# TEMPORAL TRENDS OF 2,3,7,8-TETRACHLORODIBENZO-*P*-DIOXIN (TCDD) IN FISH FROM THE TITTABAWASSEE RIVER, MICHIGAN

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## Introduction

Temporal measurements of chemicals of concern in native fish provide useful information for addressing fate and transport, ecological, and human health questions. For the Great Lakes, there are several temporal trend datasets for bioaccumulative chemicals such as polychlorinated biphenyls (PCBs), organochlorine pesticides, and mercury. However, there are relatively few datasets that are useful to evaluate long-term temporal trends of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) residues in wildlife.

The presence of PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), heavy metals, and other compounds in sediments and biota of the Saginaw Bay watershed have been studied and published in various reports over the last 10 years[1-3]. Interest in these data reflects the presence and impact of 87 licensed industrial facilities, 127 wastewater treatment plants, and intensive agricultural practices located in the watershed area. To date, much of the emphasis has focussed on residues of PCBs[4].

The Tittabawassee River is one of five rivers that drain into the Saginaw River which eventually empties into the Saginaw Bay of Lake Huron. The Dow Chemical Company and the State of Michigan have been measuring concentrations of PCDDs and PCDFs in local sediment-dwelling fish (e.g., carp) and in migratory game fish (e.g., walleye) over the past 25 years from the Tittabawassee River. These time trend data should provide insights into the history of fish residues in the Tittabawassee River that may provide useful information to address current and future concerns over human and ecological health.

## Methods and Materials

The species selected as representative of sediment-dwelling fish was the carp (*Cyprinus carpio*). Bottom dwellers, such as carp, are a preferred species for tissue residue monitoring of highly lipophilic materials, as such compounds typically bind to sediment materials. The carp is primarily a selective benthivorous omnivore that feeds by sucking up mud from the bottom, ejecting it, and then selectively consuming items while they are suspended[6]. Bottom feeding fish, such as carp, are generally perceived to be less transitory than game fish.

Migratory game fish in the Tittabawassee River were characterized by the walleye, (*Stizostedion vitreum*). This species is strictly carnivorous in nature and largely a nocturnal feeder. Young walleye eat plankton, and as they age, they mostly consume other fish such as yellow perch and freshwater drum, but can also eat insects, crayfish, and snails[7].

Walleye and carp were generally collected using an electroshocking technique, although in some years, carp were sampled using Fyke nets. Several class sizes were established in harvested fish and the target size for analytical chemistry analysis of TCDD in carp and walleye were 45-65 and 45-55 cm, respectively, in total body length. Fish were sampled most years in late summer/early fall. Samples used for fillet analysis were immediately eviscerated and filleted. Edible portions of walleye (skin-on) and whole body carp were collected and immediately frozen.

Fish were sampled below the industrial dam (i.e, the "Dow dam") in Midland, MI and were collected over a varying timeframe from 1976 to 2002. Chemical analysis was conducted on solvent-extracted homogenized carp (whole body) and walleye (fillet) tissue for TCDD using gas chromatography and high-resolution mass spectrometry (GC/MS). Concentrations of TCDD are expressed on a wet weight basis.

**Results and Discussion**

*Concentrations of TCDD in carp from the Tittabawassee River from 1977 – 2002*

The concentrations of TCDD in carp from the Tittabawassee River have been declining for some time and continue to decrease (Figure 1). The concentration of TCDD in whole body carp collected from the Tittabawassee River ranges from a high of 118 picogram/g or pg/g (ww) in 1976 to a low of 5.6 pg/g (ww) in 1996. Most recently, carp collected in 2002 have a mean TCDD concentration 7.6 pg/g (ww). Thus, over the past 26 years, concentrations of TCDD in carp collected from the Tittabawassee River have decreased approximately 15-fold. This substantial decrease is consistent with results from caged fish studies conducted during this time. Taken together, these data indicate that the bioavailable amounts of TCDD have been declining over this time period.

Periodic measurements of TCDD concentrations in carp collected from the Tittabawassee River were used to evaluate time trends; the residue data are presented in Figure 1. In this analysis, an exponential model was used to describe the rate of decrease between 1976 and 2002. The equation describing the decrease in concentrations of the mean TCDD concentrations in carp is as follows, $y=125.6e^{-0.0865x}$ and was found to be highly significant ($r^2 = 0.8465$; $p = 0.0012$). This predictive equation indicates that the pseudo first-order half-life of decline in TCDD concentrations in whole carp of approximately 8 years. It is also noteworthy that sample variability of carp TCDD residues declined significantly over time.

*Concentrations of TCDD in walleye fillet from the Tittabawassee River from 1983 – 2002*

The concentrations of TCDD in walleye fillet from the Tittabawassee River have been measured from 1983 to 2002 and have shown a gradual decline over the past 20 years, albeit more erratically than in carp, due in part to residues of TCDD approaching the detection limit of ~1 pg/g (observed range of 1.1 to 4.4 pg/g). Time trend analysis using an exponential model produced an equation describing the decrease in concentrations of the mean TCDD concentrations in walleye fillet of $y=3.83e^{-0.070x}$; the fillet residue data are presented in Figure 2. While the correlation coefficient was relatively low, the model was found to be statistically significant ($r^2 = 0.5193$, $p = 0.0437$). This predictive equation indicates a pseudo first-order half-life of decline in TCDD concentrations in this presumably more mobile game fish species (walleye) of approximately 10 years.

*Comparison of TCDD Time Trends in Tittabawassee River Carp/Walleye and Lake Ontario Lake Trout*

A similar analysis was conducted for residue data for lake trout from Lake Ontario[5]. In this study, the authors analyzed 4 year-old lake trout from Lake Ontario for 15 time points between 1977 –

1993 (Figure 3). These data are very robust since they represent the same age fish from the same location (minor difference for 1 year, but still Lake Ontario) and they were analyzed as one batch in the mid-1990's, thereby avoiding potentially confounding factors related to different analytical methods over time. These data were chosen for comparison since the concentrations of TCDD and time ranges are suitably comparable to the carp data from the Tittabawassee River. The equation describing the decrease in concentrations of the mean TCDD concentrations in Lake Ontario lake trout is $y = 71.84e^{-0.069x}$ and was likewise found to be highly significant ($r^2 = 0.7440$; $p < 0.0001$). This predictive equation indicates a pseudo first-order half-life of decline in TCDD concentrations in this anadromous Great Lakes fish species of approximately 10 years. In a similar trend noted with Tittabawassee River carp, the TCDD residue variability in lake trout appears to decline substantially over time.

While source control measures have been undertaken over this time period in both the Tittabawassee River and Lake Ontario, the similar rates of decline of TCDD residues in Tittabawassee River carp (benthic feeder) and walleye (game fish) to Lake Ontario lake trout suggest similar attenuation processes for this chemical in the Great Lakes aquatic system.

**Conclusions**

In conclusion, the Tittabawassee River carp and walleye residue data demonstrate a continuing decline in tissue concentrations of dioxin. The more recent carp data demonstrate reduced tissue concentration variability suggesting a reduction in sediment hot spots in the river. The declining carp dioxin concentration are highly suggestive of natural attenuation taking place in the river with a significant improvement over conditions that existed 20 to 30 years ago . The findings in carp are consistent with a number of caged fish studies that Dow and others have conducted over the past 30 years[6]. The comparable dissipation rates for residues of TCDD in Tittabawassee River fish and Lake Ontario lake trout (pseudo first-order half-life of ~10 years) are suggestive of similar attenuation processes for this compound in the Great Lakes aquatic system.

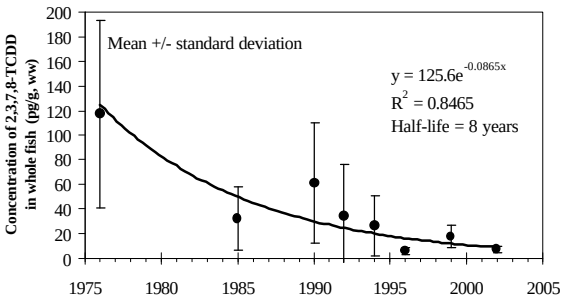


**Figure 1.** Time Trend for Concentrations of 2,3,7,8-TCDD in Carp from the Tittabawassee River, MI.

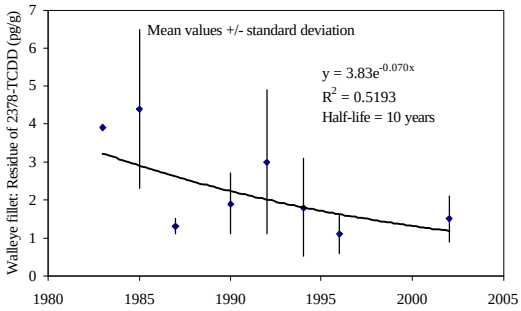


**Figure 2.** Time Trend for Concentrations of 2,3,7,8- TCDD in Walleye Fillet from the Tittabawassee River, MI

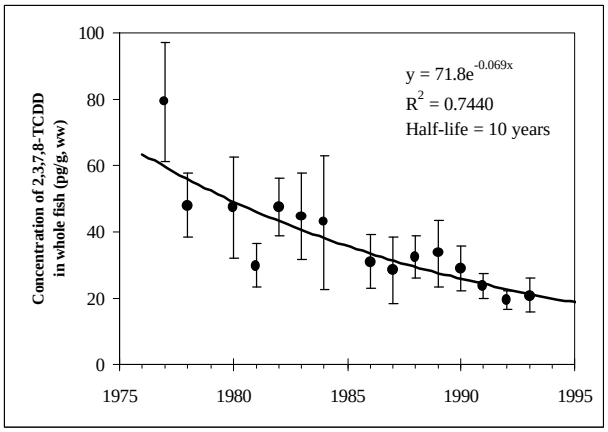


**Figure 3.** Time Trend for Concentrations of 2,3,7,8-TCDD in whole body Lake Ontario Lake Trout (Data from Huestis et al., 1997)[5].

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