TRENDS OF CONGENERS AND ENANTIOMER RATIOS OF TOXAPHENE IN LAKE TROUT FROM LAKE SUPERIOR

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Introduction

The measurement of enantiomer ratios for chiral pollutants in environmental samples is a useful method of determining sources, pathways and fate of these compounds [1]. Atmospheric deposition is the the primary source of toxaphene to the lake basin today [2, 3]. In Lake Superior, levels of toxaphene in the lake trout population have not declined significantly since 1980 and have recently increased in concentration [4].

The objectives for this study was to provide evidence for that the changes in feeding patterns for lake trout was responsible for the increased body burdens in the fish [4]. The shift from the less contaminated smelt as a major diet item to the more contaminated lake herring could be reflected in both changes in enantiomer ratios and higher toxaphene body burdens.

The objective of the study was to determine if changes in congener and enantiomer pattern in lake trout samples from 1980 through 1998 were reflective of changes in the diet and feeding pattern over that time period. In addition, the major food items of lake trout, lake herring and smelt were analysed enantioselectively.

Materials & Methods

Samples of lake trout were captured from open water sites throughout Lake Superior from 1980 through to 1998. Smelt and lake herring were caught near the Apostle Islands in June 1998. All lake trout samples were processed and analyzed as individual whole fish. Total toxaphene and congener specific (Parlar 22) were performed using a Varian 3600 gas chromatograph (GC) with dual electron capture detectors (ECD) as described in ref [4]. Extracts from these analyses were stored in iso-octane @ 4° C in 14 ml vials with teflon septa and screw caps. Retrospective enantioselective analysis was conducted with low resolution ECNIMS using an HP6890 GC connected to a HP5973 MSD [5]. Installation of a Gertstel DCS2 heart-cut valve in combination with a Gerstel liquid nitrogen cold trap into the GC oven allowed the use of multidimensional GC (MDGC). Details about the enantioselective analysis can be obtained in ref [5]. Isomer separation was performed on a HP-5 (30m x 0.25mm i.d. x 0.25 µm film thickness) prior to heart-cut onto the chiral columns BGB-172 (30m x 0.25 mm i.d. x 0.18 µm film thickness), BGB-TBDM (30 m x 0.25 mm i.d. x 0.15µm film thickness) or ChirasilDex (25 m x 0.25 mm i.d.).

Results and Discussion

Analysis of stable isotope signatures in the food web provides an indication of changes in feeding patterns. The relationship between 13C/12C stable isotope ratios and contaminant bioaccumulation in a lake trout dominated food web has been previously demonstrated [6]. Based on changes measured in the δ13C signatures measured in the Lake Superior food web in 1993 and in 1996, the data indicate that lake trout have shifted from a diet dominated by sculpin and smelt to one dominated by lake herring, which is in accordance with Selgeby et al. [7]. This change is based on a reduction in the availability of large smelt (>20 cm.), the preferred diet item of lake trout, in comparison to lake herring. Since herring have significantly higher total toxaphene levels than smelt and sculpin (Table 1), an increase in herring consumption would result the in higher body burdens of total toxaphene in lake

Table 1. Total Toxaphene concentrations in the Lake Superior food web. (1995-98)

Food Web Component	Total Toxaphene (µg/g wet weight)
Lake Trout	1.926 ±0.299
Lake Herring	1.024 ± 0.136
Smelt	0.291 ± 0.013
Sculpin	0.546 ± 0.035
Diporeia	0.197 ± 0.022
Mysis	0.091 ± 0.009
Plankton	0.062 ± 0.015

The Lake Superior homologue pattern in lake trout changed significantly over almost two decades. A nonachlorobornane (Palar # 50) was consistently the most predominant congener in Lake Superior lake trout throughout the period (1980-1998). In the 1990's there was a significant decline in 2 lower chlorinated toxaphene congeners – [Parlar #21-heptachloro- and Parlar #40-octachloro-] in archived lake trout whole fish homogenates (see figure 1).

The enantiomer ratios (ERs) of selected toxaphene congeners in smelt deviated more from racemic compared to lake herring (see figure 2). This is consistent with the large burden of toxaphene in lake herring, which most likely degrade toxaphene more slowly compared to smelt. The food items of the forage fish (zooplankton, mysis, diporeia) was also analyzed enantioselectively to confirm enantioselective metabolic activity in the forage fish.

ERs of selected toxaphene congeners were more similar between lake herring and lake trout compared to smelt. Recalcitrant congeners such as hep-sed, P50 and P62 deviated more from racemic in smelt compared to lake trout. In addition the ER of P50 in lake trout from 1982 (0.70 ± 0.03) was comparable to the ER of the same congener in smelt (0.62 ± 0.03). The ER of P50 in lake trout from 1998 (0.92 ± 0.02) was more similar to the ER of P50 in lake herring (0.82 ± 0.01).

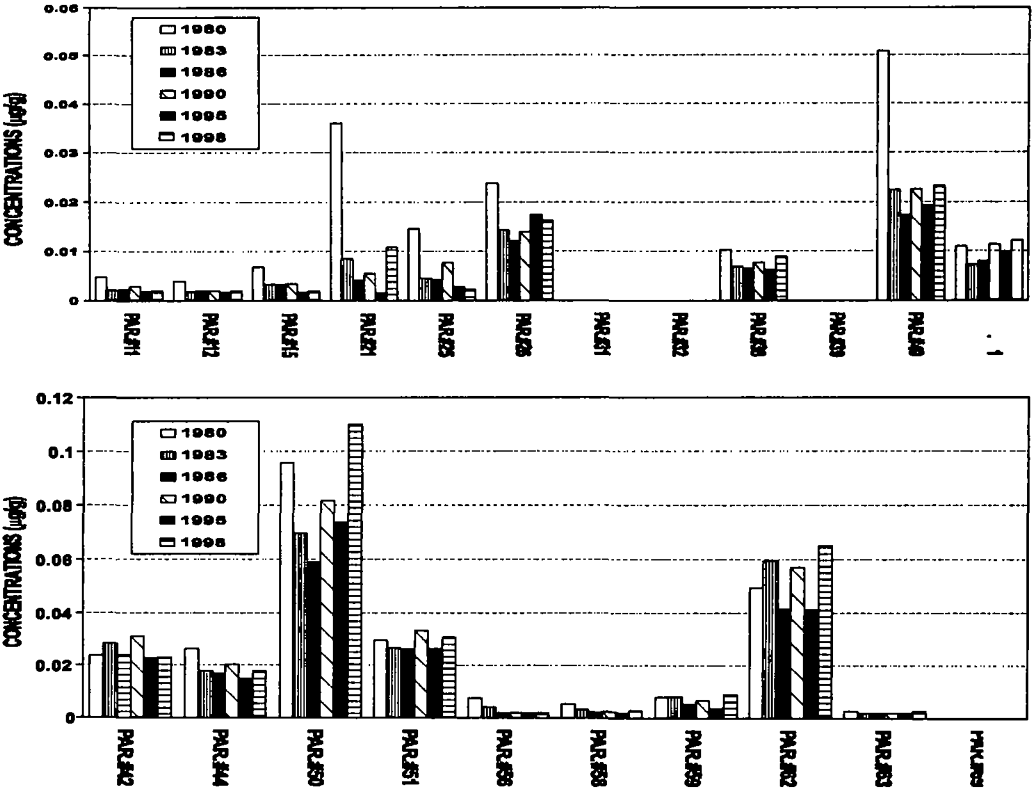

Figure 1. Temporal Trends in the Distribution of the 22 Parlar Toxaphene Congeners (PARLAR#) in Lake Superior Lake Trout (1980-1998)

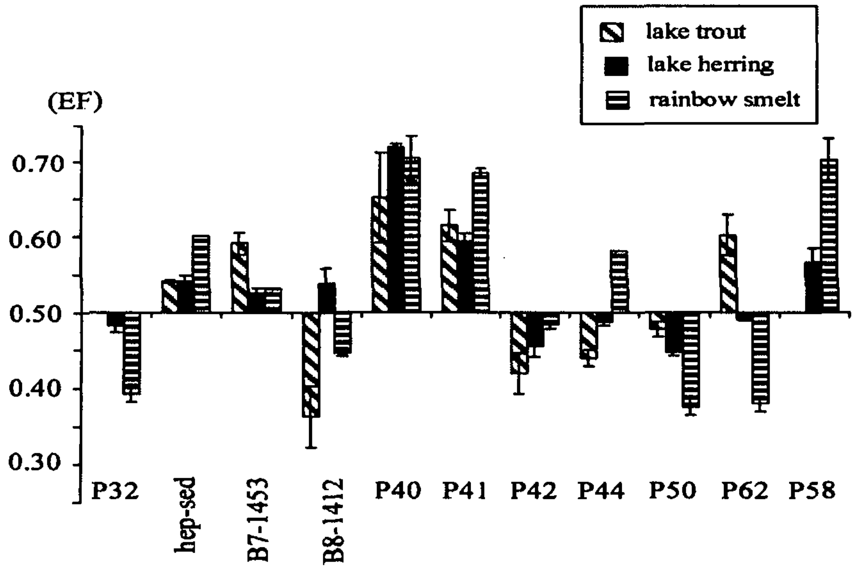

Figure 2. EFs of selected toxaphene congeners in lake trout and its prey species. Note that EFs has been used in order not to graphically discriminate the second eluting enantiomer

Biogmagnification factors were higher between lake herring and lake trout compared to zooplankton and lake herring. In addition, the biomagnification of P42, P44, P50 and P62 were more enantioselective at the higher trophic level (see figure 2).

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