

**TEMPORAL TRENDS OF POLYCHLORINATED NAPHTHALENES,
POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS, AND
DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN LAKE ONTARIO LAKE
TROUT (1979-2004)**

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Abstract

Polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), and dioxin-like PCBs (DL-PCBs) are classes of highly toxic compounds. Of these chemicals, PCNs have been the least well studied and their temporal trends have yet to be measured in any environmental media in the Laurentian Great Lakes. Here we evaluated the temporal trends of PCNs, PCDDs, PCDFs, and DL-PCBs in Lake Ontario lake trout (*Salvelinus namaycush*) collected between 1979 and 2004. Concentrations of the sum of each of these three compound classes have decreased since the late 1970s. Elimination rate constants (k_2) for PCNs that had two pairs or three adjacent carbons unsubstituted with chlorine were not significantly different from zero, which indicated that these congeners had not declined in the fish. This was not surprising considering that these PCNs are known to be metabolized by vertebrates. In contrast, the k_2 values for PCNs that did not have adjacent carbons unsubstituted with chlorine generally increased with hydrophobicity and degree of chlorination, which we hypothesized was due to metabolic dechlorination of higher chlorinated PCN congeners, PCN 74 and 75, to lower chlorinated ones. PCNs contributed between 5 to 10% of total dioxin-like activity in the fish.

Introduction

Polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), and non- and mono-ortho PCBs (dioxin-like or DL-PCBs) are classes of structurally similar compounds that are highly toxic and ubiquitous in the environment.¹⁻³ Of these three groups of contaminants, PCNs have been the least well studied and highly sensitive analytical congener-specific methods have only recently become available.^{3,4}

PCNs are a group of 75 compounds that have been manufactured for a range of industrial applications such as dielectrics for flame resistance and insulation in capacitors and cables.³ They are also present as impurities in PCB formulations and are produced through combustion processes such as municipal solid waste incineration.³ Although the production and use of PCNs is thought to have ceased in most countries, they continue to be emitted into the environment through sources such as combustion emissions, evaporation from PCB and PCN mixtures in disposal sites, and older electric equipment currently in use.⁵⁻⁷

PCNs have been nominated as possible additions to the list of banned/restricted substances under the United Nations Economic Commission for Europe Persistent Organic Pollutants Protocol of the Long-Range Transboundary Air Pollution Convention. A main objective of this protocol is to monitor concentration trends in both the abiotic and biotic environment. However, unfortunately there have been few studies that have examined the temporal trends of this compound class and to our knowledge, PCN time trends have yet to be measured in fish.⁴ This information is needed because fish are likely a major exposure route of PCNs to humans.

The objective of this study is to evaluate the temporal trends of PCNs, PCDDs, PCDFs, and DL-PCBs in Lake Ontario lake trout (*Salvelinus namaycush*). This study represents the first time that the temporal trends of PCNs have been evaluated in any environmental media in the Laurentian Great Lakes system.

Materials and Methods

Four and five year old lake trout collected from Lake Ontario in 1979, 1983, 1988, 1993, 1998, and 2004 were

obtained from the archive maintained by the Great Lakes Laboratory for Fisheries and Aquatic Sciences. Individual whole fish were homogenized and stored frozen in glass jars at -80°C until analysis.

Chemical extraction methods have been reported elsewhere.^{8,9} Briefly, fish samples were either fortified with ^{13}C -PCDD/Fs and DL-PCBs or ^{13}C -PCNs. The samples were digested in hydrochloric acid and extracted with hexane. The extracts were then cleaned on sulphate and sulphuric acid-modified silica columns followed by alumina and carbon columns for PCDD/Fs and DL-PCBs and a carbon column only for PCNs. The samples were analyzed by isotope dilution Gas Chromatography-High Resolution Mass Spectrometry.

Results and Discussion

Table 1 shows concentrations of total PCNs (ng/g lipid) as well as the sum of 2378-substituted PCDDs and PCDFs and DL-PCBs (pg/g lipid toxic equivalents or TEQs¹). Both groups of contaminants showed a declining trend between 1977 and 2004, and decreased 8- and 7-fold, respectively, between these two time periods.

Table 1: Concentrations (mean \pm SE) of total PCNs (ng/g lipid) as well as the sum of 2378-substituted PCDDs and PCDFs and DL-PCBs (pg/g lipid TEQ) in Lake Ontario lake trout collected between 1979 and 2004.

Year	Total PCN	Sum of 2378-substituted PCDDs and PCDFs and DL-PCBs
1979	71.9 \pm 12.0	1886 \pm 208
1983	70.0 \pm 7.4	2438 \pm 234
1988	69.7 \pm 7.9	1892 \pm 155
1993	56.9 \pm 11.3	1834 \pm 308
1998	15.8 \pm 1.4	573 \pm 58
2004	8.93 \pm 1.7	277 \pm 53

Using the approach of Paterson et al.¹⁰ we calculated elimination rate constants (k_2) for individual PCN, PCDD, PCDF, and DL-PCB congeners as follows:

$$(1) \quad \ln[\text{contaminant}] = a(\text{year}) + b$$

$$(2) \quad k_2 = |a|$$

where [contaminant] is the lipid normalized concentration of the congener in question, and a and b represent the slope and intercept of the least squares regression line. The k_2 values are directly proportional to the rate of contaminant decline in the lake trout.

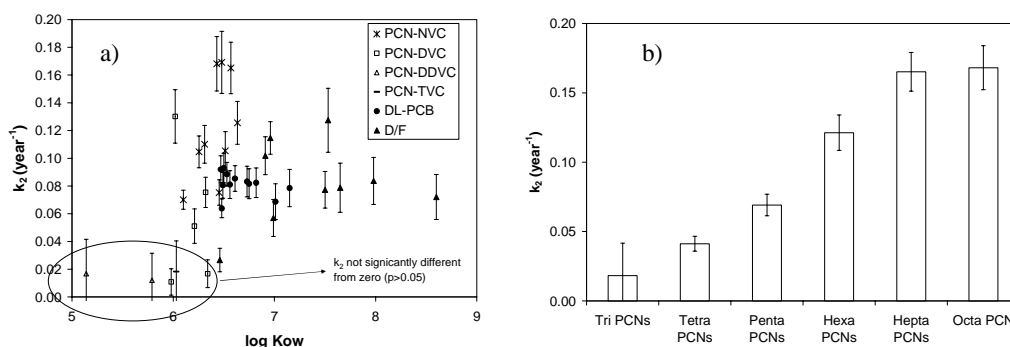


Figure 1: Elimination rate constants (k_2) for a) individual congeners of PCNs, 2378-substituted PCDDs and PCDFs, and DL-PCBs, and b) PCN homologue groups.

The k_2 values for the individual congeners evaluated in this study as a function of $\log K_{ow}$ ¹¹⁻¹³ are shown in Figure 1a. The k_2 values for PCDDs, PCDFs, and DL-PCBs were similar (mean = 0.08) and did not vary with K_{ow} . PCNs that do not have adjacent (or vicinal) carbons unsubstituted with chlorine (PCN-NVC) are resistant to metabolism and are more likely to bioaccumulate.³ In contrast, congeners having two (PCN-DVC), three (PCN-TVC) or 2 pairs (PCN-DDVC) of adjacent carbon atoms unsubstituted with chlorine can be metabolized by vertebrates.³ The

k_2 values for all of the PCN-TVCs and PCN-DDVCs were not significantly different from zero ($p > 0.05$), which indicates that these congeners, unlike the other PCNs, have not declined in Lake Ontario lake trout. This is not surprising considering that these congeners are metabolized more rapidly than both PCN-NVCs and PCN-DVCs.³ The k_2 values for all of the PCN-NVCs and all but two of the PCN-DVCs were significantly different from zero ($p < 0.05$) and tended to decrease with increasing $\log K_{ow}$. This can also be seen by examining the tri- to octa- PCN homologues, where k_2 increased (i.e. the rate of concentration decline increased) with the degree of chlorination of the homologue group (Figure 1b). This contradicts what was found by Paterson et al.¹⁰ for non DL-PCBs and what is expected based on thermodynamics.¹⁴

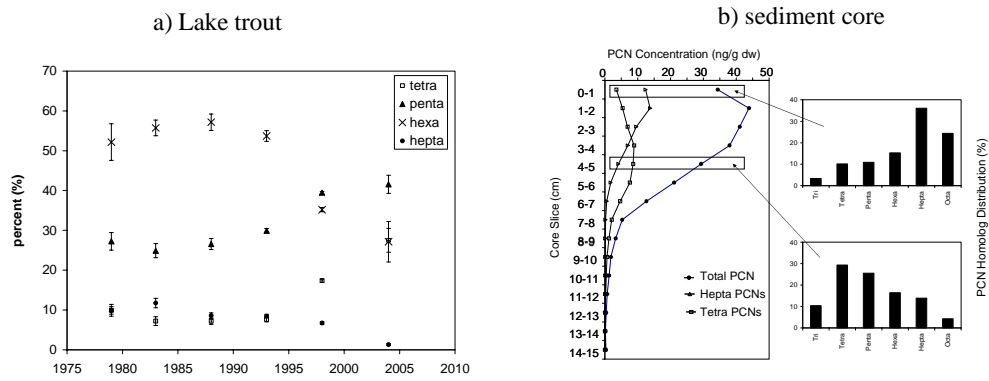


Figure 2: a) temporal trends of the percent contribution of the tetra-, penta-, hexa-, and hepta-chlorinated homologue groups to total PCN in Lake Ontario lake trout (mean \pm SE) and b) concentrations of total PCN as well as tetra- and hepta-homologues and the PCN homologue distribution in the 0-1 slice and 4-5 cm slice in a Lake Ontario sediment core.¹⁵

The PCN concentration in Lake Ontario lake trout was dominated by the hexa- (primarily PCN 66/67), penta- (primarily PCN 52/60) and the tetra- (primarily PCN 42) homologue groups (Figure 2a). The proportion of the more chlorinated homologue groups (i.e. hexa, hepta, and octa) decreased over time, whereas the less chlorinated homologue groups (i.e. tri, tetra, and penta) increased over time (Figure 2a). Although this result corresponds with that found in Figure 1, it contradicts what was found for non DL-PCBs in similar sized fish¹⁶ and again what would be expected based on thermodynamics.¹⁴ This pattern was not due to changes in either the source or formulation of PCNs over time since an opposite pattern was found in a Lake Ontario sediment core collected in 2004 where the proportion of the less chlorinated and more chlorinated homologue groups decreased and increased over time, respectively (Figure 2b). We hypothesize that the relative contributions and differences in the rate of decline of individual PCN congeners and homologue groups is due to dechlorination of higher chlorinated congeners (such as PCN 74 and 75) to lower chlorinated ones through metabolic biotransformation.

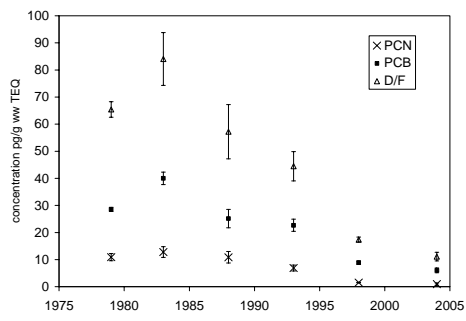


Figure 3: Temporal trends of TEQ concentrations for PCNs, DL-PCBs, and PCDDs and PCDFs. The TEFs used for this figure were all derived in the same manner using *in vitro* H4IIE bioassays.^{17,18}

The TEQ concentrations of all three compound classes in this study decreased with time (Figure 3), with the percent contribution of PCN to total dioxin-like toxicity decreasing from 10% in 1977 to 5% in 2004.

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