount of toxaphene in their diet.

Similarly, in 1977, the National Academy of Science (NAS) estimated that the acceptable daily intake (ADI) of toxaphene for humans was 1.25  $\mu\text{g/kg}$  of body weight. The ADI was based on a study in which rats evidenced increased liver weight and hepatic cell enlargement after exposure to toxaphene in their diet for two years.

Based on these estimates, a 68-kilogram (150-pound) human who consumed 225 grams (0.5 pound) of a 640-millimeter (24-inch) Lake Superior lake trout caught near Bayfield, Wis., in 1982 would have been exposed to about five times the NAS acceptable intake level and about twice maximum safe dose set by the USEPA.

In contrast, if the same person ate the same amount of a 320-millimeter (12-inch) whitefish from the Bayfield area at that time, his/her exposure would have been slightly less than the NAS' ADI and well below the USEPA's MSDD. A person consuming fish containing 5.0 mg/kg toxaphene (the USFDA tolerance level) would be exposed to approximately 6.5 times the ADI and 2.5 times the MSDD.

These exposure levels were calculated from a whole, uncooked lake trout with a toxaphene concentration of 3.7 mg/kg and a mean raw whitefish concentration of 0.75 mg/kg, and assumed a 50 percent reduction in the toxaphene concentration in the fillet, or edible portion, as compared to the whole fish.

Proper preparation and cooking of the fish fillet (i.e., removing all skin; trimming dorsal, lateral and belly fat; and broiling or baking the fillet rather than boiling or deep frying it) will further reduce its toxaphene concentration.

While these consumption guidelines indicate that toxaphene exposure through the eating of Great Lakes fish could adversely affect human health, the margin for safety in such estimates is high. ADI and MSDD concentrations are derived by extrapolation of animal test data to humans, and a large degree of uncertainty exists because of the unknown sensitivity of humans versus test animals.

To ensure adequate protection of human health, the NAS and USEPA use large safety factors in establishing the ADIs and MSDDs for various contaminants. In the case of toxaphene, the USEPA used a safety factor of 500, while the NAS used a safety factor of 1,000.

### Questions Remain

Though toxaphene has been identified as a ubiquitous Great Lakes contaminant, three key questions regarding the fate and effects of toxaphene in the Great Lakes remain to be answered:

- How long will it take for toxaphene concentrations in fish to decline to acceptable levels now that toxaphene usage is limited and will probably eventually cease?
- Are current toxaphene body burdens in lake trout great enough to contribute to reproductive failure, thereby thwarting efforts to reestablish a self-sustaining lake trout population in Lake Michigan?
- Is environmentally altered toxaphene as toxic to fish and humans as technical toxaphene?

Research on toxaphene and other organochlorine contaminants found in the Great Lakes must continue if answers to these questions are to be found.

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