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Mercury in Fish from Northeastern Minnesota Lakes: Historical Trends, Environmental Correlates, and Potential Sources

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ABSTRACT—High mercury concentrations in fish of some Minnesota lakes and rivers were first noted in 1971. Major anthropogenic sources of mercury to Minnesota rivers generally have been identified and controlled, but it has been difficult to identify mercury sources to remote northeastern Minnesota lakes containing fish with elevated mercury levels. Analysis of sediments from these lakes suggests that mercury deposition has increased by a factor of about 3.5 since white settlement in the state. Because the increase is spatially constant across northeastern Minnesota, atmospheric pollution appears to be responsible for the increase. Given that fish mercury varies considerably among lakes, local environmental processes apparently control the conversion of inorganic mercury into the methylmercury found in fish. Mercury levels in Minnesota fish are related to water chemistry, which in turn is influenced by watershed geology. Fish from lakes in limestone-rich watersheds are less likely to have high mercury levels than lakes in low-alkalinity regions. Lakes with colored water are more likely to contain fish with high mercury levels. Trend analysis shows that mercury levels in fish increased significantly between the 1930s and 1980s (comparison between museum specimens and recent samples) and between the 1970s and 1980s. Rates of increase are highest in low-alkalinity lakes.

Introduction

Mercury contamination of fish in Minnesota was first investigated in 1969 after the reports of fish contamination in Sweden (1) and Canada (2) from direct industrial discharges to surface waters. Initial attention in Minnesota and elsewhere was focused on rivers, which received the bulk of point-source discharges. Significant mercury (Hg) contamination was found in the Mississippi, Red, and lower St. Louis rivers (3), prompting efforts to identify and reduce its sources within the state. Use of Hg in agriculture and paper manufacturing was phased out during the 1960s, and Minnesota had no chlor-alkali or vinyl chloride plants, which had been identified as sources elsewhere. In 1972, about 125 sewage treatment plants had trickling filters that contained a mercury seal; these were replaced within a few years. Analysis of walleye and northern pike from rivers from 1970 through 1977 showed a 60 percent decline in Hg concentration, from a mean of 0.94 μg/g in 1970 to 0.38 μg/g in 1977 (4).

Researchers in Sweden (1), Minnesota (3), and elsewhere found high Hg concentrations in fish from lakes that were unaffected by point discharges. Subsequently, a quiet debate has ensued as to whether natural or anthropogenic sources are responsible for elevated Hg concentrations in fish in remote lakes. We examine Hg levels of fish in northeastern Minnesota lakes in relation to geology and water chemistry, assess temporal trends, and consider hypotheses concerning Hg pathways into fish. An understanding of the causes of Hg contamination in Minnesota is needed to safeguard human health and also the health of piscivorous wildlife. Methylmercury magnifies in food chains, and fish-eating birds and mammals are particularly at risk (5, 6). In some Minnesota lakes, Hg concentrations of fish are high enough to be deleterious or lethal to mink (7), otter (8), loon (9, 10), and perhaps eagle and osprey, species for which there are few data.

Correlation of Fish Mercury with Water Chemistry

Relationships between Hg concentrations of fish and environmental variables were examined using data in STORET (11) that had been stored by the Minnesota Pollution Control Agency (PCA). Only lakes that had Hg data for northern pike or walleye were used; consequently, the set of lakes is non-random. Lakes are chosen for Hg analysis in fish based on three factors: (1) selection by the Minnesota Department of Natural Resources (DNR) for routine fish management; (2) angling pressure, and (3) predicted high concentrations of fish Hg because of low pH, high aluminum, high color, or low total phosphorus (12). Data reported here are all analyses of skin-on fillets of axial muscle collected between 1977 and 1988, expressed as μg Hg per g wet tissue.

Formation of the lakes and soils of the study area (Figure 1) was largely determined by Quaternary glacial activity. The landscape is characterized by non-calcareous bedrock formations overlain by thin non-calcareous tills in the east and thick calcareous tills in the west.

Patterns in fish Hg levels among lakes were examined by first normalizing concentrations to those in northern pike,

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Esox lucius, with a standard total length of 55 cm (14). Within a given lake, Hg concentration is positively correlated with fish length (12), but the slope of the relationship varies among species. For lakes where data were available only for walleye, *Stizostedion vitreum vitreum*, (22 of 127 lakes), seven length-normalized concentrations were converted to northern pike units by the method of Sorensen *et al.* (14). Normalized fish data were merged with average water quality data (alkalinity, pH, color, aluminum, sulfate, and total phosphorus) for each lake, and Spearman correlation coefficients were calculated (15). As found earlier (12, 16), Minnesota lakes with high color (>100 Pt-Co units), low alkalinity (<20 mg/L), and pH < 7.0 have higher fish Hg (Table 1).

It is clear that the distribution of fish Hg concentrations among northeastern Minnesota lakes is not spatially random (Figure 1). On average, the alkalinity of lakes in the calcareous region is 4X that of lakes in non-calcareous tills and bedrock (86 vs. 21 mg/L, $P<0.001$, t-test). Normalized average mercury concentrations of northern pike were 27 percent less in the calcareous region than in noncalcareous watersheds (0.32 vs. 0.44 μg/g, $P<0.001$), but high and low levels of fish Hg were found in both regions. In the noncalcareous region, fish Hg is significantly correlated with alkalinity, pH, color, and aluminum (Table 1).

The source of variation of Hg in fish in the calcareous region is unclear. There is a notable lack of correlation between water quality variables and fish Hg (Table 1). For instance, the correlation coefficient between fish Hg and water color is -0.03, in contrast to a relatively strong correlation in the non-calcareous region of 0.55. The poor correlation between fish Hg and alkalinity in the calcareous region (-0.28) may be due to relatively few low-alkalinity lakes (only four lakes < 20 mg/L). Nevertheless, it seems likely that fish Hg in the calcareous region is largely controlled by some factor not quantified here (see *Information Needs*).

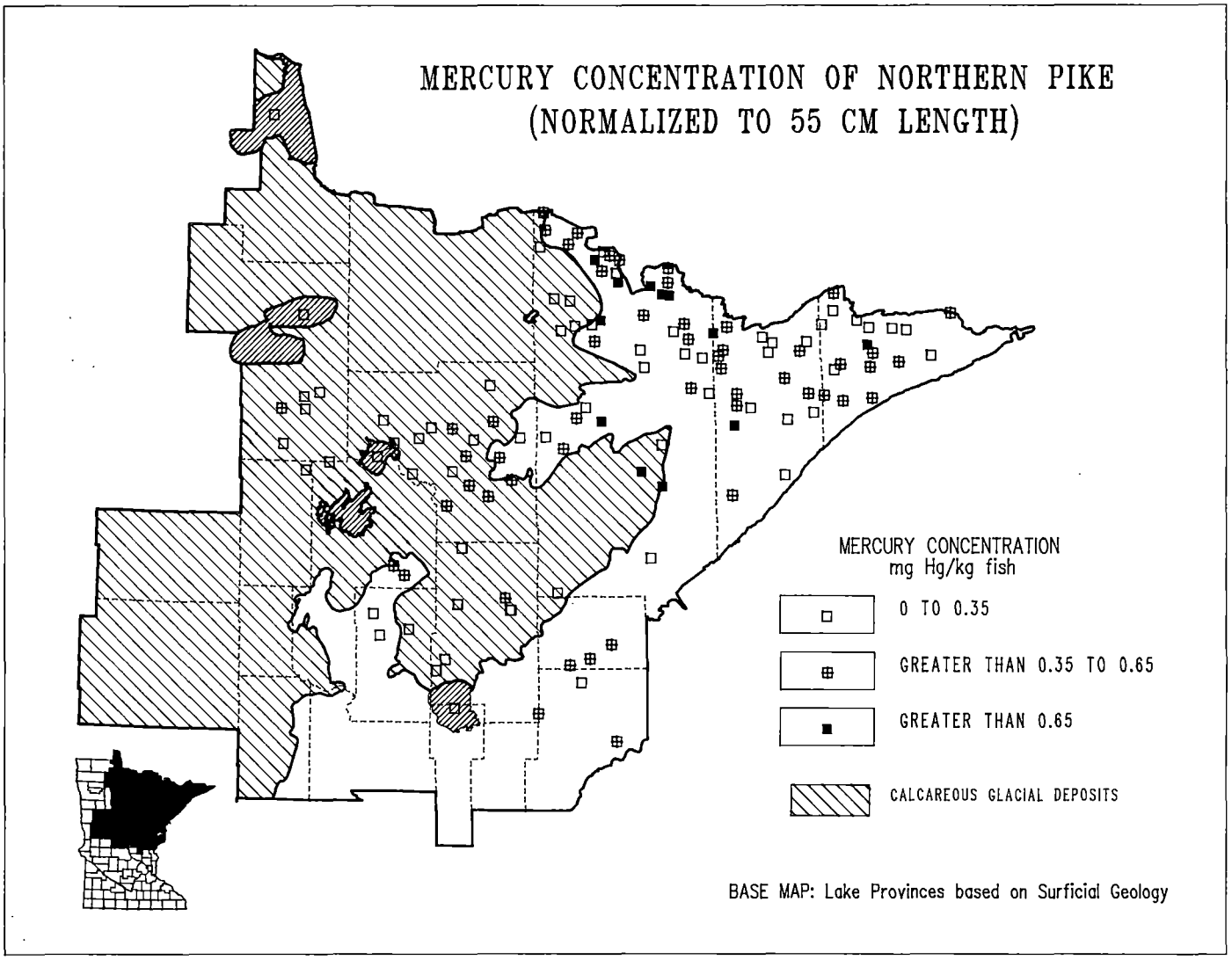

Figure 1. Mercury concentration of northern pike (normalized to 55-cm length) in northeastern Minnesota. Geological provinces are based on the dominant surficial geology that is most likely to determine water chemistry (13), although peatlands isolate some surface water from the underlying geology. The shaded region indicates the approximate extent of calcareous glacial deposits from the Des Moines and Wadena Lobes. The unshaded area is bedrock with little overlying till, or non-calcareous glacial tills deposited from the Rainy Lobe and the Superior Lobe.

Time Trends of Mercury Contamination in Minnesota

Fish Collected between 1970 and 1988

The Minnesota DNR and PCA had fish tissue analyzed for Hg by the Minnesota Department of Health (MDH) since 1970. Some lakes have been sampled twice, allowing analysis of temporal trends in Hg concentration. We compared data collected at least five years apart within a given species and size class (6.4 cm increments).

Twenty-five lakes had data pairs, with time periods between paired samples ranging from five and sixteen years. There was no significant difference between the lengths of fish in the paired samples (paired t-test, N=25, P=0.32); the mean length of all fish was 51 cm. Differences in mercury concentration were divided by the number of years between samples, to estimate the rate of change of mercury concentration (μg/g per year). The average change in fish Hg concentration was positive 0.013 μg/g per year (paired t-test, N=25, P<0.02). Seven lakes showed decreases in fish Hg, and four of these lakes were potentially affected by municipal sewage discharge. The nine lakes potentially affected by sewage effluent show no statistically significant trend (mean change = -0.005 μg/g per yr, P=0.27). If the data set is restricted to northern pike and lakes not potentially affected by municipal sewage effluent, the results are similar to the whole set: a significant increase of 0.017 μg/g per year (paired t-test, N=14, P<0.02). For these, the mean increase in Hg concentration in northern pike was 0.11 μg/g, from 0.36 to 0.47 μg/g, over an average time span of 7.2 years.

We separated the lakes not affected by sewage discharge into those in the region of calcareous glacial deposits and those in the noncalcareous region; some relationships analogous to the patterns of Hg concentrations discussed above were revealed. There is no significant change in the calcareous region (paired t-test, P=0.22, N=12). For the noncalcareous region, the average rate of increase is 0.026 μg/g per year (paired t-test, P<0.01, N=12), but this average is affected by two high points. The median rate of increase is 0.013 μg/g per year. Just as Hg concentrations in the noncalcareous region are inversely correlated with alkalinity, the rate of Hg increase is significantly higher at low alkalinity (r= 0.66, P<0.025, Figure 2). In contrast, there is no significant relation between the rate of mercury increase and water color (r=0.09), although there is a correlation between fish Hg levels and water color. Although these findings are limited by small sample size, they provide intriguing information on which to formulate hypotheses.

Table 1. Spearman correlation coefficients between water chemistry and normalized fish mercury concentration (normalized to 55-cm northern pike; ug Hg/g wet tissue). "***" indicates significance at the 0.001 level, "**" at the 0.01 level, "*" at the 0.05 level, and "NS" indicates that there is no significant correlation (P>0.05).

	All Lakes (N=127)	Calcareous Region (N=41)	Non-Calcareous Region (N=86)
Alkalinity	-0.50***	-0.28 NS	-0.44**
pH	-0.46***	-0.05 NS	-0.45***
Color	0.41***	-0.03 NS	0.55***
Sulfate	0.26*	0.36 NS	0.20 NS
Total Phosphorus	-0.19*	-0.24 NS	-0.06 NS
Total Aluminum	0.56***	0.27 NS	0.60***

Fish Collected in the 1930s vs. the 1980s

We also compared the Hg content of fish in museum collections to the concentration in similarly-sized fish collected recently. Analyses of museum specimens from the oceans have shown no temporal increase in Hg (17, 18, 19), whereas analyses of museum specimens (walleye) from Michigan have shown significant recent increases (20, 21).

Twelve northern pike and walleye collected from six lakes in 1935 and 1936, and stored at the Bell Museum of Natural History (University of Minnesota-Minneapolis), were analyzed for total Hg. Lakes were selected to represent a range of recent fish Hg concentrations. Skin-on fillet samples were scaled, chopped, and dried at 55 °C. Analyses were performed by the MDH with the same technique used for recent fish samples. Samples of fresh fish were dried to determine conversion factors between dry and wet weights; all fish Hg concentrations are expressed as μg Hg/g wet tissue. The northern pike conversion factor was 0.204 g dry/g wet tissue (s.d. = 0.004), and the walleye factor was 0.185 (s.d. = 0.013). Museum fish were chosen to match, generally within one cm, the length of at least one recent (1983-1986) fish already analyzed for Hg, so that a paired t-test could be applied.

The data show a significant increase in fish mercury from a mean of 0.13 μg/g in the 1930s to a mean of 0.31 μg/g in the 1980s (P<0.01, N=12, Figure 3). The average rate of increase for these lakes (in μg/g per year) ranges from no increase in Winnibigoshish, to 0.002 in Alton, 0.004 in Side, 0.005 in Sawbill, and 0.009 in Brule. These rates are less than the average rate of increase (0.017 μg/g per year) between 1970 and 1988, which suggests that the data are reasonable, even though concern has been expressed that preservation in formaldehyde may leach mercury from specimens (22).

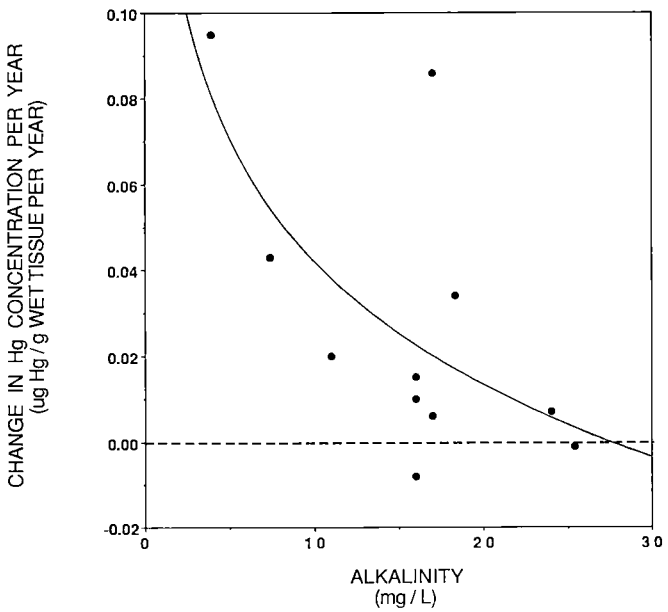

Figure 2. Relation between rate of increase in mercury concentration of recent fish samples (collected 1970 to 1988) and alkalinity in the non-calcareous region of northeastern Minnesota: RATE = 0.14 - 0.10 (LOG ALKALINITY), r=0.66, P<0.025. If the two points with the highest rates are removed, the regression is still significant: RATE = 0.09 - 0.07 (LOG ALKALINITY), r=0.66, P<0.05.

Sediment Concentrations from the 1800s to the 1980s

Lake sediments record the history of a lake and its watershed as they accumulate. Henning (23) performed experiments showing that the vertical stratigraphy of Hg in sediments is a reliable record of the Hg concentration of the sediment at the time of deposition. When radiometric sediment dating is performed, it is possible to calculate changes in deposition rates and estimate the timing of any changes.

Data from Meger (24) show that sediment concentrations had increased since white settlement by an average of 2.9X in single cores from both Kabetogama and Crane Lakes in northern Minnesota (range of 2.3 to 3.6X). Given that no known Hg sources exist for either lake, Meger attributed the increases in loading to atmospheric sources. Similar increases in sediment Hg concentrations were observed from stratigraphic analyses of cores from Lake Superior and inland lakes in Wisconsin and southern Ontario. Kemp *et al.* (25) showed that Hg concentrations in six Lake Superior cores increased by an average of 2.6X (s.d. = 0.8). Rada *et al.* (26) found an average of 2.7X (s.d. = 0.6) in cores from 11 lakes in north-central Wisconsin, and Johnson *et al.* (27) found an average increase of 2.7X (s.d. = 0.7) in cores from nine Ontario lake basins.

Henning (23) analyzed at least ten cores from each of four lakes across the non-calcareous region of northeastern Minnesota and found that sediment concentrations increased by factors of 3.4 to 3.9. Detailed lead-210 dating allowed the estimation of the timing of increases and deposition rates. The increases occurred in two periods, the first immediately after settlement (1860-1890), and the second between 1920 and 1950 (Figure 4). Modern deposition rates of 18-26 $\mu g/m^2$ per year were estimated to be 3.2-3.6X those during pre-settlement. Based on a North American average atmospheric deposition rate of 15 $\mu g/m^2$ per year (28), Henning concluded that direct deposition to the lake surface could account for 60 to 80 percent of the measured accumulation rate in each lake (23). Presumably, the remaining Hg influx was from watershed inputs.

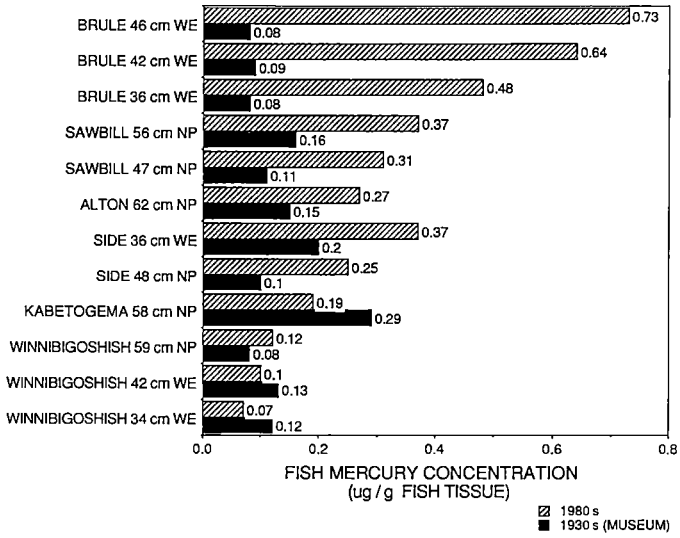

Figure 3. Comparisons of fish mercury concentration in 1930s museum specimens and fish collected in the 1980s. The lake, total length of fish, and species are indicated (NP = northern pike, WE = walleye). Samples were skin-on fillets of axial muscle, with data expressed as μg mercury per g wet tissue. The t-tests for the two lakes with three samples show no significant change in walleye from Lake Winnibigoshish, but a significant increase in walleye from Brule Lake (0.080 vs. 0.055, $P<0.01$).

Discussion

Potential Sources

Henning (23) showed that there is little spatial variation in recent rates of Hg accumulation in lake sediments across northeastern Minnesota. Two studies from Minnesota (23, 24) and three studies from surrounding areas (25, 26, 27) show an approximate tripling in sediment concentrations of Hg over the past 150 years. The consistency of these data suggest that atmospheric deposition is spatially constant, at least across northern Minnesota, if not the upper Midwest. All five studies attributed the increases to increased atmospheric deposition, although it is difficult to conclusively show that this is so.

About half of the anthropogenic Hg emissions to the atmosphere in Wisconsin were attributed to Hg-based fungicides added to latex paint, and an additional one-third of the total Hg emission was estimated to derive from coal and oil combustion (28). The error in each of the estimates was thought to be 15 to 30 percent. These estimates suggested that anthropogenic emissions are about equal to degassing from

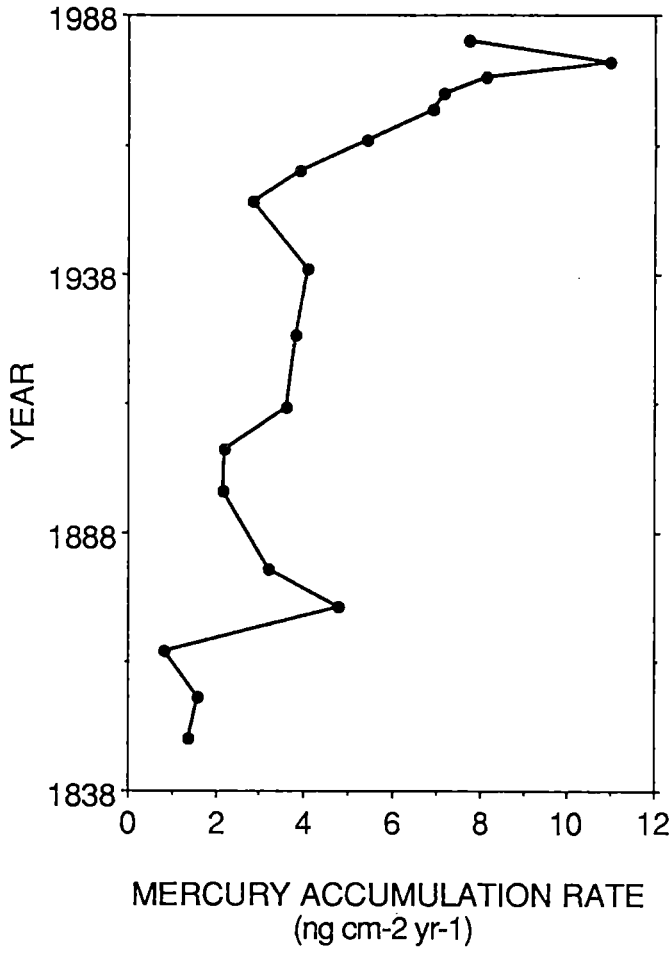

Figure 4. An example of an estimated mercury accumulation rate, as determined in a sediment core from Kjostad Lake (from 23). The trend of increases in accumulation rate in the late 1800s and 1920-1950 were observed in other cores; peaks based on individual points are not significant.

the earth, a process that mobilizes Hg from natural sources and past human activities.

Historical Trends

Two separate trend analyses indicate that the mercury concentration of fish is increasing in northeastern Minnesota. Analyses of fish since 1970 show an average annual increase of 0.017 μg/g per year (about 5 percent increase per year, not compounded). Analyses of museum specimens show an average annual increase of 0.004 μg/g per year, or about 3 percent per year, based on the 1930s average of 0.13 μg/g. Higher recent rates of increase are consistent with the thought that anthropogenic Hg sources have increased in recent times. These upward trends also are consistent with the finding that Hg concentrations in lake sediments have increased by factors of 2.9 to 3.9 over the past 100 to 150 years (23, 24). An increase in sediment Hg concentrations by a factor of about 3.5 over about 125 years represents an annual rate of increase of about 2 percent per year. The calculation of these percentage annual increases, although gross averages, shows that the estimated increases are similar for the different methods.

Environmental Correlates

If atmospheric deposition of Hg has little spatial variation across northeastern Minnesota, then local biogeochemical differences presumably cause the variation in observed Hg concentrations in fish. Equal rates of deposition do not necessarily imply equal Hg concentrations in water or sediment, an important observation, because methylation can be proportional to Hg concentration (30, 31). Sedimentary Hg concentration may be higher in lakes with large watersheds relative to lake volume, as some studies have found (32, 33).

The critical process controlling Hg bioaccumulation may be the production of methylmercury, but methylation is not well-understood. Research to date has suggested many potential environmental factors affecting Hg bioaccumulation (34). A brief review of these hypotheses reveals that we are far from a comprehensive understanding of Hg accumulation in fish.

First, statistical work, including that reported here, has identified alkalinity, pH, calcium, color, and dissolved organic carbon (DOC) as significant correlates of fish Hg (12, 16, 35, 36, 37). Color and alkalinity are unlikely to be causative factors in themselves but are more likely correlated with water quality characteristics that do affect Hg cycling or bioaccumulation in a lake ecosystem. For instance, color is a surrogate measure for dissolved organic carbon, including humic and fulvic acids, which chelate metals and transport them from peatlands (38), catalyze Hg methylation (25), directly methylate mercury (39), and perhaps even act as an energy source for bacteria that methylate Hg (40). In our survey of 127 northeastern Minnesota lakes, color is significantly correlated not only with fish Hg ($r=0.41$), but with aluminum ($r=0.77$, $P<0.0001$), total organic carbon ($r=0.88$, $P< 0.0001$), pH ($r=-0.22$, $P=0.04$), total phosphorus ($r=0.26$, $P=0.01$) and sulfate $r=(0.40$, $P=0.0003$), but not with alkalinity ($r=-0.14$, $P=0.19$).

Similarly, alkalinity is a surrogate measure for calcium and pH, with which alkalinity is highly correlated ($r=0.90$, $P<0.0001$). Under laboratory conditions, calcium concentration is inversely related to the uptake rate of methylmercury by rainbow trout (41). In general, metals are less toxic in hard water (42), but there is little information regarding the effects of calcium on the toxicity of organometals such as methylmercury. The pH of water directly affects virtually all chemical processes; some workers have found that net Hg methylation is higher at low pH (31), and lower pH is in general correlated with greater mobility of metals out of sediments (43). Wiener *et al.* (44), who studied age-1 yellow perch in an experimentally acidified Wisconsin lake, found significantly higher Hg concentrations at pH 5.6 compared to the pH 6.1 reference basin.

The methylmercury available for bioaccumulation in a lake is the balance between methylation and losses of methylmercury. Methylmercury can be lost by conversion to dimethylmercury, which is readily lost to the atmosphere (45), or by demethylation. Each of these processes is a function of environmental conditions, including pH (31, 46, 47), oxidation-reduction potential (46), temperature (48), oxygen (49), and organic substrate concentration (31, 48). A comprehensive Wisconsin study found that net methylation is determined more by the demethylation rate than the methylation rate, and that most methylmercury is produced in surface sediments under anoxic conditions (50). Wood (51) suggested that methylation rates may be limited in some lakes by cobalt availability, an essential component of methylcobalamin, which is thought necessary for biomethylation of mercury (52).

The availability of sedimentary mercury for methylation is not only affected by pH and humic acids, but also by sulfur, which forms highly insoluble sulfides in anoxic sediments with many metals, including Hg (53). Selenium, just below sulfur in the periodic table, also can bind strongly to various Hg forms. When present in elevated concentrations, selenium interferes with Hg bioaccumulation (54). As yet, there is very little environmental data concerning the interplay of Hg and selenium in lakes.

This discussion has assumed that the amount of methylmercury in the system is the main determinant of fish concentrations. It has been suggested, however, that the biomass of fish may be the most important factor that determines Hg concentration in fish (55). If one assumes a relatively constant production rate of methylmercury among lakes and efficient uptake by organisms, then fish Hg would be highest in lakes with the lowest biomass of fish. The negative correlation between productivity and fish Hg is probably significant, just as it is for alkalinity. But significant correlation does not provide evidence for cause and effect.

Information Needs

Statistical analysis of lake surveys has yielded an abundance of environmental correlations with the Hg content of fish. Such results describe what is observed in the environment, but do little to isolate cause and effect. Even though color is significantly correlated with Hg in fish ($P<0.001$, Table 1), its correlation coefficient of 0.55 means that only 30 percent of the variation in fish Hg is explained by water color; alkalinity explains only 25 percent of the variation. Multiple regression models with three variables can explain more of the variance of fish Hg; one model including pH, aluminum, and phosphorus explained 40 percent (12), and one including calcium, phosphorus, and chlorophyll explained 60 percent of the variance (36). Richman *et al.* (34) caution that Hg bioaccumulation is likely governed by an array of factors that vary in importance from lake to lake.

A major problem with lake surveys is that environmental variables tend to co-correlate in lakes; pH tends to be higher in lakes with higher alkalinity, which is produced mainly from

calcium carbonate derived from relatively phosphorus-rich rocks such as limestone. Consequently, pH, alkalinity, calcium, and phosphorus tend to correlate with each other, which makes it difficult to separate, for instance, the effect of pH from that of productivity. Much more work is needed in which a critical variable is manipulated while others are held constant. This can be done in the laboratory (41), or *in situ* with enclosures (54) or by dividing a lake (44). Experimental manipulations should be aimed at understanding Hg methylation and its relation to uptake by biota.

If Hg contamination is to be reduced, we need to know more about atmospheric deposition, the role of water and sediment chemistry in methylation, and how the food chain works to magnify methylmercury. We are beginning to understand why certain water quality parameters such as pH and color yield statistical correlations with fish Hg, but we need much more information concerning the mode of action of these and other potentially important parameters as such as oxygen, calcium, phosphorus, sulfur, selenium, and perhaps even cobalt. The ecological structure of the food web in a particular lake also plays a role in determining the Hg concentration of predators such as northern pike (34). It will be difficult to reduce Hg contamination in fish until we understand the processes that lead to that contamination.

Acknowledgements

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