Toxaphene Congeners in the Canadian Great Lakes Basin: Temporal and Spatial Food Web Dynamics

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Introduction

Samples of top predator and major forage fish species from throughout the Great Lakes and 3 lake systems within the basin were analysed for body burdens of total toxaphene and 22 toxaphene congeners. In addition, samples of major invertebrate dietary items, such as *Mysis*, *Diporeia* and plankton, were similarly analysed. Whole lake trout samples, archived at -80 C, were reanalysed to determine historical trends of toxaphene congeners plus carbon and nitrogen stable isotopes. The Lake Superior foodweb consistently has the highest levels of total toxaphene of all the Great Lakes monitored. The primary source of toxaphene to Lake Superior has been identified as atmospheric transport and deposition from sites in the southern US, Mexico and Central America (1). Of the offsystem lakes surveyed, Lake Nipigon, situated due north of Lake Superior and with a lake basin area of about 6% of Lake Superior, has total toxaphene levels in lake trout equivalent to about 45% of those found in lake trout from Lake Superior. Temporal trend analysis was conducted on archived whole fish samples collected over the period 1980 through to the 1990's. Initially a nonachlorobornane congener (Parlar # 50) was predominant, with congeners #40, # 62 and # 21 being the next most prominent in the 1980 samples. Samples from the 1990's showed a significant decline in the presence of lower chlorinated congeners # 40 and # 21. Analysis of total toxaphene in foodwebs, indicated elevated levels in lower trophic level species such as *Diporeia* and *Cottus sp.* which had a benthic association. The stable isotope temporal trend δ 13 C signature identifies a significant shift in the lake trout diet over the period 1993 to 1996

Background

Toxaphene, a mixture of chlorobornanes, is a ubiquitous contaminant within the Great Lakes ecosystem. (2) Next to PCB and DDT, toxaphene is the most predominant organic contaminant in all aquatic biota within the basin. Although the use of toxaphene was banned or severely restricted in Canada and the US in the early 1980's, there is little evidence that Great Lakes basin levels have declined significantly since then. Toxaphene

formulations are still used in Mexico and South America. Atmospheric transport from these regions has been identified as the most likely source of toxaphene to the Great Lakes. No new local sources of toxaphene have been identified. Recently imposed consumption guidelines for fish from Lake Superior and Lake Huron are based on elevated levels of total toxaphene.(3) Traditional measurements of total toxaphene have been replaced by homologue and individual congener analysis. These techniques, when applied to historical samples, provide a means of identifying possible changes in the sources of toxaphene. Retrospective analysis of stable isotope (N and C) ratios assists in the determination in the change in foodweb structure and dynamics over time. Changes in foodweb function can alter contaminant accumulation patterns and whole animal concentrations.

Materials and Methods

Invertebrate and fish samples were sorted/homogenized and stored @ -80C prior to analysis.

All samples of fish were analysed on a whole fish basis.

Samples were extracted with methylene chloride (MC), lipids were removed via GPC and extracts were cleaned up on 1% deactivated silica gel columns with MC.

All data are expressed on a wet weight & whole animal basis.

Total toxaphene levels were determined using GC-ECD methodology.

Quantification of toxaphene congeners was completed by GC-ECD utilizing a 22-component Parlar toxaphene analytical standard -.

The stable isotopic ratio was calculated as:

$$\delta X = [(R_{SAMPLE}/R_{STANDARD}) - 1] \times 10^3 \text{ (per ml)}$$
where $X = {}^{15}N$ or ${}^{13}C$ and $R = {}^{15}N/{}^{14}N$ or ${}^{13}C/{}^{12}C$

Results

Lake Superior has the highest levels of total toxaphene in all trophic levels.

Total toxaphene levels in Lake Superior top predator lake trout are at least 60% greater than all other Great Lakes surveyed

Lake Nipigon has a basin area ~ 6% of Lake Superior but toxaphene levels are 45% of those measured in Lake Superior lake trout.

There are similarities in foodweb BMFs f(biomagnification factors) for most of the Great Lakes surveyed: ie: Ontario - 30.5, Erie - 5.4, Huron - 24.3 & Superior - 31.0.

The homologue pattern has changed significantly from 1980 to 1995 with a decrease in the lower chlorinated (hexa & hepta) congener groups.

A nonachlorobornane (Palar # 50) is consistently the predominant congener through time (1980-95) in Lake Superior lake trout.

In the 1990's there has been a significant decline in 2 lower chlorinated congeners – [#21-hepta and #40-octa] in archived lake trout whole fish homogenates.

Changes in δ^{13} C from 1993 to 1996 indicate a significant shift in diet of Lake Superior lake trout.

Discussion

Although toxaphene has not been used in the Great Lakes basin for more than 15 years, concentrations in biota have not declined significantly in some lakes. Recently consumption advisories have been issued for large sport fish species from Lake Superior whose muscle tissue levels exceeded 0.2 μg/g (3). Currently 68% of the consumption advisories for Lake Superior are related to elevated toxaphene concentrations. There has been speculation on a lake specific loading of toxaphene to Lake Superior (2). The reduction in the levels of lower chlorinated toxaphene homologues (hexa-hepta) noted in lake trout samples from 1980 to 1995 may indicate an increase in the contribution of atmospheric sources to the total loadings to Lake Superior over that time period. Atmospheric transport tends to result in the degradation of the hexa- and hepta-chlorinated homologues. The most rapid decline was observed in Parlar #21, a heptachlorobornane. Conversely there was little or no decline in the concentration of the 6 nonachlorobornane congeners measured in lake trout samples. Analysis of stable isotope signatures in the foodweb presents an indication of changes in feeding patterns. (4) and(5) have previously demonstrated the relationship between $^{13}C/^{12}C$ stable isotope ratios and contaminant bioaccumulation in a lake trout foodweb. Based on $\delta^{13}C$ signatures measured in the Lake Superior foodweb in 1993 and in 1996, the data indicate that lake trout have shifted from a diet dominated by sculpins and smelt to one dominated by cisco. Cisco have significantly higher total toxaphene levels than smelt and sculpin (Thus, increased cisco consumption would result in higher body burdens of total toxaphene in lake trout.

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