# Spatial trends in dioxin-like PCBs in three species of fish from the Canadian Great Lakes

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## Introduction

Polychlorinated biphenyls (PCBs) are among the most widespread environmental pollutants and a predominant contaminant of the Great Lakes[1,2]. They are persistent, lipophilic and bioaccumulate in aquatic organisms. As a result, fish with high fat content can accumulate high levels of PCBs. Individual PCB congeners exhibit different physiochemical properties and biological activities that result in different toxicity profiles and environmental distirbutions[3].

The toxicity of PCB congeners varies largely with the number of chlorine atoms and their substituted positions in the biphenyl rings, with the coplanar PCBs being especially toxic[4]. The twelve PCB congeners with structure, orientation and toxicological properties similar to 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (TCDD) are referred to as dioxin-like PCBs (DLPCBs)[5]. The World Health Organization (WHO) have identified Toxic Equivalency Factors (TEFs)[6] for these DLPCBs relative to 2,3,7,8-TCDD, from which Toxic Equivalencies (TEQ) can be derived.

This paper compares the trends in DLPCB levels from three species of sport fish (lake trout (*Salvelinusnamycush*), lake whitefish (*Coregonusclupeaformis*) and carp (*Cyprinuscarpio*) from the Great Lakes. The spatial patterns of the twelve DLPCBs are also considered together with their contribution to the overall TEQ.

## Methods and Materials

Sport fish were collected from the Canadian waters of the Great Lakes (Lake Ontario, Lake Erie, Lake Huron, Georgian Bay, North Channel of Lake Huron, Lake Superior, and Lake St. Clair) between 2000 and 2004. A skinless, boneless fillet of dorsal muscle was taken for analysis. A congener-specific method developed by the Ontario Ministry of the Environment (MOE)[7] was used to identify and quantify the twelve DLPCBs. The tissue samples were acid digested, then extracted with hexane via liquid-liquid digestion. The extracts were cleaned through a column containing anhydrous $Na_2SO_4$ and $H_2so_4$ impregnated silica. The sample was then chromatographed on an alumina column. The remaining mono-orthoDLPCBs were further separated using a 5% Amoco PX21 carbon/silica column. The analyses were performed on a MicromassAutospec GC-HRMS.

## Data Analysis

An Analysis of Variance (ANOVA) was conducted on each fish species to determine if there were significant differences in fish length among lakes. If there were length differences then differences in the DLPCB congeners among lakes may have been due to fish length rather than environmental concentration. Differences in DLPCB concentrations between years are not considered in this paper. The concentration of each DLPCB congener was then compared in each fish species among lakes using an ANOVA, these analyses were conducted to determine if there were any significant spatial trends in concentration. Congener distribution patterns in each species were then compared using Pearson Correlation analysis. The relationships of the DLPCB congeners between each of the lakes and among species could then be determined.

The TEQ for each DLPCB congener was determined using the WHO TEF values[6]. The total TEQ value for each fish was then determined by summing the individual congener TEQs. As with the individual DLPCB concentrations, the TEQs for each species were compared among lakes using an ANOVA. The relative contribution of each congener to the overall toxicity was calculated as a percentage of the total TEQ in the sample.

The DLPCB congener patterns and TEQ contributions were also compared to fish collected from inland waters with known PCB sources (e.g. Lyons Creek, Canagagigue Creek, Lake Gibson, Rice Lake and Sturgeon Lake) as well as

a waterbody with no known point source (Lake Simcoe).

**Results and Discussion**

In most cases, there were no significant differences ($p>0.05$) observed among lakes in the mean length for each of the three fish species, thus, length was not considered to be a major variable. The exceptions were lake whitefish from Georgian Bay which were significantly larger ($p=0.001$) than in the other lakes and carp from Lake Erie which were smaller ($p=0.012$) than in the other lakes. If length corrections were made for these two cases, lake whitefish from Georgian Bay would have been assigned somewhat lower concentrations and carp from Lake Erie, higher concentrations.

Total DLPCB concentrations in lake trout were significantly higher in Lake Huron ($p=0.016$) than in any of the other lakes (Figure 1a). Concentrations in both whitefish and carp were significantly higher in Lake Ontario ($p<0.001$) than in any other lake (Figure 1b & c). Typically, DLPCB concentrations declined from lower Great Lakes to the upper Great Lakes (e.g. Lake Ontario>Lake Erie>Lake Huron>Lake Superior) reflecting a similar decline in the level of urbanization and industrialization; a trend that has been observed by others for total PCB concentrations[8]. Despite the differences in industrial activities and therefore apparent sources of PCBs to the different lakes, the congener distributions of the DLPCBs among lakes was highly correlated ($r>0.99$, $p<0.001$), and the obvious similarities are apparent in Figure 1 (a-c). Similar observations have also been made in DLPCB concentrations in caged mussels[9].

The congener patterns observed in fish from the Great Lakes (both among lakes and species) were all highly correlated ($r>0.98$, $p<0.001$) to fish from inland systems, with congener 118, 105 and 156 accounting for up to 59%, 25% and 11% respectively of the overall DLPCB concentrations.

Consumption advisories for sport fish in the Canadian Great Lakes[2] are based on TEQ values. The most toxic DLPCB congener is congener 126, and previous studies[10] have shown it to account for 79-99% of the overall DLPCB toxicity. However, congener 126 contributes less than 0.7% of the overall DLPCB concentration in Great Lakes fish. Patterns in TEQ concentrations, as with the DLPCB congeners, were highly correlated both among lakes ($r>0.89$, $p<0.001$) and species ($r>0.99$, $p<0.001$) (Figure 1d-f). However, the congeners contribution most of the TEQ did not fully reflect the congener patterns observed in the fish. The primary congener with regard to toxicity was 126, contributing up to 81% of the overall toxicity. Congeners 118, 105 and 156 constituted the majority of the overall DLPCB concentration, and contributed the next three highest amounts (<18%, <6%, and <13% respectively) to the overall toxicity. These trends were also observed in the inland systems (Figure 2d-f).

**Conclusions**

Trends in concentrations of DLPCBs, and their associate TEQs were spatially correlated, with the highest values in the lower Great Lakes. Despite differences in concentrations, there were no observed differences in the distribution patterns of either the relative proportions of DLPCB congeners or the congener TEQs. The similarity in congener pattern among locations, fish species and trophic levels was not expected and is worthy of further investigation. We can only speculate at this point; however, the similarity in congener pattern suggests, firstly that the rate of breakdown in the environment of all DLPCBs is similar, and secondly all DLPCBs are treated equally in the biological uptake process. The TEF factors assigned to each congener drives the overall TEQ, with congener 126 contributing a major portion of the overall toxicity, despite its relatively low contribution to the overall DLPCB concentration.

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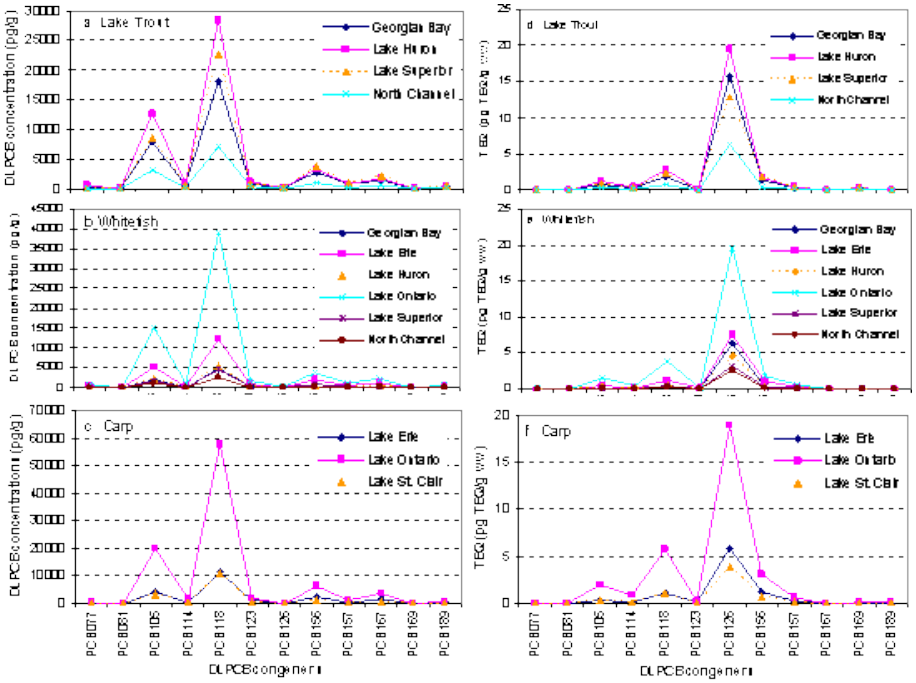


Figure 1: Dioxin-like PCB congener distributions (pg/g) in lake trout (a), whitefish (b) and carp (c) from the Canadian Great Lakes. Distribution of TEQ values for each DLPCB congener (d-f).