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Relationship between Mercury Accumulation in Young-of-the-Year Yellow Perch and Water-Level Fluctuations

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A three-year (2001−2003) monitoring effort of 14 northeastern Minnesota lakes was conducted to document relationships between water-level fluctuations and mercury bioaccumulation in young-of-the-year (YOY) yellow perch (*Perca flavescens*) collected in the fall of each year at fixed locations. Six of those lakes are located within or adjacent to Voyageurs National Park and are influenced by dams on the outlets of Rainy and Namakan lakes. One site on Sand Point Lake coincides with a location that has nine years of previous monitoring suitable for addressing the same issue over a longer time frame. Mean mercury concentrations in YOY yellow perch at each sampling location varied significantly from year to year. For the 12-year monitoring site on Sand Point Lake, values ranged from 38 ng gww^{-1} in 1998 to 200 ng gww^{-1} in 2001. For the 14-lake study, annual mean concentrations ranged by nearly a factor of 2, on average, for each lake over the three years of record. One likely factor responsible for these wide variations is that annual water-level fluctuations are strongly correlated with mercury levels in YOY perch for both data sets.

Introduction

Mercury contamination of the food web and water-level management of Rainy Lake and Namakan Reservoir (comprising Namakan, Kabetogama, Sand Point, Crane, and Little Vermilion lakes) are two of the most significant water resource issues for Voyageurs National Park (VNP), located in northern Minnesota. Interestingly, preliminary evidence has suggested that these two issues may be linked. That is, the changing water levels may affect the magnitude of mercury contamination in fish.

While the creation of reservoirs is known to cause a substantial increase in mercury concentrations throughout the food web (*1*), we do not have a good understanding of how long the initial "reservoir effect" lingers or what effect subsequent water-level fluctuations (WLFs) have on mercury bioaccumulation (*2*). However, one study of 19 reservoirs in Finland (*3*), in which mercury levels in fish were modeled using reservoir age and WLF amplitude (as well as other variables) as predictors, concluded that the "reservoir effect" lasts from 15 to 30 years. Moreover, the results of the study suggest that mercury levels in fish decreased with reduced WLFs.

As part of another study, young-of-the-year (YOY) yellow perch were collected in late September or early October of each year from 1991 to 1994 at one site on Sand Point Lake and analyzed for mercury content (*4*). Significant differences observed in annual concentration averages prompted us to continue monitoring that site through 2000 (except for 1995). Because preliminary observations of that nine-year data set indicated that mercury concentrations in fish correlated with annual WLFs, an expanded study from 2001 to 2003 was initiated. This included the analyses of YOY yellow perch collected in the fall from 29 sites on 14 lakes in northeastern Minnesota.

This study design has two important attributes. First, mercury concentrations in YOY perch, collected at the end of the growing season, represent bioaccumulation conditions for that year's growth. This allows the direct comparison of water conditions and mercury bioaccumulation for each year. Second, multiple years of that data allow the investigation into possible reasons for annual variations within individual lakes, thus eliminating many variables that complicate lake-to-lake comparisons.

Methods

The methods used for the expanded study from 2001 to 2003 are described below. Procedures used for measurements from 1991 to 2000 (Sand Point Lake) were generally the same and were described earlier (*4*). Relevant methodological differences between the two time periods are noted.

Lake Selection. Study lakes were divided into two categories: those with water levels controlled by dams at the outlets of Rainy and Namakan lakes (six lakes, designated as VNP lakes), and those that were not (eight lakes, designated as non-VNP lakes) (Table 1). Lakes in the first group were selected to include all large lakes in that category. Lakes in the second group (all impoundments except for Sturgeon Lake) were selected to represent different regions and water-level fluctuation conditions across northeastern Minnesota (Figure 1). The east and west basins of Vermilion Lake are treated as separate lakes because they have contrasting water quality properties and only join near the outlet of the lake.

Sampling. YOY yellow perch were collected in either late September or early October of each year, near shore, using 15.2 and 30.5 m nylon bag seines with 6.4 mm bar mesh. Fish specimens were placed in zippered bags (double bagged) and kept on ice until they could be transported to the laboratory where they were kept frozen until they were processed for analysis.

Sampling goals for yellow perch were to collect 20 specimens from each of two separate sites for each lake. Specific sampling areas for 2002 and 2003 were kept as close as possible to those defined by the 2001 sampling efforts. The only sampling that fell significantly short of our goals was for Sturgeon Lake site 2 during 2003 where only two fish were collected (total number of successful samplings was $29 \times 3 - 1 = 86$). From 1991 to 2000, an average of 12 fish were sampled each year at Sand Point Lake site 0 (minimum of four collected in 1999).

During fish sampling, a water sample was collected and field measurements were made in deeper water, just outside the area disturbed by the fish sampling. Water samples were

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TABLE 1. Background Information and Sampling Locations for Study Lakes

lake name [ID no.]	sampling locations station	latitude	longitude	area[a] (km^2)	mean depth[b] (m)	mean WLR[c] (m)
			Sites Influenced by Dams at Rainy or Namakan Lakes (VNP Lakes)[d]			
Crane [69−616]	1	48.3132	92.4998	12.0	9.1	1.90 ± 0.32
	2	48.3055	92.4784			
Kabetogama [69−845]	1	48.4275	92.8677	104.3	9.1	1.90 ± 0.32
	2	48.4342	92.8182			
Little Vermilion [69−608]	1	48.3038	92.4298	5.4	7.6	1.90 ± 0.32
	2	48.2975	92.4222			
Namakan [69−693]	1	48.4317	92.6816	101.7	13.6	1.90 ± 0.32
	2	48.4261	92.6877			
Rainy [69−694]	1	48.5970	93.0586	893.6	9.9	0.98 ± 0.29
	2	48.6044	93.0929			
Sand Point [69−617	0	48.3313	92.4756	35.9	12.0	1.90 ± 0.32
	1	48.3813	92.5206			
	2	48.4023	92.4890			
			Sites Not Influenced by Dams at Rainy or Namakan Lakes (Non-VNP Lakes)[e]			
Boulder [69−373]	1	47.0783	92.1880	15.7	2.1	1.38 ± 0.62**
	2	47.0570	92.1952			
Fish [69−491]	1	46.9588	92.2563	13.2	2.4	0.62 ± 0.21**
	2	46.9198	92.2725			
Island [69−372]	1	47.0065	92.1790	29.7	4.6	2.52 ± 1.39**
	2	47.0170	92.1680			
Sturgeon [69−939]	1	47.6862	93.0678	6.7		0.53 ± 0.22
	2	47.6895	93.0394			
Vermilion, E. Basin [69−378]	1	47.8170	92.2973	116.0‡		0.36 ± 0.12
	2	47.8017	92.3610			
Vermilion, W.Basin [69−378]	1	47.9025	92.5890	48.0‡		0.36 ± 0.12
	2	47.8997	92.5603			
White Iron [69−004]	1	47.8690	91.8200	13.9	6.1	0.44 ± 0.23*
	2	47.8815	91.7920			
Whiteface [69−375]	1	47.2849	92.1890	22.7	4.6	1.04 ± 0.47**
	2	47.2956	92.1685			

[a] From the Minnesota Department of Natural Resources (MDNR) (*5*) except entries marked as ‡ which are estimates. [b] From Kallemeyn et al. (*6*) and Minnesota Power (MP) (*6*), average for both basins of Lake Vermilion is 5.7 m. [c] Water level range (WLR) statistics are based on data from the Lake of the Woods Control Board (LWCB) (*8*) for Rainy and Namakan Lake dams and on data from MDNR (*5*) and MP (*9*) for all other lakes. Statistics are for 1990−2003 except those marked with asterisks: * = 1996−2003 and ** = 1997−2003. [d] Impoundments on Namakan and Rainy lakes were created in 1914 and 1909, respectively (*10*). [e] Impoundments on Boulder, Fish, Island, Vermilion, White Iron, and Whiteface lakes/reservoirs were created in 1920, 1911, 1909, 1892, 1925, and 1923, respectively. No dam exists on Sturgeon Lake (*10*).

collected at a 1 m depth using a Van Dorn sampler and 1 L polyethylene bottles. The bottles were kept on ice until they could be transported to the laboratory, where they were refrigerated at 4 °C until the samples were analyzed. No water samples were collected from Sand Point Lake site 0 from 1995 to 2000.

Field Measurements. Field measurements of temperature, conductivity, and pH were performed as a check against the analyses of water samples conducted in the laboratory. For VNP lakes, these parameters were measured using a YSI Sonde meter, model 6820CE (Yellow Spring Instrument Co.). For non-VNP lakes, temperature and conductivity were measured using a YSI model 33 meter and pH was measured using an Orion (Cambridge, MA) model 407A meter with an Orion 91-02-00 combination electrode (used during 2001 and part of 2002) and an Orion model SA250 meter with a VWR (So. Plainfield, NJ) gel epoxy combination pH electrode (used during 2002 and 2003). Conductivities were adjusted to values at 25 °C (*11*). Single measurements of secchi depth were performed in the fall for all lakes except for Sand Point Lake, where biweekly measurements were made (May through September 1991−2003). For Sand Point Lake site 0, both seasonal averages and fall secchi values were used for correlations with other data.

Laboratory Analyses. All laboratory analyses, with the exception of the organic carbon and fish age determinations, were performed at the UMD Environmental Physics Laboratory. Organic carbon levels and fish ages were determined by the Natural Resources Research Institute (Duluth, MN) and the U.S. Geological Survey (International Falls, MN), respectively.

Yellow perch were processed by first measuring both their total length and wet weight. Specimens were then dried for 24 h at 70 °C and weighed again to determine moisture content (average content was 79% for fresh weight). After drying, fish were shredded using a small scissors, then ground by mortar and pestle, and finally stored in a freezer in small zippered bags until they could be analyzed. Dried fish aliquots of approximately 70 mg were analyzed for total mercury using cold vapor atomic absorption and USEPA method 245.6 (*12*).

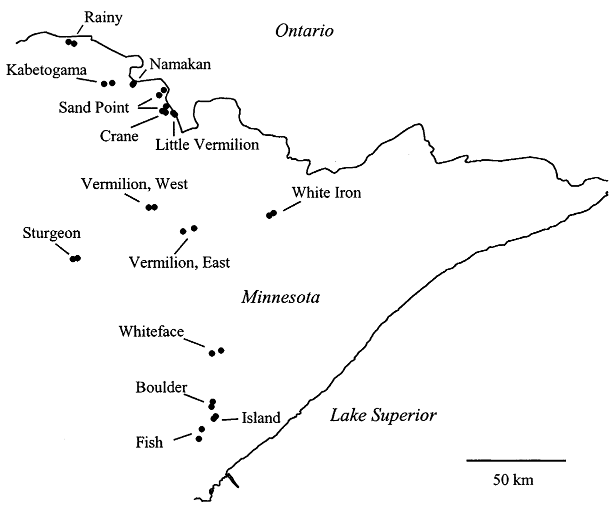

FIGURE 1. Location of study sites in northeastern Minnesota.

The method detection limit was about 3 ng gww^{-1}, the precision averaged about 3%, and the average spike and certified standard recoveries averaged 100 ± 4% (SD). To test the effects of the drying process on mercury concentration measurements, 14 samples were run as wet and dried pairs. The results indicated no significant differences [average concentration ratio = 1.00 ± 0.01 (SE)]. From 1991 to 2000 (Sand Point Lake data) most fish were analyzed whole and undried.

In northeastern Minnesota lakes, YOY yellow perch are readily identified by size distributions, with total lengths generally between 4.5 and 7 cm by October (*13*). To ensure against including possible second-year perch with YOY fish, a subset of specimens from various lakes and sampling years, with lengths ranging from 6.2 to 8.7 cm, were aged using scale circuli. Based on those results, cutoff lengths were assigned for each lake to reject possible second-year specimens.

Methods for measuring acid neutralizing capacity (ANC), pH, conductivity, turbidity, and water color (unfiltered) are similar to those used in earlier studies (*14*). Total (TOC) and dissolved (DOC, for 2003 samples) organic carbon were determined by persulfate oxidation with ultraviolet irradiation activation of the reagents to convert organic carbon to carbon dioxide which was then directly measured by a nondispersive infrared analyzer (*15*). Aliquots used for DOC analyses were first passed through a 0.45 μm glass fiber filter and then preserved using 0.1 mL H_2SO_4 per 100 mL sample. The average difference between TOC and DOC concentrations, for samples collected in 2003, was 6%.

Water Levels. Water-level data for the Rainy and the Namakan Reservoir lakes were obtained from the Lake of the Woods Control Board (*8*). Water-level data for other lakes were obtained from the Minnesota Department of Natural Resources (*5*) and the Minnesota Power Company (*9*).

Although minimum water levels occur just prior to spring melt, maximum levels can occur over a broader time window between June and late fall, depending on the year. If water levels have an influence on mercury bioaccumulation, it is likely that there would be a time lag for the effect to be expressed in fish. For example, if the maximum water level occurred in September, it is unlikely that mercury levels in YOY fish collected in September would be influenced significantly by that recent event. To accommodate this concept we used various time ranges (March−June, March−July, March−August, and March−September) for calculating various water-level parameters and the corresponding correlation coefficients with mercury levels in YOY perch.

Wet Mercury Deposition. Wet Mercury deposition data are from the Fernberg, MN, monitoring site (located 52 km southeast of Sand Point Lake site 0). Data for 1996−2003 are from the National Atmospheric Deposition Program (*16*), and from earlier monitoring work during 1990−1995 (*17*). Wet deposition was calculated as the sum of the weekly concentration measurements multiplied by the weekly precipitation depths.

To calculate correlations between wet mercury deposition and mercury concentrations in YOY perch, we considered the mass of mercury entering the lake during the snowmelt plus amounts falling by rain up to a selected cutoff date during the fish growing season. For each year, December 1 of the previous year was selected to represent the beginning date of snow accumulation. As with the effects from water levels discussed above, we considered different end dates for cumulative deposition in an effort to account for time lag between mercury deposition and its possible accumulation in fish.

Statistical Analyses. To test for a significant difference between the average values of two data sets, 2-tailed *t* tests were used with a critical level of $p = 0.05$. Because comparisons among lake sites required numerous *t* tests, Bonferroni corrections were applied to protect against making type 1 errors. For example, the critical significance level of $p = 0.05$ for a standard *t* test becomes $p_B = 0.0037$ under a Bonferroni correction for a group of 14 tests.

Pearson correlation coefficients between YOY yellow perch mercury concentrations and fish lengths were calculated for each sampling event to assess whether a relationship exists. Because of the large matrix of sites and years involved ($n = 86$), Bonferroni adjustments were applicable.

Correlation statistics were also used to assess which parameters were related in the 12-year Sand Point Lake data set. Because these data have approximately normal distributions, Pearson correlation coefficients were used. For the correlations involving three years of data (14-lake study), Spearman coefficients were used. This was done for two reasons: (1) Pearson correlations coefficients are too sensitive to a spurious distribution for such a small number of data pairs and (2) ranked Spearman coefficients may be combined across a group of lakes to increase statistical power for making statements applicable to that set of lakes. The sum of Spearman coefficients yields a distribution that may be calculated exactly, thereby allowing the assignment of a significance level to the sum or average. For example, the possible Spearman outcomes for one lake (three data pairs) are −1.0, −0.5, −0.5, 0.5, 0.5, and 1.0. The possible outcomes for the sum of the Spearman coefficients for two lakes are (number of occurrences for each value in parentheses) −2.0 (1), −1.5 (4), −1.0 (4), −0.5 (4), 0.0 (10), 0.5 (4), 1.0 (4), 1.5 (4), and 2.0 (1). Thus, the probability for obtaining an outcome in any range may be computed. The probability (significance) of obtaining a value of 0.5 or more for one lake is 3/6 = 0.5. For comparison, the probability of observing an average of 0.5 (sum = 1.0) or more for two lakes is 9/36 = 0.25. Enumerating the possible outcomes for the sum of Spearman values for more than three lakes required the use of a computer program.

For the long-term data set, stepwise multiple regression analysis, using first-order linear combinations of all tested variables with no interactions, was used to test which combinations of measured variables were significant in explaining the variability of mercury levels in YOY perch.

Results and Discussion

Mercury Concentration and Fish Length. Before addressing statistics of YOY yellow perch mercury concentrations, we used the 2001−2003 data set to look for possible dependences of those concentrations on fish size. Although game fish

TABLE 2. Mercury Concentrations of YOY Yellow Perch from 2001 to 2003

site	average mercury concentration ± standard error (ng gww^{-1})[a]						max yr/min yr	
	2001		2002		2003			
	site 1	site 2	site 1	site 2	site 1	site 2	site 1	site 2
Crane	225 ± 21	281 ± 12	80 ± 6	114 ± 4	98 ± 8	107 ± 4	2.8	2.6
Kabetogama	48 ± 2	63 ± 2	50 ± 2	56 ± 2	35 ± 2	37 ± 2	1.4	1.7
Little Verm.	104 ± 8	101 ± 4	63 ± 3	78 ± 3	94 ± 5	112 ± 8	1.6	1.4
Namakan	114 ± 3	101 ± 3	75 ± 1	67 ± 3	46 ± 1	47 ± 2	2.5	2.2
Rainy	61 ± 2	67 ± 2	74 ± 4	71 ± 2	35 ± 2	39 ± 2	2.1	1.8
Sand Point	191 ± 10	150 ± 8	77 ± 3	63 ± 4	62 ± 2	68 ± 5	3.2	3.1
Boulder	49 ± 1	46 ± 2	57 ± 2	58 ± 3	38 ± 2	37 ± 2	1.5	1.6
Fish	30 ± 1	28 ± 1	32 ± 2	37 ± 2	21 ± 1	24 ± 2	1.5	1.6
Island	56 ± 2	66 ± 4	58 ± 3	72 ± 6	26 ± 1	59 ± 3	2.2	1.2
Sturgeon	40 ± 2	36 ± 2	45 ± 1	38 ± 2	36 ± 2	32 ± *	1.3	1.2
Vermilion, E.	101 ± 6	126 ± 5	89 ± 9	105 ± 7	35 ± 1	57 ± 3	2.9	2.2
Vermilion, W.	28 ± 1	49 ± 2	20 ± 1	15 ± 0.4	22 ± 1	17 ± 1	1.4	3.3
White Iron	73 ± 3	91 ± 3	60 ± 3	69 ± 2	53 ± 5	72 ± 1	1.4	1.3
Whiteface	59 ± 3	55 ± 3	79 ± 5	86 ± 6	85 ± 6	86 ± 4	1.4	1.6

[a] The number of fish per average is approximately 20 except for one Sturgeon Lake entry (denoted as *) where two fish were sampled at site 2 in 2003.

TABLE 3. Water Quality Values Averaged across Sites 1 and 2 for Selected Parameters from 2001 to 2003

lake	cond (μS cm^{-1})			ANC (μequiv L^{-1})			apparent color (Pt−Co)			TOC (mg L^{-1})			secchi depth (m)		
	2001	2002	2003	2001	2002	2003	2001	2002	2003	2001	2002	2003	2001	2002	2003
Crane	74.0	79.4	79.4	489	527	522	105	55	65	14.3	10.8	13.8	1.1	2.3	2.0
Kabetogama	89.2	78.4	90.9	801	611	801	53	53	30	10.6	10.3	10.2	1.5	1.8	1.7
Little Verm.	28.4	32.3	32.4	165	151	201	120	70	65	14.7	11.9	12.8	1.1	1.4	1.6
Namakan	44.1	44.6	47.9	289	283	315	59	50	30	10.0	9.5	8.5	2.4	2.9	3.8
Rainy	48.7	50.0	50.9	339	307	347	57	58	42	10.0	10.4	9.0	2.2	2.6	2.5
Sand Point	59.4	65.9	69.7	381	420	455	109	59	50	14.7	11.5	10.6	1.1	2.3	2.3
Boulder	59.7	68.6	70.2	535	593	587	60	110	60	12.3	17.6	13.9	1.2	1.0	1.5
Fish	83.9	89.3	97.1	738	693	794	50	70	50	11.4	13.6	11.7	1.3	1.3	1.4
Island	84.6	94.8	102.6	728	735	853	55	65	53	10.7	12.5	11.9	1.4	1.4	1.3
Sturgeon	69.0	76.2	80.5	608	660	691	38	50	43	9.7	11.1	10.1	3.2	2.5	2.8
Verm., East	96.8	115	123	737	796	748	100	123	63	14.0	16.4	12.9	2.6	2.2	2.5
Verm., West	115	126	109	694	788	495	120	130	125	15.1	17.6	15.5	2.2	1.5	1.3
White Iron	59.1	66.4	73.7	396	409	469	73	50	70	12.3	11.2	11.8	2.0	1.6	1.5
Whiteface	51.2	58.7	63.6	383	424	479	112	97	95	15.8	15.8	14.9	1.3	1.3	1.5

generally show a strong positive correlation between mercury concentration and fish size, no consistent correlation was observed between mercury in YOY yellow perch and size in this study. This observation agrees with an earlier survey, which included three of the study lakes (*18*), as well as surveys in Michigan (*19*) and Wisconsin (*20*). Of 86 samplings, only 5 had statistically significant correlations after applying a Bonferroni correction. Therefore, comparisons of mercury levels in YOY perch (among sites and years) in this report do not use values adjusted for fish length.

Data Representativeness. We also used the 2001−2003 data set to assess data representativeness. Descriptive statistics for mercury concentrations found in YOY yellow perch from 2001 to 2003 are given in Table 2 for each site and sampling year. Mean mercury concentrations ranged from 15 to 281 ng/g, with the highest values found at Crane and Sand Point Lakes in 2001. On comparing fish mercury levels between separate sites of each lake (site 1 vs 2), we found that 12 of 41 cases ($14 \times 3 - 1$) exhibited a statistically significant difference. Thus, in terms of the absolute mercury concentration, a single sampling site should not be considered as representative of other sites for a given lake.

Although mercury concentrations of YOY yellow perch were often different between the two sites of the same lake, the significant changes from year to year were similar for the site pairs. Because the average Spearman correlation between sites 1 and 2 across the three years is highly significant ($r = 0.79$, $p < 0.00001$), it is not proper to consider multiple sites on the same lake as independent measurements for purposes of trend/correlation analyses. Thus, the average concentration of the two sites was used to represent each lake for those purposes.

Because there were no significant differences in water quality between the site pairs, results from 2001 to 2003 were averaged across sites 1 and 2 of each lake. A summary of those averages is given in Table 3.

YOY Yellow Perch Mercury Level Variations at Sand Point Lake, 1991−2003. Nine years of previous work along with the three additional years of expanded monitoring in this study has produced a 12-year record of mercury levels in YOY yellow perch at Sand Point Lake site 0. A summary of those concentrations is presented in Table 4 where a strikingly wide range of mean values is observed. In fact, the highest average concentration, which occurred in 2001, is approximately 6 times the lowest one, observed in 1998. These results suggest that there are important physical processes influencing mercury bioaccumulation that change from year to year. We examined this data set to determine which factors correlate with these annual mercury concentrations.

A summary of correlations between annual mercury levels in YOY perch from Sand Point Lake and various water-level parameters is given in Table 5. Correlations corresponding to the cutoff date yielding the highest correlation are presented along with those corresponding to the full period from March to September. We note that the highest correlations occurred for cutoff dates earlier than September,

TABLE 4. Summary of Mercury Analyses of YOY Yellow Perch Collected from Sand Point Site 0 from 1991 to 2003

year	mean Hg concn (ng gww^{-1})	SE (ng gww^{-1})	*N*
1991	124	4	37
1992	67	3	10
1993	122	5	14
1994	111	3	10
1996	102	8	10
1997	64	11	5
1998	32	4	5
1999	120	10	4
2000	53	3	9
2001	200	18	10
2002	75	4	20
2003	63	6	21

TABLE 5. Correlation Coefficients among Mercury Concentrations in YOY Perch and Selected Water Level and Water Quality Variables for Sand Point Lake, 1991−2003[a]

		correlation coefficient[b]			
variable	time period[c]	Hg in YOY perch ($n = 12$)	secchi depth[d] ($n = 12$)	color ($n = 7$)	conductivity ($n = 7$)
Hg in perch			−0.79**	0.86**	
max WL	March→ Sept	0.77**	−0.82**		
max WL	March→ July	0.80**	−0.88**	0.69	
Δ max WL	March→ July	0.86**	−0.72**	0.80*	−0.78*
mean WL	June→ Sept	0.63*	−0.74**		
mean WL	June→ Aug	0.66*	−0.80**		
Δ mean WL	June→ Aug	0.70*	−0.67*	0.68	
WLR	March→ Sept	0.53			
WLR	March→ June	0.61*	−0.63*		
Δ WLR	March→ June	0.86**	−0.74**	0.70	−0.72

[a] Δ = change relative to previous year, YOY = young-of-the-year, WL = water level, WLR = max WL−min WL. [b] Statistical significances: no entry = $p > 0.10$, no asterisk = $p \leq 0.10$ and > 0.05, * = $p \leq 0.05$ and > 0.01, ** = $p \leq 0.01$. No significant correlation occurred for turbidity or minimum water level. [c] Range of months used for calculating indicated water-level variable. [d] Secchi depth correlations are for biweekly averages; single fall measurement had no significant correlations.

with some occurring for the March−June period. Because, on average, 94% of the total annual water-level range (WLR) occurs from March to June, it is reasonable to consider shorter time intervals for defining some WLF parameters.

In Table 5 we observe that WLR (March−June) correlates significantly with mercury concentrations in YOY perch. As one possible WLR-related mechanism for increased exposure to methylmercury (MeHg) for fish, we considered the hypothesis that during low water conditions MeHg-enriched water drains into a lake from wetlands and leaches out of newly exposed sediment. However, this hypothesis is not supported by the nonsignificant correlation between mercury in fish and annual minimum water levels.

Another WLR-related parameter is the maximum water level. The correlation between maximum water levels and fish mercury concentrations is significant, and is highest for water levels defined in the range from March to July ($r = 0.80$, $p = 0.002$). One reason for this correlation may be that as water levels rise, areas of increasing organic content are inundated. This would promote increased microbial activity responsible for methylmercury production. Another intriguing possibility may be inferred from a recent study of MeHg production in the Everglades (*21*) where it was concluded that drying and rewetting of sediments increases mercury methylation by increasing sulfate levels. That is, when water levels fall, exposed sulfides in sediments are

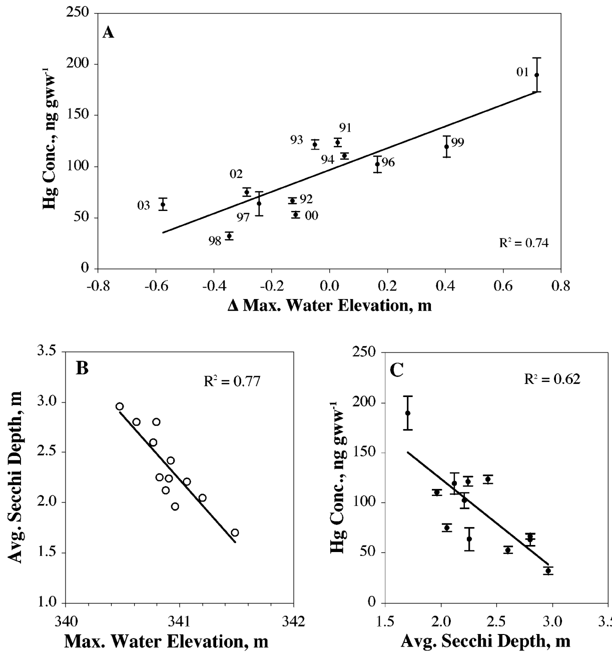

FIGURE 2. (A) Relationship between mercury concentrations in young-of-the-year yellow perch and maximum water levels (from March−July), relative to the previous year, for Sand Point Lake from 1991 to 2003. (B) Relationship between secchi depths and maximum water levels. (C) Mercury concentrations in yellow perch. Bars represent standard error ranges.

oxidized to sulfate. When water levels rise again, the mobilized sulfate provides fuel for sulfate-reducing bacteria, which are responsible for mercury methylation. Higher water levels would thus mobilize more sulfate and translate to more MeHg production.

If sulfate concentrations tend to rise in dried sediments/soil from oxidation of sulfides and perhaps from atmospheric deposition, then the amount of sulfates available for mobilization may depend on the length of time that has passed since the last mobilization event (last inundation by lake water). That is, the amount of sulfate mobilized from an area that is dried and rewetted on an annual basis may be less than the sulfate mobilized from an area that has not been inundated by lake water for several years. Thus, we might expect higher than usual sulfate mobilization for a year when the maximum water level exceeded the maximum attained during the prior year, and less sulfate for the converse. Assuming that more sulfate mobilization translates into more MeHg production (*22*), we might expect that mercury concentrations in YOY perch would correlate more strongly with the difference in the maximum levels between successive years than with the maximum levels themselves.

In Table 5 we see that the correlation using the maximum water levels (March−July) relative to the previous year (Δ max water level) is very strong ($r = 0.86$, $p = 0.0003$) and is consistent with the above reasoning. A plot of this relationship is shown in the upper panel of Figure 2 where results for each year are indicated. Standard error bars for mercury concentrations indicate the significances of the year-to-year differences.

We also observe that the mercury correlation against the change in WLR (Δ WLR, March−June) relative to the previous year is also strong ($r = 0.86$, $p = 0.0003$). Unfortunately, we have no data on sulfate concentrations and thus cannot properly address the sulfate hypothesis. However, the above observations provide strong evidence that some variable or process affecting mercury bioaccumulation is influenced by water-level dynamics.

Mercury in Fish and Water Quality. For the 12 years of YOY yellow perch mercury level data for Sand Point Lake, there also exists 12 years of secchi depth readings and 7 years of data for water color, conductivity, and turbidity. Table 5 and Figure 2 show that YOY yellow perch mercury levels correlate significantly with average secchi depth, which, in turn, correlates with WLFs. However, it is interesting to note that when secchi depths are based on a single fall measurement, correlations with other parameters are nonsignificant. This suggests that a fall measurement of a water quality parameter may be inadequate for characterizing a water body for that growing season. It also suggests that the correlations observed for the other water quality variables, defined by fall measurements, may differ from those using seasonal averages. Mercury in perch was also found to correlate significantly with water color but not with conductivity or turbidity. Average secchi depth consistently showed significant correlations across various water-level parameters, whereas water color correlations were less significant.

The correlation of secchi depth with WLFs suggests that the mobilization and/or production of ingredients which contribute to lake water clarity may be enhanced by changing water levels. This, in turn, implies that WLFs may affect organic carbon levels, which correlate with color in northeastern Minnesota lakes (*14, 23*), consistent with observations in an experimental reservoir (*22*).

Mercury in Fish and Atmospheric Wet Deposition. Because an increase in precipitation depth provides greater mercury loadings (*17*) and higher water levels in a natural system, wet mercury deposition would seem to be a promising candidate for explaining the annual variations in mercury concentrations in YOY perch. That is, mercury deposition is likely to co-vary with maximum water levels and, in turn, mercury in YOY perch. The only significant correlation between mercury deposition and mercury in yellow perch was the accumulated deposition through Aug 31 ($r = 0.59$, $p = 0.04$). Thus, water-level dynamics appear to have a stronger relationship with mercury levels in YOY perch than does wet mercury deposition.

This observation does not imply that atmospheric deposition is not the predominant source of mercury in YOY perch. Depositional mercury must first be transported to a methylating site before being incorporated in the food web. The time required for this to occur will vary depending on where the deposition fell, and would tend to obscure any correlation with mercury in fish.

Fish Mercury and Water Temperature. Because MeHg production is linked to lake water temperature (*22*), we compared annual variations in mercury concentrations of YOY perch with variations in water temperature. To accomplish this, we used cumulative degree days (referenced to 10 °C) in the surface to the 10 m depth zone, that are available in two-week increments (*6*). We observed no significant correlations between water temperature and fish mercury for any cumulative degree-day computation dates.

Multiple Regressions. Stepwise multiple regression analyses indicated that water-level parameters were the best variables for explaining variations of mercury levels in fish. None of the other variables described above were statistically significant in combination with water-level parameters.

YOY Yellow Perch Mercury Level Variations in 14 Lakes, 2001−2003. *Mercury in Fish Correlates.* Table 1 shows the wide range of water-level dynamics for the study lakes, with Island Lake having the largest fluctuations and Sturgeon, Vermilion, and White Iron lakes having the smallest. Although the minimum levels may have been missed for some of the study years for Sturgeon and White Iron lakes, results for Sand Point Lake indicate that the maximum water-level data are more important.

TABLE 6. Correlation Coefficients between Mercury Concentrations in YOY Yellow Perch and Selected Variables for 14 Lakes in Northeastern Minnesota[a]

	average Spearman correlation with mercury in YOYperch for indicated lake subset[b]			
variable[c]	all ($n = 14$)	VNP ($n = 6$)	non-VNP ($n = 8$)	non-VNP[d] ($n = 7$)
min WL		0.65		
max WL	0.63**	0.77*	0.52	0.68*
Δ max WL	0.59**	0.69	0.52	0.68*
mean WL (June→ Sept)	0.75**	0.77*	0.73**	0.82**
mean WL (June→ Aug)	0.75**	0.77*	0.73**	0.82**
Δ mean WL (June→ Aug)	0.64**	0.69	0.61*	0.68*
color	0.66**	0.75*	0.59	0.55
TOC	0.66**	0.98**		
conductivity	−0.48*	−0.65		−0.54

[a] pH, ANC, turbidity, and secchi depth had no significant correlations and are not listed. [b] VNP lakes are Crane, Kabetogama, Little Vermilion, Namakan, Rainy, and Sand Point. Non-VNP lakes are Boulder, Fish, Island, Sturgeon, Vermilion, E., Vermilion, W., White Iron, and Whiteface. Statistical significances: no entry = $p > 0.10$, no asterisk = $p \leq 0.10$ and > 0.05, * = $p \leq 0.05$ and > 0.01, ** = $p \leq 0.01$. [c] Abbreviations: Δ = change in value with respect to the previous year, WL = water level, min = annual minimum, max = maximum. Results for WLF and Δ WLF (not listed) are the same as those for max and Δ max, respectively. [d] Whiteface Reservoir excluded.

For the full set of 14 lakes, we observed (Table 6) significant positive correlations between mercury in fish and all water-level measures, except for minimum water levels. Water color, TOC, and conductivity also correlated significantly with mercury levels in fish. Water-level variables and water color results are similar to those for the long-term study of site 0 on Sand Point Lake. As observed for the 12-year data set for Sand Point Lake, the fall measurements for the 14-lake study also showed no correlation with fish mercury.

One important observation shown in Table 6 is that the direct water-level variable, rather than its change relative to the previous year, correlates best with mercury levels in fish. This contrasts with observations of the long-term data set for Sand Point Lake. Although this does not exclude a "sulfate hypothesis" it does indicate that mechanisms involving sulfate may be more complicated than those discussed above. We are currently seeking more years of data for the 14-lake set to better assess this observation.

For the two lake subsets (VNP and non-VNP) we observed both similarities and differences. Both sets indicate that mercury in fish correlate with WLFs, with the mean summer water level correlating strongly and significantly for both groups. If we exclude the Whiteface Reservoir (where trends appeared contrary to the other lakes) from the non-VNP set, we see that the water-level correlations with fish mercury become significantly stronger and they tend to agree with those for the VNP set. The strong fish mercury correlations with water color and TOC for the VNP lakes contrast with the weaker correlation with water color and the nonsignificant correlation with TOC for the non-VNP lakes.

We also tested for a relationship between mercury in YOY perch and total wet mercury deposition (measured at the Fernberg monitoring site) and found no significant correlations for any of the lake sets described above.

Water Quality vs Water Levels. Significant negative correlations were observed between conductivity and all water-level parameters, except for the minimum water level, for each set of lakes. Water color and TOC correlated positively with the same water-level parameters, but only for the VNP lake subset.

Interpreting the Results. Because co-variance among variables in nature is commonplace, it is generally true that correlation does not imply causation. This is because we do not always know the direction of the cause and we may not be aware of a third variable which could be responsible for the co-variance between two variables of interest.

However, water-level fluctuations have a higher order of independence than most other variables, particularly those involving water chemistry and biological activity, which have complex interactions that are responsible for mercury bioaccumulation in fish. That is, even though water-level fluctuations may correlate with a water chemistry variable, a change in that variable will not affect the lake's water level. Thus, we know the direction of any influence.

It is possible that a more fundamental variable could affect both water levels and fish mercury concentrations. However, wet mercury deposition, the most promising of such variables, was found to correlate only weakly with fish mercury for the long-term monitoring at Sand Point Lake, and did not correlate at all for the 14-lake study from 2001 to 2003.

Based on results from this study, it is likely that annual water-level fluctuations have a significant influence on mercury levels in YOY yellow perch. Because of the implied potential for reducing mercury bioaccumulation in fish through water-level management (in regulated water systems), further research on possible mechanisms involved and differences in responses among the lakes should be conducted.

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