BIOMAGNIFICATION OF TOXAPHENE IN THE LAKE MICHIGAN LOWER FOODWEB

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I. INTRODUCTION

Toxaphene is a broad-spectrum pesticide that is considered to have been the most widely used chlorinated agricultural chemical in the U.S.[1]. It was the replacement for DDT when the latter was banned in 1972, and was used primarily on cotton, peanuts, soybeans, and grains, and as a cattle dip. Toxaphene consists of a complex mixture of chlorinated bornanes and bornenes, made by the chlorination of terpenes from pine tree roots. It was produced either by chlorinating pinenes (Strobane) or camphenes (toxaphene), and contains at least 670 different components [2]. It was first introduced in 1947 by Hercules [3], and was used in the 1950's and 1960's as a piscicide to kill rough fish from inland lakes in the upper mid-west and Canada [4]. It was banned in 1982 in the U.S. following concerns about it's toxicity and widespread environmental distribution.

Approximately 85% of the toxaphene used in the US was on cotton crops in the southern states from Texas eastward to Georgia. Approximately 1% or less was used in the Great Lakes basin [5]. The rate of use in the basin (including Ontario) was approximately 1 million kg/yr in the early 1970's, and would have peaked in approximately 1977. Thus the presence of toxaphene in the Great Lakes has largely been attributed to long-range atmospheric transport from the southern U.S. or Central America, followed by wet and dry deposition to the lakes [6-7].

The history, physical chemistry, toxicology, and environmental contamination of toxaphene have been nicely reviewed elsewhere [1, 8], Rice and Evans (1983), and in a special issue of *Chemosphere*[9] that was the proceedings of an international gathering focused on toxaphene. More recently, toxaphene has been identified as being a synergistic endocrine disrupter in combination with other organochlorine pesticides [10].

Toxaphene has been reported in air, sediment, and biota from around the world. It has been found in fish from the Great Lakes and Canada and in aquatic mammals from the world's oceans. Toxaphene is the contaminant found in the highest concentration of all organochlorine compounds in fish from Lake Superior, including PCBs and ΣDDT [11].

In cases where both fish and water concentrations are known, a bioaccumulation factor (BAF) can be calculated as BAF = concentration in fish tissue, ng/kg ÷ concentration in water, ng/L. Based on lake trout data from Glassmeyer et al. [11] and water data from this laboratory, the log BAFs for toxaphene in Great Lakes lake trout are estimated to be approximately 6.5 ± 0.1. The magnitude of the BAF is greater than would be expected based on it's physical-chemical properties. This observation led us to examine the lower trophic levels of the Lake Michigan foodweb to gain insight into which trophic levels were most important in contributing to the observed bioaccumulation in top predators.

II. METHODS

Samples of water (dissolved phase), net phytoplankton, *Mysis relicta*, and *Diporeia* sp. were collected from 11 sites throughout Lake Michigan on 7 occasions over a two year period from the U.S. EPA R/V *Lake Guardian*.

Samples were extracted by Soxhlet extraction using methanol and dichloromethane. Extracts were cleaned by alumina and silica gel column chromatography. Final extracts in hexane were analyzed by gas chromatographic electron capture negative ion mass spectrometry as described elsewhere [12]. The program was adjusted to also quantitate isomers of chlordane and nonachlor in addition to toxaphene and its homologs. A surrogate compound (^{13}C-chlordane) was added to all samples to monitor laboratory procedural recoveries, and an internal standard (PCB congener #204) was added at the time of instrumental analysis. Surrogate recoveries averaged approximately 85%, and all data were corrected for surrogate recovery. Precision based on replicate sample analyses was approximately ± 15 - 25% for all compounds. Concentrations were determined on a dry weight and lipid weight basis, and BAFs were calculated as described above.

III. RESULTS AND DISCUSSION

Preliminary results indicate that concentrations of toxaphene were in the range of 50 ng/g dry weight in phytoplankton, with zooplankton having about twice that amount and *Diporeia* having about 10 times that amount. The observed log BAFs were approximately 5, 5.4, and 6 for phytoplankton, zooplankton, and *Diporeia*, respectively. The lower trophic levels of the pelagic foodweb have significantly lower BAFs than do lake trout, indicating that a substantial degree of biomagnification of toxaphene takes place in upper trophic levels. The higher BAF for *Diporeia* may also indicate the importance of the benthic component of the foodweb to overall biomagnification. Nonachlor and chlordane components had greater BAFs than toxaphene at all trophic levels considered.

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