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Mercury Concentrations of Walleye (*Stizostedion vitreum vitreum*) in 34 Northern Wisconsin Lakes

S. L. Gerstenberger, J. Pratt-Shelley, M. S. Beattie, and J. A. Dellinger

Lake Superior Research Institute, University of WI-Superior, 1800 Grand Avenue, Superior, Wisconsin 54880, USA

Mercury (Hg) occurs both naturally and from anthropogenic sources throughout the environment. The primary natural source of Hg is degassing of the earth's crust involving mainly elemental mercury vapor. In Wisconsin this contributes 66% of the total mercury (Sheffy 1987). Mercury is also used for numerous industrial applications some of which insult the environment with their by-products. Several of these anthropogenic sources include: pulp and paper, the chlorine industry, fossil fuels, mining, painting, sewage treatment, and agriculture (Brosset 1983; Airey 1982; Lindvquist 1981); these are accountable for approximately 34% of Wisconsin's total Hg (Sheffy 1987). Once within the environment, mercury is transported by the atmosphere and deposited in the form of both wet and dry precipitation into lakes and streams (Glass 1986).

Microorganisms living in the sediments convert Hg to a more toxic methylmercury which can bioaccumulate in fish and other species (Huckabee, 1978). The Hg is absorbed by the gills of fish as water passes over them or by accumulation through the food chain. Walleye are at the top of the aquatic food chain and accumulate mercury in the methylated form. These Hg contaminated fish constitute the most significant route of exposure to environmental mercury for humans (Inskip 1985). The Wisconsin Department of Natural Resources (WDNR) has issued consumption advisories for fish containing greater than 0.5 ppm of mercury (WDNR 1991). Unfortunately, if a lake is not on the Wisconsin consumption advisory, it does not always mean that the fish do not have mercury levels of concern. The Hg levels in the fish of many lakes are not routinely tested.

Northern Wisconsin lakes contain Walleyes (*Stizostedion vitreum vitreum*) which are popular table fish for humans and the main target for spearfishing in the spring by Chippewa tribal members. Great Lakes Indian Fish and Wildlife Commission (GLIFWC) is concerned about fish toxics and directed GLIFWC staff to have fish collected by spearfishing and electrofishing analyzed for contaminants. This information will then be disseminated to

Send reprint requests to Shawn L. Gerstenberger at above address.

tribal members and other concerned parties. The Voigt Inter-tribal Task Force uses the fish consumption advisories when deciding which lakes to spear. Lakes with known high levels of mercury are avoided. Lakes selected for this particular project were selected for spearing by the Voigt task force, and most had not been sampled by the WDNR but were previously harvested by GLIFWC tribal members.

The health affects resulting from ingesting methylmercury to both adult and developing nervous systems are well known. Adults may experience one or more of several common symptoms including: central nervous system damage, ataxia, loss of sensation to extremities, constriction of visual fields, and hearing loss (Tollefson 1989; Inskip & Piotrowski 1985).

The developing nervous system is also effected but to a greater extent. Prenatal life is the stage of the human life cycle most vulnerable to brain damage from methylmercury (Clarkson 1990). Specifically, infants exposed prenatally suffer neuro-behaviorally even though the mothers have mild or no symptoms (Clarkson 1989). The main effect is on neuronal migration and cell division and results in delayed achievement of developmental milestones, microcephaly, and gross neurological manifestations, such as cerebral palsy (Sheffy 1987).

MATERIALS AND METHODS

Fish were collected and filleted by GLIFWC staff prior to transporting to the Lake Superior Research Institute for analysis. Walleye samples for the analysis of Hg were received from GLIFWC on May 28, June 1, 1990, and May 3, 1991 with a total of 83 Walleye samples. Samples were stored frozen until they were readied for analysis. Prior to analysis, the samples were thawed and ground in a commercial meat grinder. The grinder attachment was washed with soap and water, rinsed with tap water, rinsed with dilute (0.1M) hydrochloric acid, and rinsed with deionized water before use and between samples. Walleye samples were all processed as skin-off filets because that is a popular way that walleye are consumed. Filets were cut into small pieces and passed through the grinder. The first few grams of each sample were discarded as waste, and the rest of the ground sample was collected in an acid-washed beaker. The sample was passed through the grinder a second time, collected in an acid washed beaker, and then thoroughly mixed with a stainless steel spatula. This homogenous walleye sample was placed in an acid-washed glass bottle and returned to the freezer for subsequent analysis.

To ensure that the grinding process was not contributing Hg to the samples, a grinder blank was also analyzed using commercially purchased ground beef. One portion of the ground beef was transferred to an acid-washed sample bottle without any treatment, and a second portion of the ground beef was passed through the grinder twice and then placed in a sample bottle.

The mercury sample preparation and analysis was completed using the methods of Hatch and Ott with the following specific steps. Digestion of the fish samples released all mercury from the fish tissue. The digestion procedure involves the following steps: (1) Flasks used for fish samples are tared, and 0.5 - 1.0 grams of fish tissue was added followed by 5 ml of deionized water, (2) 5.0 ml of concentrated nitric acid was added, (3) 10.0 ml of concentrated sulfuric acid was added, (4) The sample was heated in water bath for 1 hour at 80 - 90° C. (5) 15.0 ml of 6% potassium permanganate was added, (add more permanganate if purple color disappears) and heat for one hour at 80 - 90° C. (6) 8.0 ml of 5% potassium persulfate was added, and samples were heated for an additional hour, and (7) Cool samples to room temperature and add 50.0 ml of deionized water.

To the digested sample, 6.0 ml of 10% hydroxylamine hydrochloride - 10% sodium chloride solution was added. Just prior to connecting the sample flask to the aeration system, 5.0 ml of stannous chloride solution was added to reduce the ionic Hg to the elemental form. The flask was attached to the aeration system and the pump started. The absorbance reading of the sample was monitored to obtain the peak at 253.7 nm. The reading was compared to the values obtained for the Hg standards, spikes, duplicates and EPA reference samples and the micrograms of Hg in the sample calculated. The mass in micrograms was divided by the weight of the fish sample to determine the micrograms of Hg per gram of fish tissue. The results were recorded as micrograms of Hg per gram of fish tissue (ug Hg/g) wet weight.

Participation in a Mercury Quality Assurance program with the Government of Canada provided an opportunity for 27 labs to analyze mercury samples and compare their data. Our lab's samples lie within two standard deviations of the actual value, a statistically acceptable range for analysis.

RESULTS AND DISCUSSION

The grinder blank samples indicated that there was no detectable addition of Hg of the samples by the grinding process. The Hg content of beef samples was less then the detection limit (0.05 ug Hg/g of tissue) of the analysis for both the sample processed through the grinder as well as the sample with no treatment.

Actual results are seen in Table 1 and include both Hg concentration and fish length. The Hg contamination in Walleye was grouped according to the Wisconsin Department of Natural Resources health advisory for people who eat sport fish from Wisconsin waters (WDNR, 1990). Fifty-five percent of the Walleye collected were in Group 1 (<0.5 ppm Hg), 27% were in Group 2 (0.5-0.74 ppm Hg), 11% were in Group 3 (0.75-0.99 ppm Hg) and 7% were in Group 4 (1.0 ppm Hg or greater). It must be noted that WDNR uses skin-on fillets in making these groupings. By removing the skin for our analyses, the samples would be slightly higher because skin does not sequester as much mercury as the flesh (WDNR, 1990).

Table 1. Walleye Hg concentration by county in state of Wisconsin during 1990-1991.

County	Number	Average Length	Average ug Hg/g	Incidence/Group* 1	2	3	4
Douglas	8	17.6	0.449	4	3	1	0
Vilas	28	17.75	0.528	16	7	3	2
Bayfield	9	18.07	0.647	2	5	1	1
Gogebic	2	16.5	0.486	1	1	0	0
Florence	9	18.51	0.382	6	3	0	0
Oneida	6	18.56	0.348	5	1	0	0
Forest/Vilas	3	18.76	0.395	2	1	0	0
Burnett	5	18.16	0.288	5	0	0	0
Iron	5	19.26	0.929	0	1	3	1
Lincoln	3	18.56	0.999	0	1	0	2
Forest	4	19.77	0.519	1	2	0	0
Barron	1	15.00	0.19	1	0	0	0

*Group 1. Number of fish less than 0.49 ppm.
2. Number of fish between 0.5-0.74 ppm.
3. Number of fish between 0.75-0.99 ppm.
4. Number of fish greater than 1.00 ppm.

Nearly half of the Walleye sampled from the lakes exceeded the fish consumption advisory of 0.5 ppm set by the WDNR. Therefore, precautions should be taken when consuming fish on a regular basis, and extra caution taken for pregnant women and children as mercury is particularly toxic to the developing fetus and nursing infants.

In many cases, the source of mercury is very evident, such as in cases of the famous Minamata (Tsubaki 1977) and Iraq (Bakir et al.) incidences, but in the Great Lakes the sources are not so clearly defined. Several sources of mercury into the Great Lakes are under investigation such as incineration of municipal refuse (Glass 1990), airborne deposition (Sorenson 1990), and other natural sources. All are believed to contribute to the total Hg concentrations in northern Wisconsin.

Numerous other factors may result in increased total Hg concentration and methylation in the aquatic ecosystem. Total organic carbon (TOC), biologic activity, pH, conductance, selenium and major ions have all been investigated. Acid rain has also been thought to be a contributor to the increase in Hg concentrations, it changes the pH of the lakes by altering its

buffering capacity. The pH along with TOC has been shown to be positively correlated to the Hg concentration in aquatic ecosystems. Lake pH and Hg in zooplankton both contribute significantly to Hg in surface water, because they increase the persistence of Hg within the water column (Sorenson 1990).

It is obvious that one cannot pinpoint a single factor or condition that controls the amount of Hg found in any one of these northern Wisconsin lakes and ultimately in the Walleye. There should be a continued effort to increase public knowledge of the problem and an understanding of the potential complications it may create. Data of this sort is especially important within northern Wisconsin because the amount of fish consumed in these areas tends to be higher than other regions especially among the Chippewa tribal members.

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