# FACTORS INFLUENCING MERCURY ACCUMULATION IN YELLOW PERCH (*Perca flavescens*) AND AUFWUCHS IN SELECTED NORTH-CENTRAL WISCONSIN LAKES

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## ABSTRACT

I studied mercury (Hg) accumulation in yellow perch *(Perca flavescens)* and aufwuchs in 11 lakes with a broad range of pH (5.1 to 7.8) and alkalinity (-12 to 769 ueq/L) in north-central Wisconsin. Mercury uptake was greatest in perch in lakes with alkalinity $\leq$ 40 ueq/L. Multiple regression models, which included combinations of pH, alkalinity, and total Hg concentration and organic content in surficial profundal sediments as independent variables, accounted for 80 to 90% of the variation of Hg burden and concentration in whole yellow perch. Furthermore, preliminary data suggest that Hg concentrations in whole calendar age 2 yellow perch reflect concentrations of the metal in axial muscle tissue of walleyes in north-central Wisconsin lakes.

Aufwuchs from artificial substrates accumulated measurable amounts of Hg during 28-d incubation periods; Hg concentrations varied seasonally and were greatest in fall, lowest in spring, and intermediate in summer. Multiple regression models with combinations of five independent variables (pH, alkalinity, total Hg concentration and organic content in surficial profundal sediment, and total watershed area:lake surface area) accounted for 80 to 90% of the variability in Hg concentration and burden (areal) in aufwuchs.

When interpretative problems and costs in the use of procedurally defined aufwuchs are considered, the use of a forage fish such as yellow perch seems to be a more efficient approach to monitoring Hg bioavailability. Furthermore, determination of Hg in small yellow perch is a more direct method of assessing potential Hg contamination of gamefish--a topic with human health implications.

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# INTRODUCTION

Fish in low-alkalinity lakes often have elevated mercury (Hg) concentrations, even in watersheds lacking a direct source of Hg. Wiener (1983) found elevated Hg levels in walleyes (*Stizostedion vitreum vitreum*) from rural north-central Wisconsin lakes with low pH (< 7) and low waterborne calcium concentrations.

Hundreds of low-alkalinity seepage lakes exist in north-central Wisconsin (Eilers et al. 1983; Wiener and Eilers 1987). Low-alkalinity seepage lakes receive most (> 90%) of their hydrologic input from precipitation falling directly onto the lake surface and little, if any, surface runoff from the watershed (Lin and Schnoor 1986). Thus, there are presumably two mechanisms by which Hg can enter the water of these low-alkalinity seepage lakes, atmospheric deposition and sedimentary release. The relative Hg contribution from these sources is unknown, but the major Hg input to remote lakes with no anthropogenic source of the metal is considered to be atmospheric deposition (Syers et al. 1973; Evans 1986; Johnson 1987; Rada et al. 1987a)

Inorganic Hg entering these systems in atmospheric deposition may undergo methylation in the water column (Furutani and Rudd 1980; Callister and Winfrey 1986; Xun et al. 1987) or become rapidly adsorbed to particulate matter in the water column (Rodgers et al. 1984). The particulate matter can subsequently be incorporated into bottom sediments where the Hg may undergo methylation. The bioavailability of sediment-bound Hg is unknown, but substantial Hg methylation occurs in surficial sediments (Furutani and Rudd 1980; Callister and Winfrey

1986; Korthals and Winfrey 1987; Xun et al. 1987).

Methylmercury uptake by aquatic organisms is rapid. Generally, more than 80% of the Hg in fish is methylmercury (Huckabee et al. 1979), which is either obtained directly from the water by uptake across the gills or indirectly through the diet (Olson et al. 1973; Phillips and Buhler 1978; Phillips and Gregory 1979; Turner and Swick 1983). Methylmercury accumulation from either pathway may be substantial, but the relative contribution of each pathway may vary depending on the fish species (Norstrom et al. 1976; Huckabee et al. 1978; Phillips and Buhler 1978; Rodgers and Qadri 1982). The availability of methylmercury to aquatic organisms depends on a variety of simultaneous biological and chemical transformations (methylation, demethylation, and volatilization) that are influenced by environmental factors such as pH and temperature (Steffan 1984; Ramlal et al. 1985; Callister and Winfrey 1986; Korthals and Winfrey 1987; Rada et al. 1987a; Xun et al. 1987; Steffan et al. in review).

Chemical conditions in softwater lakes may substantially enhance Hg uptake by fish. For example, Rodgers and Beamish (1983) found that the efficiency of methylmercury uptake by rainbow trout (*Salmo gairdneri*) was greatest in waters with low calcium concentration. Low alkalinity (Scheider et al. 1979; Wiener et al. 1986), low conductivity (Wren and MacCrimmon 1983; Haines et al. 1987), and low pH (Suns et al. 1980; Wiener 1983; Wren and MacCrimmon 1983; Suns et al. 1987) have also been related to elevated concentrations of Hg in fish.

Yearling yellow perch may be a useful indicator of Hg bioavailability in low-alkalinity lakes (Suns et al. 1980). Stokes et al. (1983) found that total Hg concentrations in filamentous, attached algae in acid-stressed lakes were highly correlated with total Hg concentrations in resident yearling (age $I^+$) yellow perch in the lakes. Stokes et al. (1983) suggested that analysis of filamentous algae, harvested from artificial substrates, may be an efficient technique for monitoring the bioavailability of Hg in acid-stressed lakes. Yellow perch and attached algae are typically easier to collect than predatory gamefish. Furthermore, Hg data obtained by either of these methods would be indicative of Hg bioavailability during the year (yellow perch) or season (aufwuchs) of collection. With small yellow perch of a given age, effects of confounding variables, such as fish age, length, and weight, would also be reduced.

I evaluated yellow perch and aufwuchs attached to artificial substrates as indicators of Hg bioavailability in 11 north-central Wisconsin lakes, which varied in pH, alkalinity, and waterborne calcium concentrations. I selected the term aufwuchs to describe the community attached to the artificial substrate instead of attached algae, even though my techniques for collection were similar to those of Stokes et al. (1983) because there are other organisms, such as bacteria and fungi, in addition to attached algae that colonize the artificial substrate. The specific objectives of this study were to (1) examine total Hg concentrations in yellow perch and aufwuchs in relation to lake chemistry, (2) assess seasonal variation in Hg accumulation by aufwuchs, (3) assess seasonal biomass production of aufwuchs, and (4) develop multiple regression models for prediction of Hg in fish and aufwuchs of north-central Wisconsin lakes.

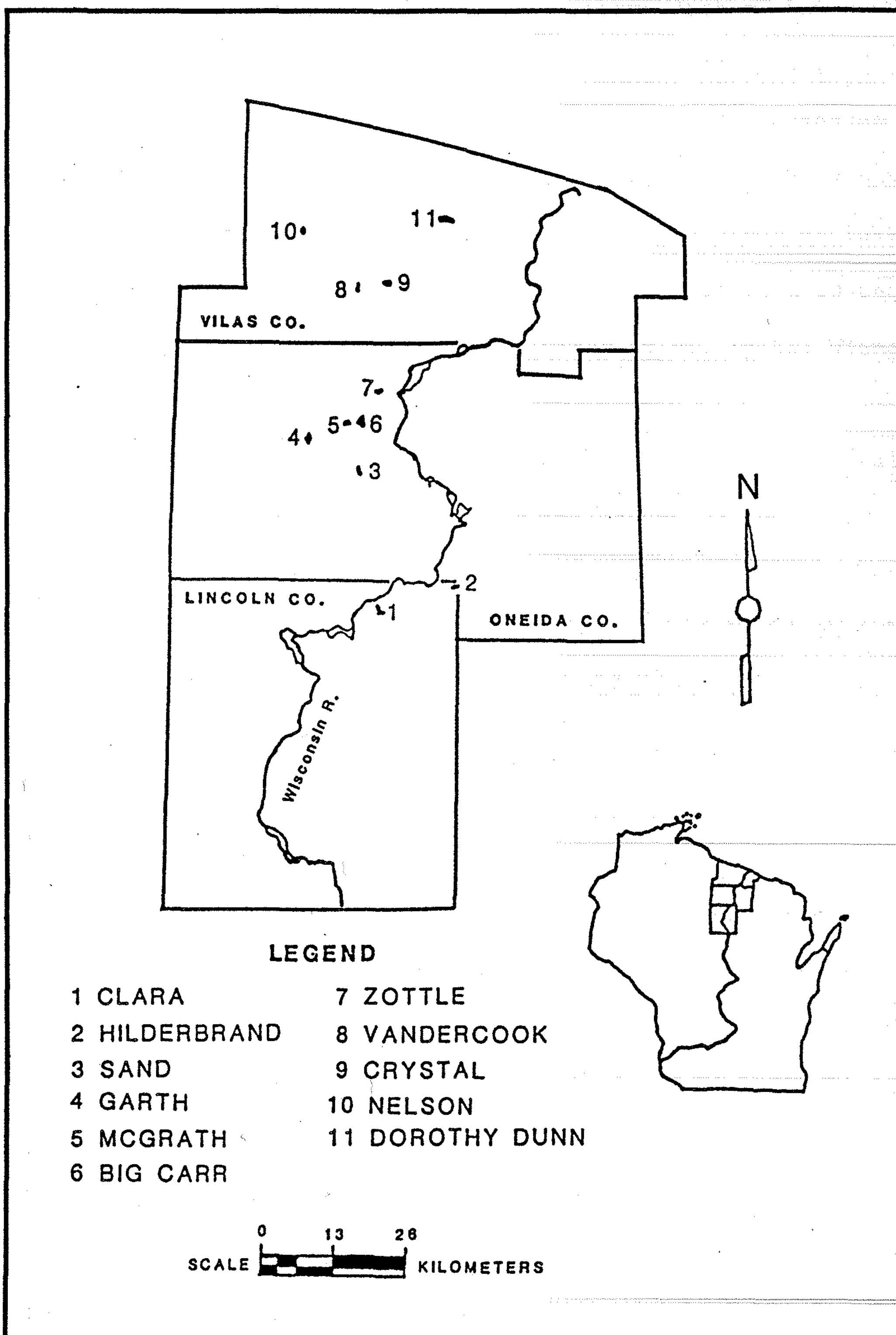
## STUDY AREA

The 11 study lakes are located in Lincoln, Oneida, and Vilas counties of north-central Wisconsin (Fig. 1). These lakes are in the Highland Lake District, which contains thousands of lakes (Martin 1965). Most lakes in this area were formed by glacial activity during the Pleistocene epoch. The study lakes are located in an area classified as pitted outwash plain (Hole 1976) and are situated well above the Precambrian bedrock in thick glacial till. The bedrock is primarily composed of granite, quartzite, and undifferentiated igneous and metamorphic rocks (Hole 1976). Soils primarily consist of acidic sands, loamy sands, and sandy loams with low cation exchange capacity and low base saturation (Hole 1976). Upland vegetation was formerly dominated by white pine, hardwoods, and hemlock, which was largely removed by logging and burning during the late 1800s and early 1900s. About 80-90% of the area has been reforested (Black et al. 1963; Andrews and Threinen 1966; Carlson and Andrews 1982) and is dominated by aspen, birch, mixed hardwoods, and conifers.

The climate of the study area is cool and humid with mean air temperatures of 19 C in July and -11 C in January (Burley 1964). Average annual precipitation is about 80 cm, of which about 60% is lost from the watershed through evapotranspiration (Hole 1976). The length of the frost-free season is about 110 d and the average annual snowfall is about 170 cm (Black et al. 1963; Andrews and Threinen 1966; Carlson and Andrews 1982).

Galloway et al. (1982) defined acid precipitation as that having a volume-weighted pH below 5.0. The annual mean, volume-weighted pH of

Figure 1. Location of the 11 study lakes in north-central Wisconsin.


VILAS CO.
LINCOLN CO.
ONEIDA CO.
Wisconsin R.
N
10
11
8
9
7
5
4
6
3
2
1
LEGEND
1 CLARA
2 HILDERBRAND
3 SAND
4 GARTH
5 MCGRATH
6 BIG CARR
7 ZOTTLE
8 VANDERCOOK
9 CRYSTAL
10 NELSON
11 DOROTHY DUNN
0
13
26
SCALE
KILOMETERS

wet deposition at Trout Lake (near the northern part of the study area) from December 1979 through November 1982 ranged from 4.64 to 4.79 (Glass and Loucks 1986). Wright and Henriksen (1978) suggested that a precipitation pH of 4.6 represents a threshold value that eventually causes acidification of low-alkalinity waters. Hundreds of lakes in north-central Wisconsin have low-alkalinity (defined as $\leq$ 50 ueq/L), and may be sensitive to acidification (Glass et al. 1986a; Wiener and Eilers 1987).

Eilers et al. (1983) studied 275 lakes in northern Wisconsin and showed that lake chemistry is strongly influenced by hydrology. The lakes with lowest alkalinity were seepage lakes, which were chemically similar to precipitation. Low-alkalinity seepage lakes lack inlets and outlets and are precipitation dominated, receiving most ($\geq$ 90%) of their hydrologic inflow by precipitation falling directly onto the lake surface (Lin and Schnoor 1986).

The 11 study lakes are small, clear-water lakes with a broad range of pH and alkalinity. The pH of the study lakes ranged from 5.1 to 7.8, and alkalinities ranged from -12 to 769 ueq/L. Seven lakes had pH $\leq$ 6.0 and eight had alkalinities < 50 ueq/L. Three lakes (Dorothy Dunn, Garth, and Nelson) had circumneutral pH and high alkalinities exceeding 200 ueq/L. All lakes were relatively clear with low color ($\leq$ 14 PCU), low turbidity ($\leq$ 3 NTU), and low total suspended solids ($\leq$ 3.4 mg/L) (Table 1). Other chemical, biological, and morphometric characteristics of the study lakes are presented in Table 2. Ten were seepage lakes and one (Clara) was a drained lake (intermittent outlet but no inlet). The hydraulic residence times of seepage and drained lakes in the Highland Lake District are long, about 4-5 years (Schnoor et al. 1986).

Table 1. Characteristics of water and sediments in the study lakes[a].

| Lake | Water chemistry: pH | Water chemistry: Alkalinity (ueq/L) | Water chemistry: Color (PCU) | Water chemistry: Turbidity (NTU) | Water chemistry: Total suspended solids (mg/L) | Water chemistry: Conductance (us/cm) | Characteristics of surficial sediment: Hg concn (ug/g dry wt) | Characteristics of surficial sediment: Al concn (mg/g dry wt) | Characteristics of surficial sediment: Organic content (%) | Characteristics of surficial sediment: Clay content (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Big Carr | 6.0 | 24 | 1.3 | 1.2 | 0.8 | 18 | 0.19 | 12.19 | 43 | 33 |
| Clara | 6.3 | 40 | 8.8 | 2.1 | 0.3 | 31 | 0.17 | 11.92 | 53 | 27 |
| Crystal | 5.7 | 9 | 1.3 | 0.8 | 0.6 | 13 | 0.15 | 14.06 | 43 | --[c] |
| Dorothy Dunn | 7.1 | 295 | 4.0 | 2.2 | 2.1 | 34 | 0.15 | 7.25 | 41 | 38 |
| Garth | 7.8 | 769 | 14.0 | 3.0 | 1.7 | 75 | 0.12 | 3.45 | 49 | 24 |
| Hilderbrand | 5.3 | -3 | 14.0 | 1.4 | ND[b] | 16 | 0.15 | 6.96 | 54 | 20 |
| McGrath | 5.1 | -12 | 1.3 | 1.3 | ND | 15 | 0.19 | 9.89 | 54 | 26 |
| Nelson | 6.9 | 310 | 1.3 | 1.6 | 0.3 | 37 | 0.13 | 5.62 | 25 | 28 |
| Sand | 5.2 | -10 | 1.3 | 0.8 | 0.6 | 22 | 0.18 | 13.35 | 48 | 31 |
| Vandercook | 5.6 | 7 | 1.3 | 1.3 | 3.4 | 13 | 0.10 | 10.68 | 35 | 31 |
| Zottle | 5.8 | 24 | 4.0 | 1.9 | 1.2 | 12 | 0.09 | 10.44 | 40 | 28 |

[a] Data from Rada et al. (1987a).
[b] ND = not detectable.
[c] Data unavailable.

Table 2. Morphometric characteristics and environmental variables of the 11 study lakes.

| Lake | Depth (m) | | Drainage basin area (ha) | | Volume ($m^3$ X $10^5$) | Total watershed area/lake surface area | Total watershed area/lake volume | Total organic carbon (mg/L)[a] | Secchi depth (m) |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | Maximum | Lake surface area[b] | Total watershed area[b] | | | | | |
| Big Carr | 10.2[b] | 21.6[b] | 84 | 176 | 85.7 | 2.1 | 2.1 | 2.9 | 8.5[b] |
| Clara | 5.1[c] | 11.4[c] | 34 | 111 | 17.3 | 3.3 | 6.4 | 3.7 | 4.2[c] |
| Crystal | 10.1[b] | 20.4[b] | 36 | 218 | 36.8 | 6.0 | 5.9 | 1.5 | -- |
| Dorothy Dunn | 2.7[c] | 8.2[c] | 28 | 85 | 7.6 | 3.0 | 11.2 | -- | 3.7[c] |
| Garth | 3.7[c] | 6.7[c] | 49 | 110 | 18.1 | 2.2 | 6.1 | -- | 2.4[c] |
| Hilderbrand | 4.2[c] | 8.0[c] | 24 | 114 | 10.1 | 4.8 | 11.3 | 2.8 | 3.2[c] |
| McGrath | 3.0[c] | 7.3[c] | 21 | 44 | 6.4 | 2.1 | 6.9 | 2.8 | 6.0[c] |
| Nelson | 6.7[c] | 15.8[c] | 43 | 113 | 28.8 | 2.6 | 3.9 | 3.1 | 5.1[c] |
| Sand | 3.2[b] | 5.8[b] | 15 | 72 | 4.8 | 4.8 | 15.0 | 0.9 | 6.7[b] |
| Vandercook | 3.5[b] | 6.7[b] | 40 | 131 | 14.0 | 3.3 | 9.4 | 4.2 | 3.4[b] |
| Zottle | 4.3[c] | 11.6[c] | 11 | 50 | 4.7 | 4.5 | 10.6 | 2.2 | 4.7[c] |

[a] Data provided by G. E. Glass (U.S. Environmental Protection Agency, Duluth, MN) and represent averages for samples collected during 1979-1983.
[b] Data provided by K. E. Webster (Wisconsin Department of Natural Resources). Secchi depth was determined during the summer of 1979.
[c] Data from Schmidt (1985). Secchi depths are mean values measured from June 1982 through June 1984.

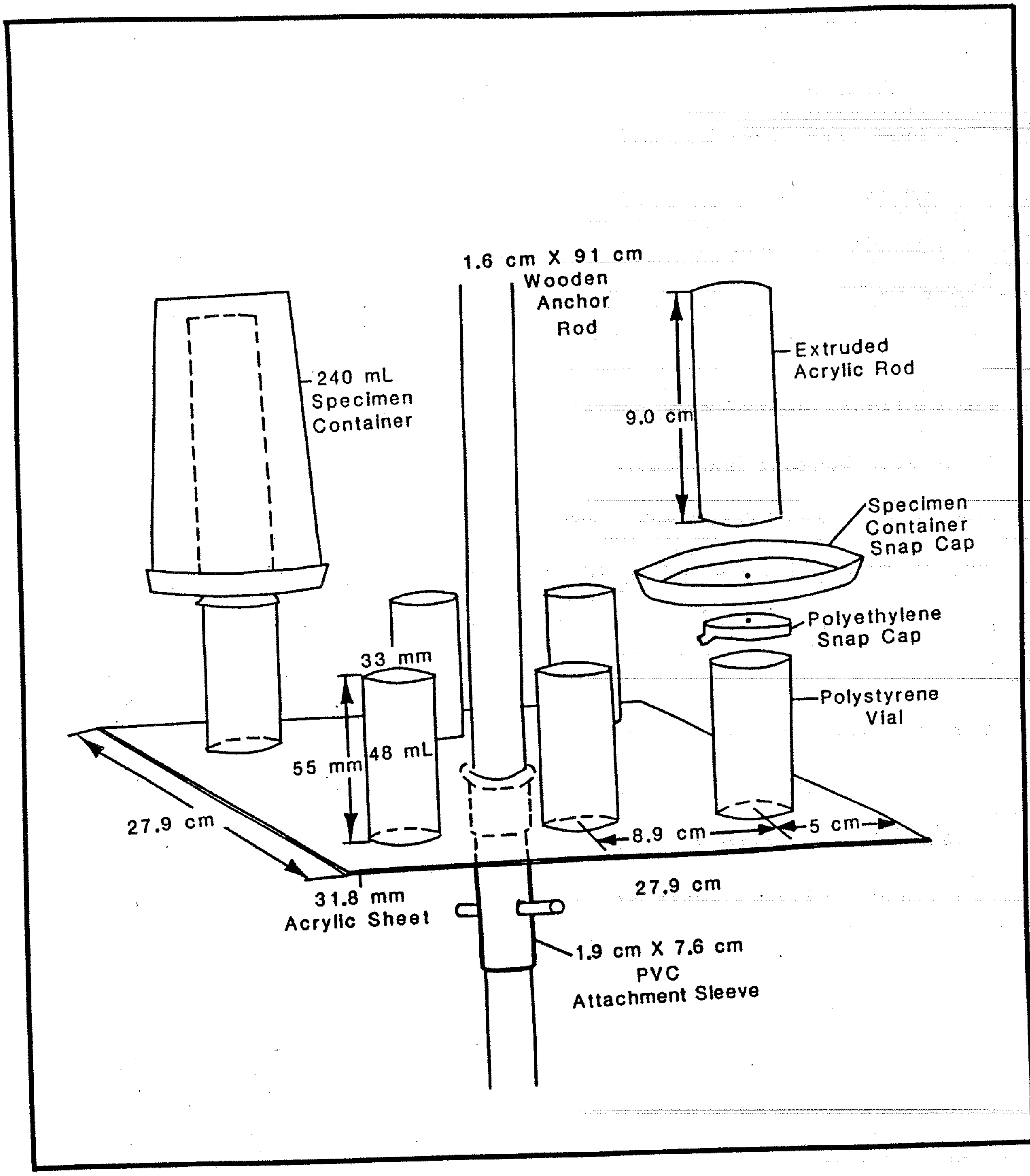
## METHODS

### Sample Collection

Yellow perch. Yellow perch were collected during April 17-27, 1986 with minnow traps (2.54-cm diam opening) fished in littoral habitats. This sampling period was shortly after ice-out, while yellow perch were spawning. Four to six traps were set overnight in each lake and checked the following morning. Most traps were set adjacent to emergent vegetation or submerged logs--locations that yielded the greatest catch. Fish were held live in polyethylene buckets containing lake water and were processed once on shore. Each fish was assigned an identification number, measured (total length, mm), and weighed (Ohaus model C501 electronic balance) to the nearest 0.1 g. The fish were then placed into labeled Ziploc$^R$ bags and transported to a field laboratory where they were stored frozen at about -20 C. Fish were transported to the University of Wisconsin-La Crosse in frozen condition and stored at about -20 C until scale collection and subsequent lyophilization.

Aufwuchs. Aufwuchs samples were collected during the summer 1985 (July to August), fall 1985 (September to October), and spring 1986 (June to July) with an artificial substrate sampler modified from Stokes (1984) (Fig. 2). Four artificial substrate samplers were placed in each of the 11 study lakes for a 28-d incubation period. The outer surface of each extruded acrylic rod was covered with a sheet of single matte Mylar$^R$ (80-um thick), which is a suitable substrate for growing and harvesting attached algae (Dreier et al. 1980; Stokes et al. 1983). The total area of Mylar$^R$ available for colonization was 90 $cm^2$. Mylar$^R$

Figure 2. Diagram of aufwuchs artificial substrate sampler.



1.6 cm X 91 cm
Wooden
Anchor
Rod
240 mL
Specimen
Container
Extruded
Acrylic Rod
9.0 cm
Specimen
Container
Snap Cap
Polyethylene
Snap Cap
33 mm
Polystyrene
Vial
55 mm
48 mL
27.9 cm
8.9 cm
5 cm
31.8 mm
Acrylic Sheet
27.9 cm
1.9 cm X 7.6 cm
PVC
Attachment Sleeve

was secured to the acrylic rod by two size-8 rubber bands (one at top and one at bottom). Samplers were placed in areas of lakes where the natural growth of aufwuchs appeared most abundant. The samplers were situated about 6.4 cm above the lake sediment at depths of 0.5-1.0 m by inserting the wooden anchor rod into the sediments to the wooden pin that secured the sampler to the wooden anchor rod (Fig. 2). This prevented the sampler from being covered with suspended sediments (caused by wave action or other disturbances) and ensured that the distance from the sediment-water interface was the same for all four samplers in a lake.

After the 28-d incubation period, a 240-mL specimen container was placed over each acrylic rod bearing the Mylar$^{R}$ and snapped into the cap that formed the base of the cylinder. The individual samples were removed from the sampler without disturbing the remaining samples and placed on ice and transported within 8 h to the field laboratory for processing.

At the laboratory, two of the six samples from each sampler were randomly selected for analysis of taxonomic composition, chlorophyll *a* (Chl *a*), pheophytin *a* (Pheo *a*) and biomass. The Mylar$^{R}$ sheets were removed from the acrylic rod with stainless steel forceps and placed onto a sheet of acrylic plexiglass. Aufwuchs was removed from the Mylar$^{R}$ with a plexiglass scraper and placed into a 500-mL graduated cylinder. For the summer and fall collections, the remaining contents of the two specimen containers were also placed into the graduated cylinder. This material was mainly organic debris that accumulated in the cap of the specimen container during the incubation period. It also included a small amount of material that dislodged from the Mylar$^{R}$

during sample handling and transport. In contrast, only aufwuchs scraped from the Mylar[R] was used during the spring 1986 collection, i.e., the material in the specimen containers was discarded. All other sample processing procedures were the same for all seasons. The contents of the graduated cylinder were diluted to 500 mL with deionized water, placed in a 1-L erlenmeyer flask, and shaken vigorously to homogenize the material. A 50-mL subsample was withdrawn and placed in an amber bottle with 1.0 mL of $M^3$ fixative and held for microscopy. A 150-mL subsample was filtered onto a Gelman glass fiber filter (Type A/E, 47-mm diam), which was wrapped in aluminum foil, frozen, and held in the dark at -20 C for pigment analysis. A 300-mL subsample was filtered onto a pre-weighed Gelman glass fiber filter (Type A/E, 47-mm diam), allowed to air dry, and held at -20 C for ash-free dry weight (AFDW) analysis.

Aufwuchs from the remaining four samples of each sampler was scraped into Nalgene[R] snap-cap vials, frozen at -20 C, and held in the dark at -20 C for total Hg analysis. The contents of the four specimen containers were discarded for all three sampling periods.

The pH was measured at each sampling site in each lake at the beginning and end of each sampling period with a Fisher Model 107 meter. Before use, the meter was calibrated with pH 7.0 and 4.0 buffers. Water temperature was measured with a YSI model 54A dissolved oxygen-temperature meter.

## Sample Analyses

Yellow perch. Fish samples were partially thawed, and scales for age estimation were taken near the area of insertion of the left pectoral fin. Age of yellow perch was estimated by examining at least six scales from each fish. The age assigned to each fish was equal to the total number of completed scale annuli and expressed as calendar age (Nielsen and Johnson 1983; Summerfelt and Hall 1987). Calendar age is based on an arbitrary birth date of January 1, rather than the true date of hatch. For example, calendar age 1 fish are those without a completed scale annulus but have passed their first January 1. In many north-central Wisconsin lakes, yellow perch older than calendar age 2 cannot be reliably aged by enumeration of scale annuli; therefore, there may be errors in age estimates for yellow perch of calendar age 3 and greater. After scales were taken, individual fish were lyophilized in their respective Ziploc$^R$ bag for 48-96 h at -60 C and ground to a fine powder with a porcelain mortar and pestle. Total Hg concentrations were measured on 0.150-g subsamples of lyophilized whole-body tissue that was placed into 300-mL Fleakers$^R$ and digested with 5 mL of concentrated $H_2SO_4$, 2 mL of concentrated $HNO_3$, 1 mL of concentrated HCl, 20 mL of saturated $KMnO_4$, and 8 mL of 5% (w/v) $K_2S_2O_8$ (modified from Environment Canada 1979). The $K_2S_2O_8$ was added to increase the boiling point to prevent loss of material during autoclaving. The HCl was added to promote decomposition of fish tissue. If oxidizing conditions did not persist for 15 min after addition of $KMnO_4$ (as evidenced by the lack of a purple color), more $KMnO_4$ was added. After oxidizing conditions persisted for 15 min, the Fleakers$^R$ were covered with heavy-duty aluminum foil and autoclaved for 15 min at 121 C (U.S. Environmental Protection Agency 1981). If oxidizing conditions were not maintained during autoclaving, more $KMnO_4$ was added until oxidizing conditions were re-established, and samples were again autoclaved. Digestates were cooled and diluted to 100 mL with deionized water. Total Hg concentrations in the diluted digestates were determined with cold vapor atomic absorption at 253.7 nm with an Instrumentation Laboratory 551 atomic absorption spectrophotometer equipped with an Instrumentation Laboratory AVA 440 cold vapor generator.

Aufwuchs. Samples were analyzed for Chl *a*, Pheo *a*, and AFDW according to APHA (1985). Pigment determinations were performed on a Beckman DU-6 spectrophotometer. Total Hg concentrations in aufwuchs scraped from four sheets (360 $cm^2$) of Mylar$^R$ from each sampler were measured. Aufwuchs samples held for total Hg analyses were lyophilized in their respective Nalgene$^R$ snap-cap vials for 24-48 h and weighed (Scientech model 3300 electronic balance) to the nearest milligram. Lyophilized aufwuchs samples were placed into 300-mL Fleakers$^R$ and digested with 5 mL of concentrated $H_2SO_4$, 2 mL of concentrated $HNO_3$, 5 mL of saturated $KMnO_4$, and 5 mL of 5% (w/v) $K_2S_2O_8$. The rest of the Hg analysis was the same as described for fish.

## Quality Assurance

Yellow perch sampling equipment. Polyethylene holdling buckets, measuring boards, and weighing cups were washed with Liquinox$^R$ detergent, rinsed with tap water, soaked in 50% $HNO_3$ for 24 h, and rinsed thoroughly with deionized water. Buckets were sealed with a lid during transit. Measuring boards and weighing cups were transported in large Ziploc$^R$ bags.

Aufwuchs sampling equipment. Before each setting, the artificial substrate samplers were washed with Liquinox$^R$ detergent, rinsed with tap water, soaked in 50% $HNO_3$ for 12 h, and consecutively rinsed in tap and deionized water. Mylar® and rubber bands were washed with Liquinox® detergent, rinsed with tap water, soaked in 5% $HNO_3$ for 12 h, and rinsed thoroughly with deionized water. Nalgene® snap-cap vials were washed with Liquinox® detergent, rinsed with tap water, soaked in 50% $HNO_3$ for 24 h, and rinsed 10 times in deionized water. All other sampling equipment (such as plexiglass sheets, plexiglass scrapers, forceps, and filtration equipment) were given the same washing procedure as the artificial substrate samplers but were soaked for 24 h in 50% $HNO_3$ and rinsed thoroughly in deionized water. All sampling equipment and storage containers were transported to the sampling site in tightly sealed plastic garbage bags or in large Ziploc® bags.

Analytical equipment and glassware. Fleakers®, stir bars, and other equipment used in Hg analyses were washed with Liquinox® detergent, rinsed 3 times with tap water, soaked a minimum of 12 h in 50% $HNO_3$, and rinsed 10 times in deionized water. Stir bars used in fish analyses were given the same wash as the Fleakers®, except the bars were given an acetone wash to remove lipids before the acid soak.

Pigment analyses of aufwuchs. United States Environmental Protection Agency chlorophyll quality control samples were analyzed in triplicate with the aufwuchs chlorophyll analyses from the spring sampling period to estimate precision and accuracy and to validate procedures (Table 3). Each analysis was within the 95% confidence limits established by the U.S. Environmental Protection Agency.

Hg analyses. Instra-Analyzed® acids, $KMnO_4$, and $K_2S_2O_8$ (J.T. Baker Chemical Co.) were used in fish digestions. Other chemicals used in Hg analyses were certified as suitable for Hg analysis (J.T. Baker

Table 3. Quality assurance data for chlorophyll standards from the U.S. Environmental Protection Agency (EPA).

| Parameter | Sample | EPA certified concentration range (mg/L) | Our results: Mean concentration (mg/L) | Our results: Range (mg/L) |
|---|---|---|---|---|
| Chlorophyll a | 1 | 6.0 to 7.8 | 7.2 | 7.1 to 7.3 |
| | 2 | 1.7 to 2.2 | 1.8 | -- |
| Pheophytin a | 1 | -0.04 to 3.1 | 1.2 | 1.1 to 1.3 |
| | 2 | -0.6 to 0.4 | -0.03 | -0.003 to -0.05 |

Chemical Co.). Reagents were the same for aufwuchs analyses except that Ultrex$^R$ acids (J.T. Baker Chemical Co.) were used to digest aufwuchs. The Hg concentration of each bottle of Instra-Analyzed$^R$ acid was compared to that of the same type of Ultrex$^R$ acid (J.T. Baker Chemical Co). No differences were observed between the two types of acids for the instrumental conditions used in the Hg analyses (Student's t-test, $\alpha = 0.05$). Atomic absorption standards for Hg analyses were prepared from 1000-mg/L certified standard solutions (Curtin Matheson Scientific Co.). Procedural blanks and calibration standards were taken through digestion and analytical procedures for each batch of samples analyzed to assess contamination from reagents and glassware. United States National Bureau of Standards (NBS) albacore tuna (SRM 50), oyster tissue (SRM 1566), bovine liver (SRM 1577a), pine needles (SRM 1575), and spiked yellow perch and aufwuchs samples were analyzed with each batch of samples to evaluate accuracy and precision of procedures and analyses. Duplicate and triplicate analyses of individually digested subsamples, respectively, were conducted on 10% of the fish and aufwuchs samples to estimate precision.

A standard addition procedure (4-point) was performed on fish and aufwuchs tissue to evaluate the presence of potential interferences, which were observed during analyses of fish tissue. Therefore, a matrix similar to that of the samples--0.125 g of lyophilized, triturated fathead minnow (*Pimephales promelas*) tissue--was added to the blanks and calibration standards. The absorbances of all blanks and calibration standards were then adjusted for absorbance due to any Hg in the fathead minnow tissue. My calculated analytical detection limits (Slavin et al. 1972) for samples with low mercury concentrations were 5 ng per 100-mL diluted digestate for fish and 2 ng per 100-mL diluted digestate for aufwuchs. My analyses of NBS standard reference materials (Table 4) yielded Hg concentrations within the certified concentration ranges in 44 of the 49 analyses conducted. Two of the 24 albacore tuna analyses were slightly above (within 4%) of the certified concentration range. Three of the 16 analyses of bovine liver were outside the certified 95% confidence interval (1 above, 2 below), and the mean relative standard deviation (percent RSD) for bovine liver was also high (54%). These results were obtained because the Hg concentration in the bovine liver was near my estimated detection limit. Mean percent recovery of Hg from spiked fish and aufwuchs samples were 104 and 102%, respectively (Table 5). Percent differences ranged from 0 to 33% for duplicate analyses of fish and from 15 to 21% for duplicate analyses of aufwuchs. The RSD ranged from 4 to 5% for triplicate aufwuchs analyses (Table 6).

Statistical analysis. Statistical analyses were performed with the StatPac Gold$^{R}$ Statistical Analysis Package (Walonick Associates 1986). A Type I error of 0.05 was used to judge significance of statistical tests. One-way analysis of variance (ANOVA) was used to determine if the size (length or weight) of yellow perch of a given age class differed among lakes. The Student-Newman-Keuls (SNK) multiple range test was used to perform pairwise contrasts of fish size between lakes. One-way ANOVA and SNK multiple range test was also used to evaluate seasonal variation in aufwuchs Hg. If the ANOVA assumption of homogeneity of variances was not met, the data were $\log_{10}$-transformed. If variances remained unequal after logarithmic transformation, the

Table 4. Summary of quality assurance data for Hg analyses of U.S. National Bureau of Standards (NBS) reference materials.

| NBS reference material | NBS certified concentration range (ug/g dry wt) | Our results | | | |
|---|---|---|---|---|---|
| | | Mean concentration (ug/g dry wt) | Range | Mean RSD[a] (%) | Number of digestates analyzed |
| Albacore tuna | 0.85-1.05 | 0.98 | 0.91-1.09 | 5 | 24 |
| Oyster tissue | 0.042-0.072 | 0.054 | -- | 0 | 1 |
| Bovine liver | 0.002-0.006 | 0.003 | <DL[b]-0.007 | 54 | 16 |
| Pine needles | 0.10-0.20 | 0.14 | 0.13-0.17 | 9 | 8 |

[a] RSD = Relative standard deviation.

[b] DL - Detection limit = 0.002 ug/g dry weight.

Table 5. Recovery of Hg from spiked samples of yellow perch and aufwuchs.

| Sample type | Number of spiked samples analyzed | Percent recovery | | |
|---|---|---|---|---|
| | | Mean | Minimum | Maximum |
| Yellow perch | 46 | 104 | 89 | 115 |
| Aufwuchs | 10 | 102 | 97 | 105 |

Table 6. Precision of replicate analyses for yellow perch and aufwuchs.

| Sample type | Measurement of variation | Number of replicate analyses | Variation among replicates | | |
|---|---|---|---|---|---|
| | | | Mean | Minimum | Maximum |
| Yellow perch | Percent difference | 23[a] | 8 | 0 | 33 |
| Aufwuchs | Percent difference | 2[a] | 18 | 15 | 21 |
| Aufwuchs | RSD[b] | 2[c] | 4 | 4 | 5 |

[a] Replicates were analyzed in duplicate.

[b] RSD = Relative standard deviation.

[c] Replicates were analyzed in triplicate.

data were rank-transformed and evaluated by one-way ANOVA of ranks (Conover and Iman 1981).

Relations of Hg concentrations in fish and aufwuchs to environmental variables were evaluated by a stepwise multiple regression procedure (STEPWISE), which uses the forward inclusion ($F \geq 4.0$ to include a variable), backward elimination ($F \leq 3.9$ to remove a variable) method. This method attempts to generate the best model from the independent variables available. No variables were forced into the model.

The total number of lakes ($N = 11$) was too small to incorporate all independent variables into a single multiple regression analysis; therefore, all independent variables were subjected to correlation analysis (Pearson) with fish and aufwuchs Hg concentrations. Three sets of variables were evaluated by correlation analysis, as shown below.

| Surface water | Surficial sediment | Lake-watershed |
|---|---|---|
| pH | Hg concn | Maximum depth |
| Alkalinity | Al concn | Mean depth |
| Color | Organic concn | Lake surface area (LSA) |
| Turbidity | Clay concn | Total watershed area (TWA) |
| Total suspended solids | | Lake volume (LV) |
| Conductivity | | TWA/LSA ratio |
| Secchi depth | | TWA/LV ratio |

Data for the independent variables listed above were assembled from other studies. The majority of data was taken from the study of Rada et al. (1987a), which was simultaneously conducted on the same 11 study lakes as my study. Lakewater pH was analyzed statistically as pH and as hydrogen ion concentration. Negative alkalinity values were changed to 0.001 ueq/L to allow for $\log_{10}$ transformation. Alkalinity was analyzed statistically as ueq/L and $\log_{10}$ ueq/L. The independent variable reporting units and abbreviations are presented in Appendix 2.

The four to seven variables that were most strongly correlated with the dependent variable were made available to the STEPWISE program. All variables available for selection in the STEPWISE program had correlation coefficients that differed from zero at $p \leq 0.10$ unless the author had a specific reason to include a variable having $p > 0.10$. For fish, two dependent variables, Hg concentration ($\log_{10}$-transformed and untransformed, ug/g wet weight) and Hg burden (ug/fish), were analyzed in the correlation and the multiple regression program. Mercury burden is defined as the total quantity of Hg in a whole fish. Mercury in fish is expressed as both concentration and burden because concentration values are important from a regulatory perspective (e.g., U.S. Food and Drug Administration action level) and burden values reflect the amount (i.e., dose) of Hg a predator would ingest if feeding on one of these yellow perch. Dry weight concentrations of Hg in fish were converted to wet weight concentrations by multiplying by 0.25 (Wiener and Giesy 1979). Mercury concentrations in aufwuchs ($\log_{10}$-transformed and untransformed values, ng/g dry weight) and Hg burdens expressed on an areal basis (ng/$m^2$) were analyzed as dependent variables in correlation and multiple regression analyses. The multiple $R^2$ (adjusted for degrees of freedom) was the primary criterion for selecting the best regression equations.

# CHAPTER 1: FACTORS INFLUENCING MERCURY ACCUMULATION IN FISH

## RESULTS

### Comparison of Yellow Perch Size Among Lakes

Mean total lengths of calendar age 1 yellow perch from individual lakes ranged from 69 to 81 mm, and mean wet weights ranged from 2.9 to 4.4 g (Table 7). The variances of length and weight of age 1 yellow perch varied significantly among lakes; therefore, the length and weight data were $\log_{10}$-transformed. The mean size (length or weight) of age 1 yellow perch did not vary among lakes ($p > 0.05$, one-way ANOVA).

Mean total lengths of calendar age 2 yellow perch from individual lakes ranged from 88 to 115 mm, and mean wet weights ranged from 6.1 to 15.6 g (Table 8). Mean total lengths and wet weights of age 2 yellow perch varied significantly among lakes and were greatest in Big Carr Lake and smallest in Nelson and Zottle lakes.

### Comparison of Hg in Yellow Perch Among Lakes

Mean concentrations of total Hg in age 1 yellow perch ranged from 0.05 to 0.15 ug/g wet weight (Table 7). Mean concentrations in age 2 perch ranged from 0.06 to 0.19 ug/g. Fish from Dorothy Dunn, Nelson, and Zottle lakes had the lowest mean concentrations and those from McGrath Lake the highest mean concentration (Table 8).

Mercury concentrations in perch from a given lake usually increased with increasing age; furthermore, fish from the low-pH lakes, such as McGrath and Vandercook, generally had greater Hg concentrations than those from the high-pH lakes, such as Dorothy Dunn (Fig. 3).

Table 7. Wet weight, total length, and mercury content of calendar age 1 yellow perch from north-central Wisconsin lakes.

| Lake | N[a] | Wet weight (g) of fish analyzed | | Total length (mm) of fish analyzed | | Mercury concentration (ug/g wet weight) | | |
|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | Mean | Range | RSD (%)[b] |
| Big Carr | 12 | 4.3 | 2.0-9.8 | 77 | 63-102 | 0.12 | 0.10-0.15 | 14 |
| Clara | 15 | 4.0 | 2.6-5.7 | 80 | 72-89 | 0.15 | 0.12-0.17 | 11 |
| Dorothy Dunn | 6 | 2.9 | 1.7-4.4 | 69 | 60-81 | 0.05 | 0.04-0.08 | 32 |
| McGrath | 14 | 4.4 | 3.3-5.9 | 80 | 72-88 | 0.12 | 0.07-0.24 | 32 |
| Nelson | 8 | 3.4 | 3.0-3.9 | 74 | 70-78 | 0.08 | 0.03-0.10 | 29 |
| Vandercook | 15 | 4.2 | 3.4-5.2 | 81 | 75-87 | 0.05 | 0.03-0.07 | 25 |
| Zottle | 18 | 3.0 | 1.6-3.9 | 70 | 58-76 | 0.08 | 0.07-0.10 | 11 |

[a] N = Number of fish analyzed; age 1 perch were not obtained from four lakes (Crystal, Garth, Hilderbrand, and Sand).

[b] RSD = Relative standard deviation.

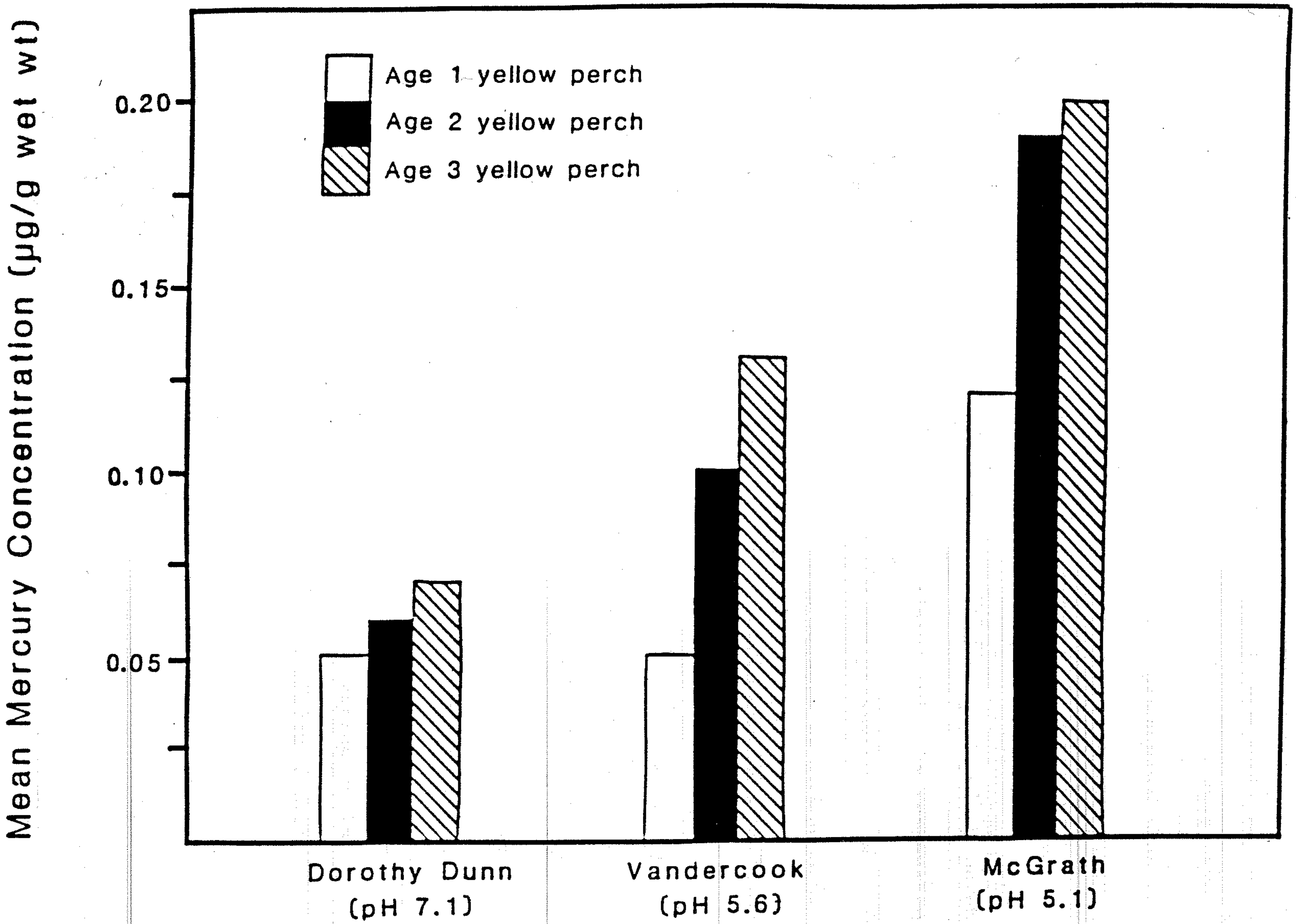
Table 8. Wet weight, total length, and mercury content of calendar age 2 yellow perch from north-central Wisconsin lakes. For a given variable, any two means not accompanied by a common letter in their superscript were judged to be significantly different ($\alpha = 0.05$), Student-Newman-Keuls multiple range test (Sand lake was not included in multiple comparisons).

| | | Wet weight (g) of fish analyzed | | Total length (mm) of fish analyzed | | Mercury concentration (ug/g wet weight) | | |
|---|---|---|---|---|---|---|---|---|
| Lake | N* | Mean | Range | Mean | Range | Mean | Range | RSD (%)¶ |
| Big Carr | 3 | 15.6$^{d}$ | 13.4-18.1 | 115$^{d}$ | 109-119 | 0.13$^{b}$ | 0.12-0.14 | 10 |
| Clara | 10 | 11.5$^{c}$ | 5.6-14.6 | 111$^{cd}$ | 90-119 | 0.14$^{b}$ | 0.11-0.18 | 16 |
| Crystal | 17 | 8.4$^{ab}$ | 4.8-11.0 | 102$^{b}$ | 87-108 | 0.14$^{b}$ | 0.09-0.22 | 26 |
| Dorothy Dunn | 5 | 12.9$^{c}$ | 10.3-16.3 | 109$^{cd}$ | 102-117 | 0.06$^{a}$ | 0.04-0.08 | 26 |
| Hilderbrand | 18 | 11.8$^{c}$ | 9.4-14.8 | 114$^{d}$ | 109-120 | 0.15$^{b}$ | 0.09-0.26 | 31 |
| McGrath | 13 | 9.5$^{b}$ | 4.2-12.5 | 105$^{bc}$ | 90-117 | 0.19$^{c}$ | 0.08-0.29 | 31 |
| Nelson | 17 | 6.2$^{a}$ | 4.5-11.1 | 90$^{a}$ | 80-108 | 0.08$^{a}$ | 0.03-0.11 | 26 |
| Sand | 1 | 12.6 | -- | 111 | -- | 0.14 | -- | -- |
| Vandercook | 15 | 8.6$^{ab}$ | 6.6-10.4 | 102$^{bc}$ | 92-111 | 0.10$^{ab}$ | 0.06-0.14 | 27 |
| Zottle | 8 | 6.1$^{a}$ | 2.9- 9.9 | 88$^{a}$ | 79-105 | 0.08$^{a}$ | 0.07-0.09 | 9 |

* Number of fish analyzed; age 2 perch were not obtained from Garth lake.

¶ Relative standard deviation.

Figure 3. Mercury concentration in yellow perch of age classes 1, 2, and 3 collected from Dorothy Dunn, Vandercook, and McGrath lakes.


Mean Mercury Concentration (µg/g wet wt)
0.20
0.15
0.10
0.05
Age 1 yellow perch
Age 2 yellow perch
Age 3 yellow perch
Dorothy Dunn
(pH 7.1)
Vandercook
(pH 5.6)
McGrath
(pH 5.1)

These relationships also existed for older fish from these lakes (Appendix 1). The negative relation between surface water pH and Hg in yellow perch also existed for body burdens (ug/fish), except that the increase in Hg burden with age of fish was more pronounced than that for Hg concentration.

Regressions for Predicting Hg in Yellow Perch

My most complete age-class data set was for age 2 yellow perch, which were collected from 10 lakes. Therefore, only the regression equations developed for age 2 yellow perch are presented. The STEPWISE multiple regression procedure was presented subsets of independent variables that were most highly correlated (Table 9) with either Hg burden or concentration.

Hg burden. The STEPWISE procedure revealed that two independent variables, Hg concentration in surficial profundal sediment and alkalinity, accounted for 90% of the variation in mean Hg burden of age 2 yellow perch. Lake pH and alkalinity were strongly correlated ($r = 0.91$; $p = 0.003$). When alkalinity was deleted from the list of independent variables, Hg concentration in surficial profundal sediment and lake pH were selected, explaining 86% of the variation in mean Hg burden of age 2 yellow perch (Table 10). The STEPWISE procedure was also used to determine if Hg in aufwuchs, alone or in combination with other environmental variables, could explain variation in Hg burden in fish. Two significant regression models were derived to explain the variation in mean Hg body burden in age 2 yellow perch with Hg content of aufwuchs as an independent variable. The first included three variables, organic content of profundal sediment, mean aufwuchs $Hg_{fall}$,

Table 9. Pearson correlation coefficients for selected independent variables with Hg burden (ug/fish) and concentration (ug/g wet weight) in age 1 and 2 yellow perch.

| Variable | Age 1 yellow perch: Hg burden | Age 1 yellow perch: Hg concentration | Age 2 yellow perch: Hg burden | Age 2 yellow perch: Hg concentration |
|---|---|---|---|---|
| pH | -0.37 | -0.29 | -0.58 | -0.78** |
| Alkalinity | -0.51 | -0.45 | -0.61 | -0.72* |
| Hg concentration in surficial profundal sediment | 0.81* | 0.75* | 0.83* | 0.66* |
| Organic content in surficial profundal sediment | 0.72 | 0.71 | 0.78** | 0.76** |
| Turbidity | -0.25 | -0.10 | -0.44 | -0.57 |
| Aufwuchs $Hg_{SUMMER}$ (ng/m2) | -0.73 | -0.70 | -0.67* | -0.64* |
| Aufwuchs $Hg_{SUMMER}$ (ng/g dry wt) | -0.45 | -0.36 | -0.31 | -0.57 |
| Aufwuchs $Hg_{SPRING}$ (ng/g dry wt) | 0.67 | 0.68 | 0.41 | 0.61 |

* Significant ($p \leq 0.05$).

** Highly significant ($p \leq 0.01$).

Table 10. Stepwise multiple regression models with multiple $R^2 \geq 0.70$ developed for the prediction of Hg burdens in age 2 yellow perch collected from north-central Wisconsin lakes. Units of expression for independent variables are presented in Tables 1 and 2.

| Independent variables available to STEPWISE program | Regression equation | Multiple $R^2$ | Independent variables selected | Standard error of slopes | p-value for slopes |
|---|---|---|---|---|---|
| pH, Alk, Turb, Sed Hg, Sed org | Hg = -0.45 + 12.5 Sed Hg - 0.0022 Alk | 0.90 | Sed Hg<br>Alk | 1.88<br>0.0005 | $< 0.005$ |
| pH, Sed Hg, Sed org | Hg = 1.58 + 12.6 Sed Hg - 0.37 pH | 0.86 | Sed Hg<br>pH | 2.24<br>0.11 | $< 0.025$ |
| Sed org, Aufwuchs $Hg_{SUMMER}$ ($ng/m^2$), Aufwuchs $Hg_{FALL}$ ($ng/m^2$), Aufwuchs $Hg_{SPRING}$ ($ng/m^2$) | Hg = -0.98 + 0.053 Sed org - 0.0098 Aufwuchs $Hg_{FALL}$ + 0.024 Aufwuchs $Hg_{SPRING}$ | 0.91 | Sed org<br>Aufwuchs $Hg_{FALL}$<br>Aufwuchs $Hg_{SPRING}$ | 0.008<br>0.002<br>0.006 | $< 0.01$ |
| Alk, Aufwuchs $Hg_{SUMMER}$ ($ng/m^2$), Aufwuchs $Hg_{FALL}$ ($ng/m^2$), Aufwuchs $Hg_{SPRING}$ ($ng/m^2$) | Hg = 2.17 - 0.016 Aufwuchs $Hg_{SUMMER}$ - 0.003 Alk | 0.75 | Aufwuchs $Hg_{SUMMER}$<br>Alk | 0.004<br>0.0008 | $< 0.025$ |

and mean aufwuchs $Hg_{spring}$, and accounted for 91% of the variation in Hg burden in fish. Mean aufwuchs $Hg_{fall}$ is defined as mean Hg in aufwuchs collected during the fall sampling period. A two-variable model with mean aufwuchs $Hg_{summer}$ and alkalinity explained 75% of the variation in fish Hg (Table 10).

Hg concentration. A two-variable model including lake pH and Hg concentration in surficial profundal sediment explained 87% of the variation in the Hg concentration (ug/g wet weight) in age 2 yellow perch (Table 11). In addition, three significant models included Hg in aufwuchs. A three-variable model that incorporated $\log_{10}$ alkalinity, mean aufwuchs $Hg_{summer}$, and Hg concentration in surficial profundal sediment accounted for 92% of the variation in fish Hg concentration. Two two-variable models each explained 87% of the variation in Hg concentration in fish--one with alkalinity and mean aufwuchs $Hg_{summer}$ and the other with pH and mean aufwuchs $Hg_{summer}$ (Table 11).

Regressions for Predicting Hg in Walleye

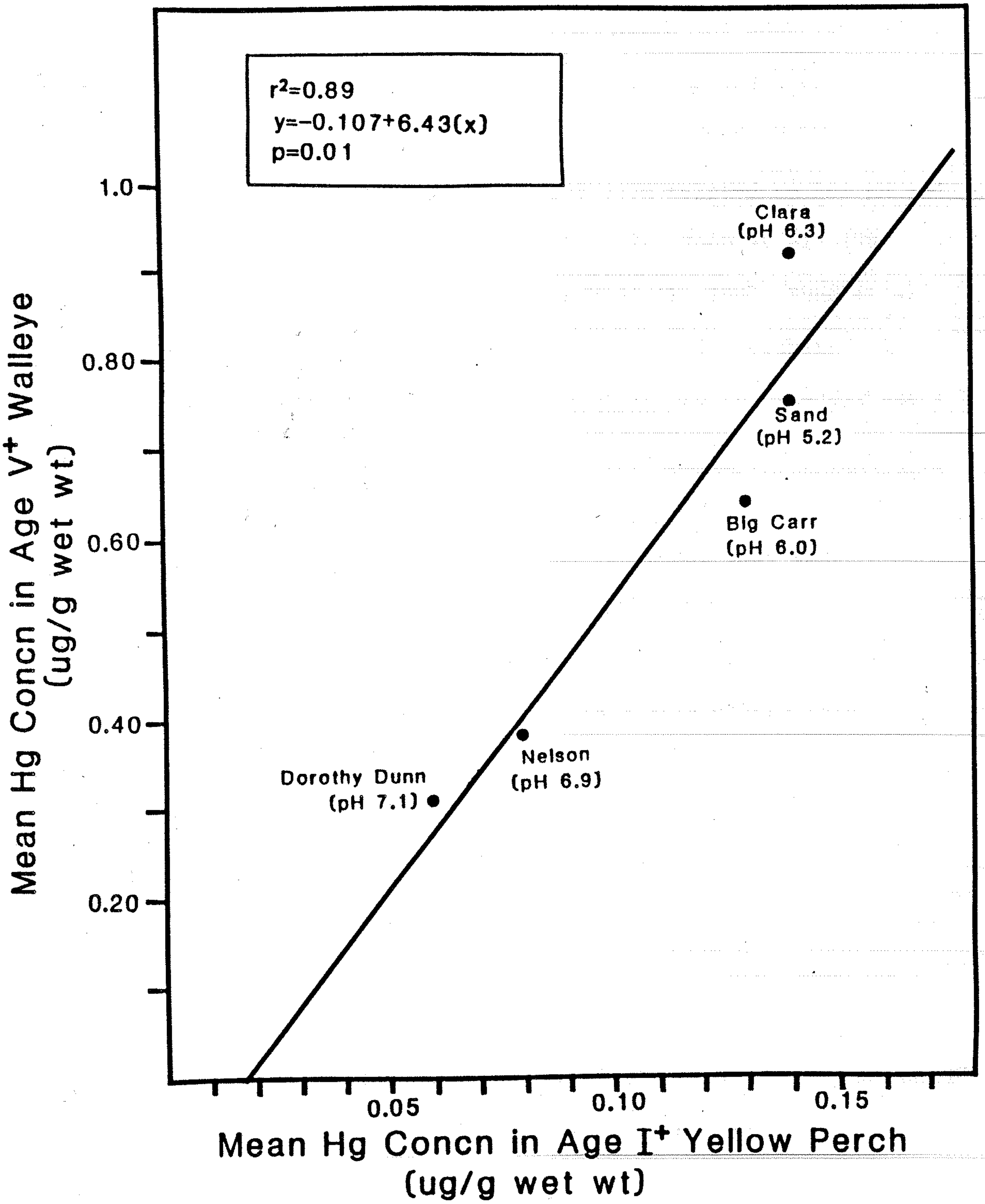
Another objective of this study was to evaluate the usefulness of yellow perch as indicators of Hg bioavailability to gamefish. Combined data on mean Hg concentrations in age 2 yellow perch and in age 5 walleye were available for five of the study lakes. Data on Hg concentrations in walleyes were obtained from other studies (Wiener 1983; Lee Liebenstein, Wisconsin Department of Natural Resources Madison, WI, personal communication; J.G. Wiener, U.S. Fish and Wildlife Service, La Crosse, WI, personal communication). Walleyes were not present in some study lakes and although present in other lakes have not been sampled and analyzed for Hg. Mercury

Table 11. Stepwise multiple regression models with multiple $R^2 \geq 0.70$ developed for the prediction of Hg concentrations in age 2 yellow perch collected from north-central Wisconsin lakes. Units of expression for independent variables are presented in Tables 1 and 2.

| Independent variables available to STEPWISE program | Regression equation | Multiple $R^2$ | Independent variables selected | Standard error of slopes | p-value for slopes |
|---|---|---|---|---|---|
| pH, Alk, Turb, Sed Hg, Sed org | Hg = 1059 - 160 pH + 2473 Sed Hg | 0.87 | pH<br>Sed Hg | 31.25<br>613.44 | < 0.01 |
| pH, $Log_{10}$ alk, Turb, Sed Hg, Sed org, Aufwuchs $Hg_{SUMMER}$ (ng/g dry wt), Aufwuchs $Hg_{SPRING}$ (ng/g dry wt) | Hg = 359 - 32.7 $Log_{10}$ alk - 0.413 Aufwuchs $Hg_{SUMMER}$ + 2208 Sed Hg | 0.92 | $Log_{10}$ alk<br>Aufwuchs $Hg_{SUMMER}$<br>Sed Hg | 8.29<br>0.09<br>522.88 | < 0.01 |
| pH, Aufwuchs $Hg_{SUMMER}$ ($ng/m^2$), Aufwuchs $Hg_{FALL}$ ($ng/m^2$), Aufwuchs $Hg_{SPRING}$ (ng/g dry wt) | Hg = 1622 - 165 pH - 3.66 Aufwuchs $Hg_{SUMMER}$ | 0.87 | pH<br>Aufwuchs $Hg_{SUMMER}$ | 30.04<br>0.87 | < 0.005 |
| Alk, Aufwuchs $Hg_{SUMMER}$ ($ng/m^2$), Aufwuchs $Hg_{FALL}$ ($ng/m^2$), Aufwuchs $Hg_{SPRING}$ ($ng/m^2$) | Hg = 732 - 0.899 Alk - 4.11 Aufwuchs $Hg_{SUMMER}$ | 0.87 | Alk<br>Aufwuchs $Hg_{SUMMER}$ | 0.16<br>0.86 | < 0.0025 |

concentrations in age 2 yellow perch and in axial muscle of age 5 walleye were positively correlated (Fig. 4). The mean total length and wet weight of the age 5 walleyes from the five study lakes were 41 cm (standard deviation, 8 cm) and 744 g (standard deviation, 393 g), respectively.

Figure 4. Relationship between mercury concentrations in age 5 walleye and age 2 yellow perch from five lakes in north-central Wisconsin.



r²=0.89
y=-0.107+6.43(x)
p=0.01
Clara
(pH 6.3)
Sand
(pH 5.2)
Big Carr
(pH 6.0)
Nelson
(pH 6.9)
Dorothy Dunn
(pH 7.1)
1.0
0.80
0.60
0.40
0.20
0.05
0.10
0.15
Mean Hg Concn in Age V+ Walleye
(ug/g wet wt)
Mean Hg Concn in Age I+ Yellow Perch
(ug/g wet wt)

# DISCUSSION

My results show that Hg uptake by yellow perch was greatest in the lakes with low alkalinity ($\leq$ 40 ueq/L). Both lake pH and alkalinity were negatively correlated with Hg concentration in fish (Table 9). Elevated Hg concentrations in fish have also been related to low pH and alkalinity in other studies (Scheider et al. 1979; Suns et al. 1980; Wiener 1983; Helwig and Heiskary 1985; Haines et al. 1987; Suns et al. 1987). In an experimental lake acidification study in northern Wisconsin, Wiener (1987) found that Hg concentrations in calendar age 1 yellow perch from the artificially acidified basin (pH 5.6) of Little Rock Lake contained higher Hg concentrations than age 1 perch from the non-acidified reference basin (pH 6.1). He concluded that lake acidification enhances Hg accumulation by fish.

Multiple regression analyses indicate that Hg content in yellow perch in north-central Wisconsin lakes may be highly predictable, if certain environmental variables are known. Two water chemistry variables (pH and alkalinity) and two sediment related variables (Hg concentration and organic content in surficial profundal sediment) appear to be most useful for predicting Hg in yellow perch. Generally, 80-90% of the Hg in fish of a given age could be predicted from two or three lake variables. For example, the Hg burden in yellow perch was highly correlated with Hg concentration in surficial profundal sediment ($r^2 = 0.69$), which was selected as the first variable entered into the model for predicting Hg burden in age 2 perch. Addition of either alkalinity or pH increased the multiple $R^2$ to about 0.90 (Table 10). Positive correlations between Hg burdens in sediments and fish have been observed in some studies (Hildebrand et al. 1980; Wren and MacCrimmon 1986; Haines et al. 1987; Johnson 1987; Parks and Hamilton 1987; Scrudato et al. 1987), but not in others (Wiener et al. 1984a; Meger 1986; Rada et al. 1986).

Other studies have also identified pH and alkalinity as variables for predicting Hg concentrations in fish. Wren and MacCrimmon (1983) developed a regression equation incorporating pH and three morphometric variables that explained 93% of the variation in Hg concentration in the pumpkinseed (*Lepomis gibbosus*) in 16 Precambrian Shield lakes in Ontario. Suns et al. (1987) found that two variables, pH and dissolved organic carbon, explained 71% of the variation in Hg concentration of age 1 yellow perch of selected Ontario lakes. Wiener et al. (in review) found that two variables, pH and total length of fish, accounted for 69% of the variation in Hg concentration in walleyes from north-central Wisconsin lakes; regression models with total length and either alkalinity or waterborne calcium as independent variables accounted for 67% of the Hg in walleyes.

Several hypotheses have been offered as possible explanations of high Hg concentrations in fish in low-alkalinity lakes. These consider the effects of lake chemistry on mechanisms of (1) direct uptake of methylmercury by fish, (2) net production of methylmercury, and (3) partitioning of methylmercury between water and sediments. The physiological mechanisms proposed to explain increased Hg uptake by fish in low-alkalinity waters include: increased efficiency of methylmercury uptake due to increased gill permeability in water with low calcium levels (Rodgers and Beamish 1983). In contrast to calcium, effect of pH on direct methylmercury uptake by fish is unclear.

Drummond et al. (1974) found that the direct uptake of methylmercury across the gills of fish is apparently enhanced at low pH (pH range 6-9). In contrast, Rodgers et al. (1987) found that accumulation of methylmercury by rainbow trout and walleye was unaffected by pH (pH range 5-7) and concluded that elevated Hg burdens in fish from low-pH waters observed in field studies were the result of other factors.

Increased Hg concentrations in fish are probably not the result of a single highly correlated variable alone, but rather related to an interaction between numerous significantly correlated variables. Increased Hg concentration in fish may be due to how these variables affect and are affected by the in-lake processes of methylation, demethylation, and volatilization that ultimately determine the bioavailability of methylmercury to fish. For example, pH may influence net methylmercury production without directly influencing Hg uptake by fish.

Increased methylmercury production in low-pH waters could result from increased methylation, decreased demethylation, or decreased volatilization (loss) of Hg from the lake surface (Steffan et al. in review). Collectively, these transformations determine the net rate of methylmercury production, which in turn influences the amount of Hg accumulated by fish (Rudd et al. 1983). Xun et al. (1987) found that the net rate of methylmercury production in the water column increases with decreasing pH. Rada et al. (1987a) also found that Hg volatilization from surface waters of Lake Clara, one of my study lakes, was positively correlated with pH and suggested that volatilization will significantly affect the amount of Hg available for methylation in the water column. Thus, in low-alkalinity lakes, smaller loss of Hg to the atmosphere may significantly enhance net methylation in the water column.

There are two potential fates of Hg that has been incorporated into the sediments of a low-pH lake. The low pH may enhance methylation activity in oxic, epilimnetic surficial sediments (Xun et al. 1987), which would provide methylmercury for uptake by fish. The second possibility is that the sediments efficiently retain Hg, serving as a sink rather than a source of the metal (Ramlal et al. 1985; Steffan et al. in review). A decrease in pH of anoxic profundal surficial and subsurficial sediments causes a decrease in net production of methylmercury (Ramlal et al. 1985; Steffan et al. in review). These studies both concluded that enhanced Hg methylation activity in profundal lake sediments is not causing the high Hg levels in fish in low-alkalinity lakes. In addition, Steffan et al. (in review) concluded that Hg volatilization in anoxic profundal surficial sediments does not significantly affect the availability of sediment-bound Hg. Other studies have also presented evidence that undisturbed bottom sediments serve primarily as a sink, not a source, for Hg (Rudd and Turner 1983; Rada et al. 1987b). Low pH may also alter the partitioning of methylmercury between water and sediment such that at low pH more methylmercury remains in the water column, thereby increasing the amount of methylmercury available to fish (Miller and Akagi 1979).

The ranges of mercury concentrations in yellow perch and the lake pH values in my study lakes were similar to those in the Ontario lakes studied by Suns et al. (1987). The 16 lakes studied by Suns and co-workers had a pH range of 5.63-7.34 (median 5.86), similar to the pH range of my study lakes (5.1-7.1, median 5.7). Mean Hg concentration in whole age 1 perch from individual Ontario lakes ranged from 0.03 to 0.18 ug/g wet weight, similar to that of my calendar age 2 perch (0.06-0.19 ug/g wet weight).

In my study, within-lake variables (two water chemistry and two sediment chemistry) were correlated with Hg in fish, whereas watershed factors were not. In contrast, studies of Ontario lakes (Suns et al. 1980; Wren and MacCrimmon 1983; Suns et al. 1987) showed that lake-watershed variables along with lake chemistry variables best predict Hg concentrations in fish. This illustrates a basic difference in factors affecting the biological availability and uptake of Hg between seepage lakes in north-central Wisconsin and headwater lakes of the Precambrian Shield in Ontario. Low-alkalinity seepage lakes generally receive more than 90% of their hydrologic inflow from precipitation falling directly onto the lake surface (Lin and Schnoor 1986). Hydrologic inflows from the terrestrial catchment (ground-water input plus overland flow) are small or negligible in these lakes. Based on the hydrology of these low-alkalinity seepage lakes, it is assumed that most Hg enters in precipitation and that watershed influxes of Hg are small. In contrast, the terrestrial influxes of Hg into headwater Ontario lakes is believed to be a significant source of Hg in sediments and fish (Evans 1986; Suns et al. 1987). After Hg has entered either type of lake system, the water chemistry variables (pH and calcium) strongly influence the bioavailability and uptake of Hg by fish.

There are no known cinnabar (HgS) deposits in Wisconsin (M. G. Mudrey, Jr., Wisconsin Geological and Natural History Survey, Madison, WI, personal communication) or known point sources of anthropogenic Hg in the watersheds of the study lakes. Mercury analysis of sediment cores indicates that there have been significant anthropogenic influxes of Hg into these lakes, presumably from direct atmospheric deposition (Rada et al. 1987a). Therefore, a potentially significant, but unknown, fraction of Hg in fish from these lakes is presumably anthropogenic in origin. Johnson (1987) analyzed sediment cores from 14 Ontario lakes and concluded that Hg concentrations in fish of these lakes were influenced by atmospheric influx of Hg into the lakes.

Dietary uptake is considered a significant fraction of the total Hg uptake in predatory fish (Phillips and Gregory 1979). Mercury concentration in piscivorous fish is often correlated with Hg concentration in forage fish. For example, MacCrimmon et al. (1983) found that Hg concentration in axial muscle of lake trout (*Salvelinus namaycush*) from Tadenac Lake in Ontario was positively correlated ($r = 0.96$; $p \leq 0.01$) with Hg concentration in rainbow smelt (*Osmerus mordax*). Similarly, Suns et al. (1987) found that Hg concentration in axial muscle of bass (*Micropterus* spp.) from the Muskoka-Haliburton lakes in Ontario was positively correlated ($r = 0.83$; $p < 0.01$) with Hg concentration in whole age 1 yellow perch. Suns et al. (1987) suggested that Hg concentration in yellow perch can be used to predict Hg concentration in bass.

Yellow perch are abundant in north-central Wisconsin lakes (Wiener et al. 1984b; Rahel 1986). When available, young yellow perch are the preferred prey of walleye (Colby et al. 1979). Thus, yellow perch represent a major trophic link for the transfer of methylmercury to gamefish in many north-central Wisconsin lakes. Therefore, perch constitute a good indicator of the potential dietary availability of Hg to walleyes and perhaps other species of gamefish. Based on my data for Hg in yellow perch, the dietary uptake of Hg is likely greater in walleyes in low-alkalinity lakes of north-central Wisconsin. However, further study will be needed to better define the statistical relation between Hg concentrations in yellow perch and walleyes.

In summary, the yellow perch is an appropriate species for monitoring Hg bioavailability in lakes of the Upper Midwest. The species is widespread and abundant in lakes of the region (Wiener and Eilers 1987), and samples of yellow perch are easy to collect. Finally, Hg concentrations in yellow perch seem to be indicative of concentrations in walleyes and other gamefish that feed heavily on perch.

CHAPTER 2: FACTORS INFLUENCING MERCURY ACCUMULATION IN AUFWUCHS

## RESULTS

### Comparison of Sample-Processing Procedures

A substantial amount of organic material was present in the specimen cap of the sampler during the summer and fall incubation periods (Fig. 2). This organic material may have been debris that accumulated during the incubation period, aufwuchs that became dislodged from the Mylar$^{R}$ during transport to the laboratory, or both. To evaluate this, I separately analyzed the material attached to the Mylar$^{R}$ and the material accumulated in the specimen cap for three of the four sampling sites in Big Carr Lake during the fall sampling period. For the other site in Big Carr Lake, the material attached to the Mylar$^{R}$ and the contents of the specimen cap were combined before analysis. The autotrophic index (AI; APHA 1985), used to evaluate the two sample processing procedures for Chl *a* and AFDW, was calculated as follows.

$$AI = [\text{biomass (AFDW)}, mg \cdot m^{-2}] \ / \ [\text{Chl } a, mg \cdot m^{-2}]$$

The mean AI was 1450 for the three Mylar$^{R}$ samples, 2250 for the three specimen cap samples, and 1530 for the combined sample. The similarity of the index for the combined sample and the Mylar$^{R}$ sample indicates that most of the material in the combined sample originated from the Mylar$^{R}$. Thus, non-photosynthetic organic material was accumulating in the specimen container cap during the incubation period. If included in the analysis of the community attached to Mylar$^{R}$, the contents of the cap and container would bias the analysis, underestimating the biomass of photosynthetic aufwuchs produced. Therefore, only material attached to the Mylar$^{R}$ should be used for evaluating AFDW and Chl *a*. I therefore changed the sample processing procedure for AFDW and Chl *a* for the subsequent spring sampling to include only material attached to the Mylar$^{R}$. For all three sampling periods, only material attached to the Mylar$^{R}$ was analyzed for Hg.

## Seasonal Variation in Aufwuchs Production

Accumulation of Chl *a* during the 28-d incubation periods ranged from 0.7 to 4.5 mg/m$^2$ in summer, 0.7 to 6.9 mg/m$^2$ in fall, and 0.3 to 4.3 mg/m$^2$ in spring (Table 12). Chlorophyll *a* concentrations were greatest during fall in 8 of the 11 lakes. The before:after acidification ratios ranged from 1.3 to 1.7 (mean = 1.6, standard deviation = 0.1) and were similar among seasons.

Mean biomass (AFDW) estimates for summer and fall were probably too high, because of the previously mentioned bias associated with sample processing procedures; therefore, biomass data are presented only for spring, when mean biomass ranged from 0.19 to 1.42 g/m$^2$ and averaged 0.67 g/m$^2$ (Table 13). The AI during spring varied from 230 to 1150 with a mean of 680 and standard deviation of 320. Normal AI values range from about 50 to 200; higher values indicate heterotrophic associations, the accumulation of nonliving organic matter, or both (APHA 1985).

## Seasonal Variation in Hg in Aufwuchs

Mean Hg concentrations in aufwuchs ranged from 185 to 803 ng/g dry weight in summer, 311 to 1609 ng/g in fall, and 48 to 466 ng/g in spring (Table 14). A seasonal trend for Hg accumulation by the aufwuchs was apparent. In 10 of the 11 lakes, the Hg concentration was

Table 12. Seasonal mean chlorophyll a accrual on artificial substrates incubated in 11 north-central Wisconsin lakes for 28 d.

| | Chlorophyll a ($mg/m^2$) | | | | | |
|---|---|---|---|---|---|---|
| | Summer 1985 | | Fall 1985 | | Spring 1986 | |
| Lake | Mean | RSD(%)[a] | Mean | RSD(%) | Mean | RSD(%) |
| Big Carr | 0.8 | 70 | 1.0 | 74 | 1.5 | 44 |
| Clara | 0.7 | 30 | 2.2 | 21 | 1.0 | 35 |
| Crystal | 0.9 | 0 | 2.5 | 6 | 1.9 | 52 |
| Dorothy Dunn | 0.9 | 47 | 1.6 | 62 | 0.6 | 49 |
| Garth | 4.5 | 85 | 6.9 | 35 | 4.2 | 9 |
| Hilderbrand | 1.9 | 46 | 4.8 | 18 | 4.3 | 29 |
| McGrath | 0.2 | 87 | 0.7 | 49 | 0.4 | 11 |
| Nelson | 0.8 | 31 | 0.7 | 5 | 0.4 | 16 |
| Sand | 1.4 | 46 | 2.3 | 40 | 0.3 | 73 |
| Vandercook | 2.2 | 60 | 0.8 | 40 | 1.7 | 17 |
| Zottle | 2.4 | 57 | 6.2 | 77 | 0.3 | 47 |
| Mean | 1.5 | 51 | 2.7 | 39 | 1.5 | 33 |

[a] RSD = Relative standard deviation.

Table 13. Biomass (ash-free dry weight) accrued on artificial substrates incubated for 28 d in 11 north-central Wisconsin lakes during spring 1986.

| Lake | Biomass accrual: Mean ($g/m^2$) | Biomass accrual: RSD[a] (%) |
|---|---|---|
| Big Carr | 0.79 | 36 |
| Clara | 0.79 | 17 |
| Crystal | 0.76 | 15 |
| Dorothy Dunn | 0.61 | 25 |
| Garth | 1.42 | 45 |
| Hilderbrand | 0.92 | 20 |
| McGrath | 0.19 | 39 |
| Nelson | 0.41 | 29 |
| Sand | 0.32 | 12 |
| Vandercook | 0.82 | 20 |
| Zottle | 0.32 | 29 |
| Mean | 0.67 | 26 |

[a] RSD = Relative standard deviation.

Table 14. Seasonal mean concentrations of total mercury in aufwuchs (ng/g dry wt) collected from 11 north-central Wisconsin lakes.

| Lake | Summer 1985 | | | Fall 1985 | | | Spring 1986 | | |
|---|---|---|---|---|---|---|---|---|---|
| | N[a] | Mean Hg concn | RSD(%)[b] | N | Mean Hg concn | RSD(%) | N | Mean Hg concn | RSD(%) |
| Big Carr | 4 | 385 | 37 | 4 | 1284 | 34 | 3 | 255 | 18 |
| Clara | 4 | 514 | 47 | 4 | 1609 | 64 | 4 | 244 | 55 |
| Crystal | 2 | 185 | 56[c] | 4 | 311 | 54 | 3 | 111 | 39 |
| Dorothy Dunn | 3 | 803 | 43 | 4 | 1037 | 21 | 4 | 48 | 125 |
| Garth | 3 | 315 | 37 | 3 | 718 | 6 | 4 | 187 | 11 |
| Hilderbrand | 3 | 392 | 46 | 4 | 517 | 14 | 4 | 171 | 9 |
| McGrath | 1 | 392 | -- | 3 | 1025 | 37 | 4 | 466 | 11 |
| Nelson | 3 | 695 | 32 | 4 | 1115 | 23 | 3 | 224 | 60 |
| Sand | 3 | 612 | 29 | 4 | 730 | 19 | 4 | 334 | 63 |
| Vandercook | 3 | 370 | 69 | 4 | 1356 | 62 | 4 | 191 | 28 |
| Zottle | 3 | 438 | 21 | 4 | 484 | 28 | 4 | 297 | 33 |
| Mean | | 464 | 38 | | 926 | 33 | | 230 | 41 |

[a] N = Number of samples analyzed.
[b] RSD = Relative standard deviation.
[c] Statistic calculated was percent difference.

highest in fall and lowest in spring. McGrath Lake was the only exception to this trend, perhaps because the summer value for McGrath was based on a single sample. Variances of Hg concentration in aufwuchs varied significantly among seasons; consequently, the data were rank-transformed before ANOVA. One-way ANOVA indicated significant seasonal variation in Hg concentrations ($p < 0.0005$), with the highest mean concentration in the fall and lowest in the spring (Fig. 5).

Mean Hg burdens in aufwuchs, expressed on an areal basis, ranged among lakes from 17 to 94 $ng/m^2$ in summer, 25 to 213 $ng/m^2$ in fall, and 6 to 57 $ng/m^2$ in spring (Table 15). Mercury burdens per unit area were highest in the fall in six lakes and lowest in the spring in eight. The mean burden of Hg accumulated by aufwuchs ($ng/m^2$) was greatest in the fall and least in the spring (one-way ANOVA, SNK multiple range test, $\alpha = 0.05$) (Fig. 5). Mean Hg burdens differed significantly among all three seasons.

Regressions for Predicting Hg in Aufwuchs

A simple correlation matrix was constructed to evaluate the relation of Hg in aufwuchs, expressed as areal burden and as concentration, to selected environmental variables (Table 16). The STEPWISE procedure did not reveal any significant two- or three-variable models for Hg in aufwuchs during spring and summer. With the fall data, the STEPWISE procedure selected a three-variable model (independent variables = alkalinity, organic content of surficial profundal sediment, and Hg concentration in surficial profundal sediment) that accounted for 91% of the variation in mean Hg burden in

Table 15. Seasonal mean burdens of total mercury in aufwuchs (ng/$m^2$) collected from 11 north-central Wisconsin Lakes.

| | Summer 1985 | | | Fall 1985 | | | Spring 1986 | | |
|---|---|---|---|---|---|---|---|---|---|
| Lake | N[a] | Mean Hg burden | RSD(%)[b] | N | Mean Hg burden | RSD(%) | N | Mean Hg burden | RSD(%) |
| Big Carr | 4 | 42 | 23 | 4 | 32 | 32 | 3 | 33 | 33 |
| Clara | 4 | 20 | 60 | 4 | 85 | 40 | 4 | 23 | 73 |
| Crystal | 2 | 55 | 28[c] | 4 | 105 | 24 | 3 | 37 | 28 |
| Dorothy Dunn | 3 | 59 | 54 | 4 | 52 | 24 | 4 | 6 | 125 |
| Garth | 3 | 73 | 66 | 3 | 213 | 63 | 4 | 57 | 49 |
| Hilderbrand | 3 | 30 | 21 | 4 | 85 | 12 | 4 | 36 | 12 |
| McGrath | 1 | 17 | -- | 3 | 33 | 24 | 4 | 16 | 20 |
| Nelson | 3 | 33 | 39 | 4 | 25 | 16 | 3 | 14 | 78 |
| Sand | 3 | 32 | 0 | 4 | 40 | 40 | 4 | 17 | 95 |
| Vandercook | 3 | 66 | 24 | 4 | 33 | 48 | 4 | 25 | 44 |
| Zottle | 3 | 94 | 39 | 4 | 94 | 20 | 4 | 10 | 40 |
| Mean | | 47 | 32 | | 72 | 31 | | 25 | 54 |

[a] N = Number of samples analyzed.
[b] RSD = Relative standard deviation.
[c] Statistic calculated was percent difference.

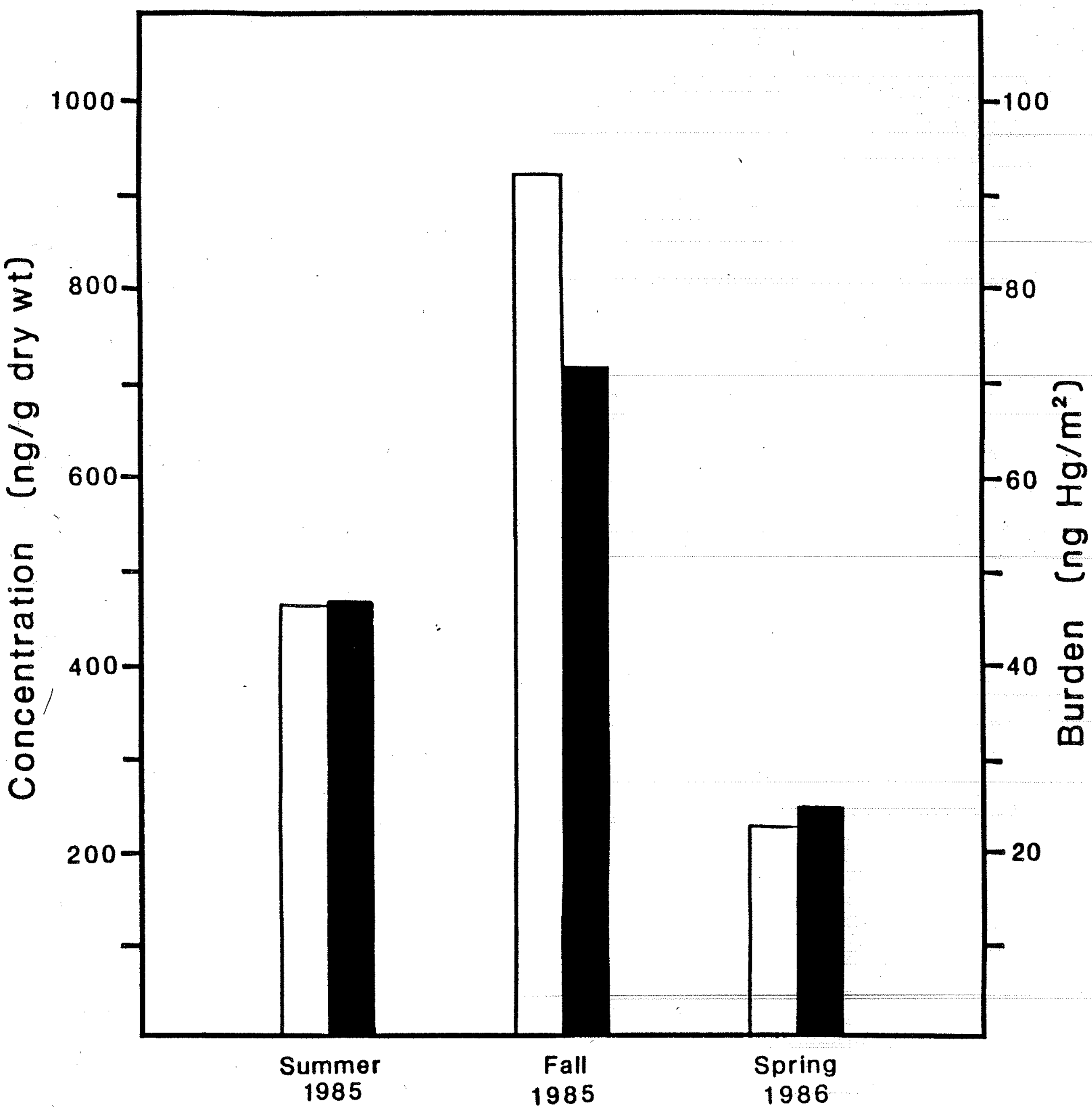
Table 16. Pearson correlation coefficients of Hg concentration (ng/g dry wt) and Hg burden (ng/$m^2$) in aufwuchs with selected variables during each season of study. Correlations with p-values $\leq 0.10$ for at least one dependent variable are presented.

| | Summer 1985 | | Fall 1985 | | Spring 1986 | |
|---|---|---|---|---|---|---|
| Variable | Hg burden | Hg concn | Hg burden | Hg concn | Hg burden | Hg concn |
| pH | 0.34 | 0.29 | 0.52 | 0.24 | 0.25 | -0.51 |
| Alkalinity | 0.33 | 0.12 | 0.66* | 0.07 | 0.44 | -0.36 |
| Turbidity | 0.37 | 0.18 | 0.65* | 0.14 | 0.23 | -0.24 |
| Color | 0.04 | -0.17 | 0.73** | -0.27 | 0.59* | -0.24 |
| Conductivity | 0.15 | 0.15 | 0.67* | 0.14 | 0.47 | -0.25 |
| Hg concentration in surficial profundal sediment | -0.80** | 0.09 | -0.35 | 0.38 | -0.03 | 0.38 |
| Clay content in surficial profundal sediment | 0.20 | 0.59 | -0.47 | 0.52 | -0.53 | -0.30 |
| TWA/LSA | 0.15 | -0.25 | 0.09 | -0.83** | -0.01 | -0.23 |
| Hg burden in age 2 yellow perch | -0.67* | -0.31 | -0.08 | 0.13 | 0.53 | 0.41 |
| Hg concentration in age 2 yellow perch | -0.64* | -0.57 | 0.07 | -0.14 | 0.51 | 0.61 |
| Hg burden in age 1 yellow perch | -0.73 | -0.45 | 0.04 | 0.49 | 0.59 | 0.67 |
| Hg concentration in age 1 yellow perch | -0.70 | -0.36 | 0.19 | 0.38 | 0.47 | 0.68 |

* Significant ($p \leq 0.05$).

** Highly significant ($p \leq 0.01$).

Figure 5. Mean total mercury content in aufwuchs collected during different seasons. Data are expressed as concentrations (ng Hg/g dry wt □) and as areal burdens (ng Hg/$m^2$ ■).



Concentration (ng/g dry wt)
1000
800
600
400
200
Burden (ng Hg/m²)
100
80
60
40
20
Summer 1985
Fall 1985
Spring 1986

aufwuchs during fall. In contrast, TWA/LSA, alkalinity, and pH were selected in the best three-variable model predicting mean Hg concentration in aufwuchs during fall (Table 17).

Table 17. Stepwise multiple regression models with multiple $R^2 \geq 0.70$, developed for the prediction of Hg concentration (ng/g dry wt) and Hg burden expressed on an areal basis ($ng/m^2$), in aufwuchs collected from north-central Wisconsin lakes during fall 1985. Units of expression for independent variables are presented in Tables 1 and 2.

| Independent variables available to STEPWISE program | Regression equation | Multiple $R^2$ | Independent variables selected | Standard error of slopes | *p*-value for slopes |
|---|---|---|---|---|---|
| pH, Alk, Sed Hg, Sed org, Sed clay | Aufwuchs $Hg_{FALL}$ ($ng/m^2$) = −26.3 + 0.15 Alk + 4.43 Sed org − 828 Sed Hg | 0.91 | Alk<br>Sed org<br>Sed Hg | 0.026<br>0.773<br>208 | $<0.01$ |
| pH, Alk, Cond, TWA/LSA | Aufwuchs $Hg_{FALL}$ (ng/g dry wt) = 244 − 225 TWA/LSA − 1.31 Alk + 258 pH | 0.86 | TWA/LSA<br>Alk<br>pH | 33.8<br>0.39<br>109 | $<0.05$ |

## DISCUSSION

Algal biomass, represented by Chl *a* concentrations, was greatest during the fall and lower during the summer and spring incubation periods. Mean seasonal Chl *a* was negatively correlated with lake pH, which agrees with the findings of Stokes (1984), who worked in Ontario lakes. The before:after acidification ratios in my study indicated that the photosynthetic component of aufwuchs was in healthy condition. The relatively high autotrophic index values imply that in addition to algae, a significant fraction of the aufwuchs was composed of heterotrophic organisms, nonliving organic matter, or both.

Aufwuchs accumulated measurable amounts of Hg during the 28-d incubation periods (Tables 14 and 15), which allowed for comparisons of Hg accumulation among seasons. Mercury concentrations and burdens in aufwuchs varied seasonally and were greatest in fall and lowest in spring (Fig. 5).

The greater accumulation of Hg by aufwuchs in summer and fall may result from temporal shifts in the atmospheric influx of inorganic Hg. These low-alkalinity seepage lakes generally receive more than 90% of their hydrologic inflow from precipitation falling directly onto the lake surface (e.g., Lin and Schnoor 1986). Therefore, hydrologic inflows from the terrestrial catchment (ground-water input plus overland flow) are small in these lakes. There are no known cinnabar (HgS) deposits in Wisconsin (M. G. Mudrey, Jr., Wisconsin Geological and Natural History Survey, Madison, WI, personal communication) or known point sources of anthropogenic Hg in the watersheds of the study lakes. However, Hg analysis of sediment cores indicates that there have been significant anthropogenic influxes of Hg into these lakes (Rada et al. 1987a). Given the hydrology of these low-alkalinity seepage lakes, it is assumed that watershed influxes of Hg are small. Furthermore, the higher Hg concentrations in aufwuchs seem to coincide with the period of greatest Hg concentration in wet deposition. For example, Glass et al. (1986b) found that Hg concentrations were much higher in rainfall than in the snow pack in the Lake Superior region. They determined that about 70% of the Hg associated with rainfall was inorganic and that the greatest wet deposition of inorganic Hg into lakes of this area occurred during June and July.

Adsorption of $Hg^{2+}$ onto the cell surface is considered the primary mechanism of Hg uptake by algae (Jennett et al. 1983; Darnall et al. 1986), but some intracellular binding of metal ions may also occur (Fujita and Hashizume 1975; Darnall et al. 1986). Surface adsorption primarily occurs through interaction of the metal ions with functional groups in the cell wall (Darnall et al. 1986) or sorptive properties associated with the glycocalyx (Jennett et al. 1983). Most algae readily concentrate Hg from solution, although their ability to bioconcentrate metals from solution varies among species (Hassett et al. 1981; Jennett et al. 1983).

My results indicate that Hg accumulation in aufwuchs in north-central Wisconsin lakes is related to physicochemical features. Two chemical variables (alkalinity and conductivity), one sediment variable (Hg concentration in surficial profundal sediment), and one morphometric variable (TWA/LSA) were most strongly related to Hg content in aufwuchs. However, lake pH was not correlated with Hg concentration or burden in aufwuchs. Stokes et al. (1983) similarly found that Hg concentrations in attached algae (aufwuchs) from artificial substrates were not correlated with pH in 11 Ontario lakes on the Precambrian Shield. In a laboratory study, Hassett et al. (1981) demonstrated that the rate of Hg uptake by 11 algal species was unrelated to pH and that the species studied removed Hg from solution across the pH range 4-10. Darnall et al. (1986) found that most metal ions were more weakly bound by algae at lower pH ($pH < 5$), but that $Hg^{2+}$ was strongly bound even at pH 2. They also noted that the algae had high metal-binding capacities for the mercuric ion--suggesting that algae effectively remove $Hg^{2+}$ from water. In addition, algae tend to remove $Hg^{2+}$ from solution more readily than $Cd^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ (Hassett et al. 1981; Jennett et al. 1983). The pH strongly affects Hg speciation, which presumably influences the bioavailability and accumulation of Hg. For example, Xun et al. (1987) found that the net methylation of Hg increased with decreasing pH in the water column and in oxic epilimnetic surficial sediments.

The accumulation of Hg by aufwuchs in summer was positively correlated with conductivity (Table 16). In contrast, Stokes et al. (1985) observed a negative correlation between Hg in algae (aufwuchs) and conductivity in 34 Precambrian Shield lakes in Ontario. Ionic strength has influenced uptake and toxicity of trace metals to algae in some studies. Stokes (1983) suggested that the concentration of calcium ion is a key factor determining uptake and toxicity of trace metals to algae, because $Ca^{2+}$ competes for metal-adsorption sites. In contrast, Jennett et al. (1983) observed no competition between calcium and magnesium with Hg for binding sites.

Mercury burdens in aufwuchs during summer were negatively correlated with Hg in age 2 yellow perch (Table 16). This relation is unexplained. In contrast, Stokes et al. (1983) found a positive correlation ($r = 0.93$; $p < 0.02$) between Hg concentrations in aufwuchs grown on artificial substrates and in yellow perch inhabiting Ontario lakes. They determined that methylmercury was the dominant form of Hg in the aufwuchs and suggested that the correlation was primarily between methylmercury concentrations in fish and aufwuchs. Methylmercury generally represents greater than 80% of the total Hg burden in fish (Huckabee et al. 1979).

In conclusion, there are several inherent problems associated with this approach for monitoring the availability and bioaccumulation of Hg in aquatic systems. First, the biotic component is composed of various organisms (e.g., algae, bacteria, fungi, etc.), the composition of which may vary among study sites. The various organisms probably differ in their ability to accumulate and transform (e.g., methylate and demethylate) Hg. Therefore, contrasts among lakes may be confounded by numerous variables. Second, the aufwuchs--procedurally defined as the material accumulating on submerged artificial substrates (Newman et al. 1985)--may also contain inorganic matter and nonliving organic matter. The Hg accumulated on the substrates may therefore be associated with any or all kinds of material on the substrate. This procedure does not distinguish between abiotic and biotic Hg accumulation; consequently, bioaccumulation per se cannot be estimated with this approach.

Some vandalism and destruction of samplers occurred during the times of peak recreational activity on some lakes. However, the samplers are durable and required only minor repair after each use.

The initial construction cost was about $13.00 per sampler, excluding labor. The cost of materials for repair and sampler preparation was about $1.50 per sampler for each period of use.

## CHAPTER 3: SUMMARY AND CONCLUSIONS

Mercury concentrations in yellow perch were negatively correlated with lake pH and alkalinity and positively correlated with Hg and organic content in surficial profundal sediment. Multiple regression models with lake and sediment chemistry parameters as independent variables accounted for 80 to 90% of the variation in Hg burdens and concentrations in yellow perch. Furthermore, preliminary data suggest that Hg concentrations in whole calendar age 2 yellow perch, which can be readily collected in early spring, reflect concentrations of the metal in axial muscle tissue of walleyes in north-central Wisconsin lakes.

Aufwuchs from artificial substrates accumulated measurable amounts of Hg during 28-d incubation periods; Hg concentrations varied seasonally and were lowest in spring, highest in fall, and intermediate in summer. Multiple regression models with combinations of five independent variables (pH, alkalinity, total Hg concentration and organic content in surficial profundal sediment, and total watershed:lake surface area) accounted for 80 to 90% of the variability of Hg concentrations and burdens (areal) in aufwuchs.

When sampler construction costs, travel costs, and problems with interpreting procedurally defined aufwuchs data are considered, the use of yellow perch seems to be a more effective means of monitoring Hg bioavailability. Furthermore, the use of a forage fish such as yellow perch is a more direct method of assessing potential Hg contamination of gamefish--a direct human health concern.

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Appendix 1. Wet weight, total length, and mercury content of yellow perch from north-central Wisconsin lakes.

| Fish age and lake | N[a] | Wet weight (g) of fish analyzed | | Total length (mm) of fish analyzed | | Mercury concentration (ug/g wet weight) | | |
|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | Mean | Range | RSD(%)[b] |
| AGE 3 | | | | | | | | |
| Crystal | 6 | 11.7 | 10.4-12.9 | 112 | 109-118 | 0.13 | 0.11-0.19 | 23 |
| Dorothy Dunn | 6 | 18.1 | 15.2-20.7 | 123 | 118-127 | 0.07 | 0.04-0.11 | 40 |
| Garth | 1 | 16.0 | -- | 121 | -- | 0.04 | -- | -- |
| McGrath | 3 | 14.8 | 13.4-16.3 | 123 | 119-126 | 0.20 | 0.18-0.22 | 10 |
| Nelson | 1 | 12.5 | -- | 115 | -- | 0.04 | -- | -- |
| Sand | 10 | 15.2 | 13.2-17.1 | 118 | 114-122 | 0.23 | 0.14-0.35 | 37 |
| Vandercook | 2 | 11.3 | 11.3-11.3 | 114 | 113-114 | 0.13 | 0.11-0.15 | 22 |
| AGE 4 | | | | | | | | |
| Big Carr | 2 | 21.6 | 20.0-23.2 | 134 | | 0.19 | 0.14-0.24 | 39 |
| Dorothy Dunn | 1 | 28.7 | -- | 141 | -- | 0.06 | -- | -- |
| Garth | 7 | 27.4 | 22.8-35.9 | 144 | 137-151 | 0.04 | 0.03-0.06 | 29 |
| Nelson | 1 | 24.2 | -- | 132 | -- | 0.08 | -- | -- |
| Sand | 2 | 17.3 | 16.6-17.9 | 125 | | 0.27 | 0.24-0.30 | 17 |
| AGE 5 | | | | | | | | |
| Garth | 6 | 34.4 | 32.5-35.6 | 157 | 153-162 | 0.07 | 0.04-0.10 | 35 |
| Nelson | 1 | 26.1 | -- | 139 | -- | 0.06 | -- | -- |
| Sand | 2 | 17.3 | 16.6-17.9 | 125 | | 0.27 | 0.24-0.30 | 17 |

[a] N = Number of fish analyzed.

[b] RSD = Relative standard deviation.

Appendix 2. Variable reporting units and abbreviations

| Variable | Abbreviation | Reporting units |
|---|---|---|
| pH | pH | pH |
| Alkalinity | Alk | ueq/L |
| Color | Color | PCU |
| Turbidity | Turb | NTU |
| Total suspended solids | TSS | mg/L |
| Conductance | $K_s$ | us/cm |
| Secchi depth | $S_d$ | m |
| Total organic carbon | TOC | mg/L |
| Hg concentration in surficial profundal sediment | Sed Hg | ug/g dry weight |
| Al concentration in surficial profundal sediment | Sed Al | mg/g dry weight |
| Organic content of surficial profundal sediment | Sed org | % |
| Clay content of surficial profundal sediment | Sed clay | % |
| Maximum depth | $Z_{max}$ | m |
| Mean depth | $\bar{Z}$ | m |
| Lake surface area | LSA | ha |

Appendix 2. Continued

| Variable | Abbreviation | Reporting units |
|---|---|---|
| Total watershed area | TWA | ha |
| Lake volume | LV | $m^3 \times 10^5$ |
| Ratio of total watershed area to lake surface area | TWA/LSA | -- |
| Ratio of total watershed area to lake volume | TWA/LV | -- |
| Hg content in aufwuchs | Aufwuchs Hg | ng/g dry weight or $ng/m^2$ |