Trends in Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/PCDFs) in Lake Trout (*Salvelinus namaycush*) from the Great Lakes

Emily Awad[1], Rachael Fletcher[1], Alan Hayton[1]

[1]Ontario Ministry of the Environment

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) are a class of toxic compounds found at all trophic levels in the Great Lakes basin[1]. They are persistent chemicals that bioaccumulate up the food chain, which makes them of particular concern to human health[2]. PCDD/PCDFs along with dioxin-like polychlorinated biphenyls (DLPCBs) are responsible for a significant proportion of the sport fish consumption advisories for the Canadian Great Lakes, ranging from 19% in Lake Erie to 65% in Lake Superior[3].

Temporal trend data on contaminants in sport fish, especially PCDD and PCDFs, are lacking in the published literature. Reiner *et al.*[4] presented levels of PCDD/PCDFs in several species of fish from the Great Lakes, which showed an overall decrease in levels between 1989 and 1994. Trends in PCDD/PCDF Toxic equivalent (TEQ) concentrations from 1989 to 2003 are analyzed here for lake trout (*Salvelinus namaycush*) from Lake Ontario, Lake Superior, Lake Huron and Georgian Bay. For Lake Erie, lake whitefish (*Coregonus clupeaformis*) was substituted because of a lack of suitable lake trout data.

Materials & Methods

Fish samples were collected by gillnetting from various locations in each of the Canadian Great Lakes. A skinless, boneless fillet of the dorsal muscle was used for analysis. The 17 most toxic congeners of PCDD and PCDF were analyzed and quantified by method DFPCB-E3418[5]. This method entails acid digestion of homogenated fish tissue, followed by extraction with hexane and clean-up by open silica chromatography and semi-automated high performance liquid chromatography. Samples were analyzed by gas chromatography-tandem mass spectrometry or by gas chromatography high resolution mass spectrometry. Resulting concentrations for each congener were multiplied by the World Health Organization (WHO) TEFs (Toxic Equivalency Factors) and summed to calculate the TEQ concentrations[6]. DLPCBs were not included in these TEQ calculations because they were unavailable for all years. Concentrations below the limit of detection were treated as zeros. Data collected from separate sites within each of the Great Lakes were pooled to give lake wide levels.

Statistical Analysis

Since fish length varied among years, an Analysis of Covariance (ANCOVA) was used to compare the slopes and intercepts of the regressions on length versus log TEQ concentration for each year of data. Once the ANCOVA results were obtained, and the slopes were determined to be parallel for each location, the individual regression intercepts (for each year) were calculated using the common slope, the mean log TEQ and the mean length. To detect any significant monotonic trends over time in the intercepts, a nonparametric Mann-Kendall test was utilized. This test evaluated temporal trends in the intercepts and determined if the slope of the trend line was zero, positive or negative. This same procedure was also used for several individual PCDD/PCDF congeners to determine if any significant trends could be detected across years. Results below detection, were assigned a value of half the detection limit.

Results and Discussion

For each of the Great Lakes, the mean and standard error of the TEQ concentrations were plotted for each sampling year (Figure 1). The highest TEQ concentrations were found in Lake Ontario lake trout. Reiner *et al.*[4] found a decrease in TEQ concentrations in Lake Ontario lake trout between 1989 and 1994. Our results support this conclusion. The Mann-Kendall test indicated a downward trend for Lake Ontario that approached significance ($p<0.10$). However, as Figure 1(a) shows, TEQ concentrations seem to stabilize after 1990, with no further downward trend evident. Since 1991 concentrations have remained within a narrow range (23-28 pg/g).

TEQ concentrations in Lake Superior and Lake Huron lake trout were similar. The Mann-Kendall test indicated a significant downward trend in TEQ concentrations for both Lake Superior ($p=0.047$) and Lake Huron ($p=0.049$). TEQ concentrations for lake whitefish from Lake Erie and lake trout from Georgian Bay have not changed significantly over the period of record.

Trends for five of the most important congeners (2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF) were investigated for Lake Ontario and Lake Superior. The Mann-Kendall test indicated a downward trend that was not significant for any of the five congeners in Lake Ontario lake trout. As Figure 2(a) shows, the pattern of decline was similar for all five congeners and similar to that found for TEQ concentrations in Lake Ontario. Concentrations declined from 1989 to 1991, after which levels have remained relatively constant with no evidence of further decline.

For Lake Superior, a significant downward trend was found for 2,3,7,8-TCDF ($p=0.011$) and 1,2,3,7,8-PeCDF ($p=0.047$). There was no significant change in the concentrations of the other three congeners. Whittle *et al.*[7] stated that Kraft pulp and paper mills are the primary source of PCDD/PCDFs to the upper Great Lakes. The downward trend in the PCDF congeners in Lake Superior most likely reflects recent changes in the pulp and paper industry processes designed to reduce discharges of PCDD/PCDF.

Conclusions

TEQ concentrations in lake trout and lake whitefish from the Canadian Great Lakes are highest in Lake Ontario. In Lake Superior and Lake Huron, TEQ concentrations declined significantly between 1989 and 2003. In Lake Ontario, the downward trend in TEQ concentration approached significance. However, any major reductions in TEQ concentration occurred between 1989 and 1991. From 1991 to 1999 TEQ concentrations have not decreased. TEQ concentrations in Lake Erie and Georgian Bay were the lowest over the period of record and have not changed significantly.

In Lake Ontario temporal trends for five of the most important congeners were similar to one another and similar to the temporal downward trend in TEQ concentration. In Lake Superior, 2,3,7,8-TCDF and 1,2,3,6,7,8-PeCDF declined significantly over time. The other three congeners did not change.

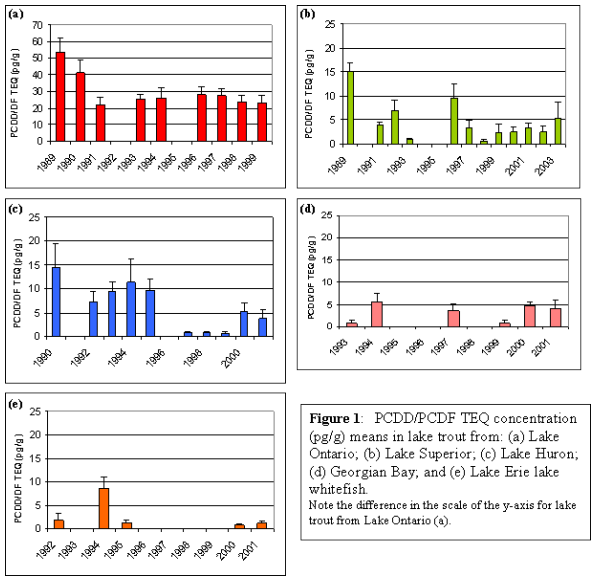

Figure 1: PCDD/PCDF TEQ concentration (pg/g) means in lake trout from: (a) Lake Ontario; (b) Lake Superior; (c) Lake Huron; (d) Georgian Bay; and (e) Lake Erie lake whitefish.
Note the difference in the scale of the y-axis for lake trout from Lake Ontario (a).

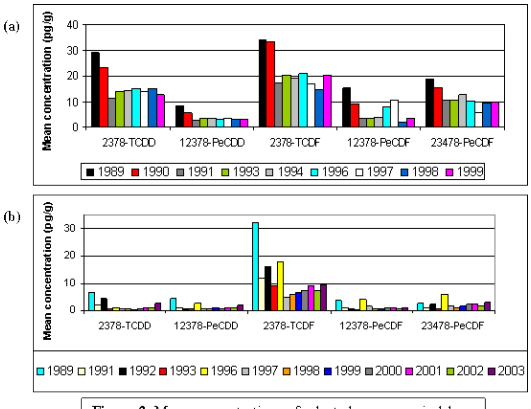

Figure 2: Mean concentrations of selected congeners in lake trout from (a) Lake Ontario and (b) Lake Superior.

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