chiometric balances made on both reactants and products demonstrated that no other substances are involved in the reaction, at least within the accuracy of the analytical methods. This was true for the completed reactions as well as those that could be monitored with time (pH > 8.35).

The reaction rate constant k_1 is independent of pH in the range of 9.5–11.6, ionic strength up to 0.04, initial concentrations of nitrite ranging from 1 to 17 mg/L as N and chlorine from 2.3 to 140 mg/L as Cl_2, and finally chlorine to nitrite molar dose ratios in the range of 0.14–6.0.

The experimental results demonstrated that the reaction is completed in fractions of a second at neutral and low pH levels. However, the kinetics of the reaction under these pH levels remain to be ascertained. The small range of temperatures investigated did not permit an accurate evaluation of the activation energy for the reaction.

Registry No. Cl, 7782-50-5.

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Airborne Mercury Deposition and Watershed Characteristics in Relation to Mercury Concentrations in Water, Sediments, Plankton, and Fish of Eighty Northern Minnesota Lakes

John A. Sorensen,[†] Gary E. Glass,*,[‡] Kent W. Schmidt,[†] James K. Huber,[†] and George R. Rapp, Jr.[†]

College of Science and Engineering, University of Minnesota, Duluth, Minnesota 55812, and Environmental Research Laboratory–Duluth, U.S. Environmental Protection Agency, 6201 Congdon Boulevard, Duluth, Minnesota 55804

■ In light of increasing fish consumption advisories in several states, a comprehensive multimedia database was created to answer a variety of questions. Mercury concentrations in precipitation, lake water and sediment, zooplankton, and fish were measured and analyzed together with extensive watershed and lake chemistry data for 80 lake watersheds in the study region of northeastern Minnesota including the Superior National Forest, Voyageurs National Park, and Boundary Waters Canoe Area Wilderness. Atmospheric deposition of mercury, transport, water column lifetimes, and sedimentation in lakes are determined. The factors relating mercury concentrations within the lake watershed components are analyzed and discussed. The notable correlates with mercury residue levels in northern pike of a standard length and weight (55 cm, 1.0 kg) were mercury concentrations in zooplankton and water, total organic carbon concentration, and pH. The primary source of mercury was found to be of atmospheric origin.

Introduction

The body burdens of toxic residue forming compounds in fish and wildlife have been studied extensively on the Great Lakes and large river systems receiving contaminated waste waters for the past several decades (1). However, residue levels in fish from inland lakes and streams are infrequently monitored, and only recently was it reported that levels of mercury (2) were readily measurable. It is now known that mercury contaminates fish in hundreds of lakes and rivers in the Upper Midwest, around the Great Lakes (3–6), and in other states and provinces as well.

In Minnesota, fish consumption advisories restricting full utilization of the resource because of high levels of mercury have been issued for 285 water bodies compared to restrictions on only 1 lake (Crane) 12 years ago (7). Wisconsin became aware of its mercury problems in inland lakes in 1983 when five inland seepage lakes were examined as part of acid rain studies (8). Michigan issued a statewide fish consumption advisory in December 1988 for all of its 10 000 lakes and Florida issued a statewide advisory in March 1989. With the growing awareness of the existence of contamination in fish and wildlife from remote regions, a number of questions are being asked: What are the sources of mercury contamination in fish? How long have they been contaminated? How is mercury transported

[†] University of Minnesota.
[‡] U.S. EPA.

within the watershed? What causes fish to be high in mercury in some lakes and low in others?

Our objectives were to build a database of relevant information in order to answer as many of these questions as possible and to give guidance to regulators and resource managers for the possible reduction of mercury residue levels in fish and other wildlife.

A number of possible explanations exist as to the sources of mercury now present in fish and wildlife: (1) regional bedrock and till, (2) industrial and municipal waste, (3) historical mining and paper manufacturing, and (4) previously implicated atmospheric deposition from airborne sources (2, 7).

The first indication that the problem was of recent origin came from a study by Meger (9), who looked at the stratigraphy of mercury in the sediments of Crane and Kabetogama Lakes. He found that the mercury flux to the sediments (from core samples) had doubled since 1880. These findings have recently been verified for other lakes of the region by Henning et al. (10) and are similar to findings by Norton et al. (11) in eastern North America and Johannson (12) in Sweden. Atmospheric sources were further suspected when rain and snow concentrations at Duluth, MN, were measured as 14–37 ng of Hg/L with an annual wet deposition of ~15 μg of Hg/m^2 for 1983 (13).

Research Framework. To build on our understanding of how atmospheric inputs and watershed processes modify the chemistry of the inputs (14), and how varying surface water quality within the region affects mercury residue levels in fish, we selected a broad and descriptive approach to building the necessary database to answer the questions raised above.

A set of 80 lakes in northern Minnesota was selected for this study. Seventy-two of these lakes had known watershed characteristics from acid rain studies (15), and mercury residue data for walleye and/or northern pike were available for 65 lakes (16). Data common to both data sets existed for 57 of the 80 lakes.

Mercury concentrations were monitored weekly in precipitation at three sites within the study region at Duluth, Marcell, and Ely, MN. This was done for the purpose of interpolating mercury concentrations and loadings for each lake and watershed. In addition, 77 of the 80 study lakes were surveyed for total mercury concentrations in the water column, zooplankton populations, and sediments.

The model for the analysis used in this study is the watershed basin, which captures and contributes to the water flows of the hydrocycle and provides the substrate on which the lake/stream ecosystem evolves. A number of studies (e.g., ref 15) have shown the importance of certain factors and processes in the functioning of watershed ecosystems.

Just as important are the biological processing and decomposition responsible for the net production of methylmercury, the specific chemical form of mercury that is 10–100 times more bioaccumulatable than the less toxic inorganic forms from which it is derived (17). The major pathways for bioaccumulation of mercury in the foodweb and in fish have been summarized by Armstrong (in ref 18), and uptake and retention have been described by de Freitas (in ref 18). The net production of methylmercury has been modeled by Bisogni and Lawrence (19), who found that the net specific methylation rate per unit biomass concentration depended on the microbial activity, mercuric ion availability, and whether the system was aerobic or anaerobic. In addition to these factors controlling the net methylation rate, other factors that need to be evaluated include the related watershed processes controlling the concentration of total mercury, nutrient concentrations affecting microbial activity, and the related chemical reactions controlling the availability of mercuric ions.

Although data for methylmercury concentrations in the water column may be useful for answering some questions, establishing quality data for a large number of lakes would be unrealistic due to the dynamics/complexities involved and the lack of certified reference samples. For example, typical seasonal variations in methylmercury concentrations at a given site can be greater than an order of magnitude (20).

Study Area. The study region encompasses over 3000 lakes and stretches approximately 180 km from north to south and 320 km east to west across Cook, Lake, St. Louis, Itasca, and Carlton counties in northeastern Minnesota (Figure 1; Table I). Many of the lakes in this study are located within the Superior National Forest, the Boundary Waters Canoe Area Wilderness, and the Voyageurs National Park; as a result, direct anthropogenic influences (other than airborne) are minimal. Additional details describing the study area are found in Rapp et al. (15).

Sampling Methods

Precipitation. Precipitation sampling at the three monitoring sites was accomplished by using an automatic moisture sensing head to activate a movable roof that covers a Teflon-lined funnel with a collection area of 0.212 m^2 (MIC Co., Thornhill, Ontario, Canada). The bottom surface of the funnel is heated in winter to melt the snow. Precipitation passes out the bottom of the funnel through a Teflon fitting and tubing into a 1-L polyethylene (Nalgene) sample collection bottle containing 6 mL of an acid dichromate preservative (2.5% $K_2Cr_2O_7$ and 25% HNO_3) and 20 mL of deionized water (DIW). The bottle is inside the enclosed base of the MIC sampler, heated during winter to 4 °C. At the Duluth station sample bottles were changed at intervals corresponding to and depending upon the volume of individual precipitation events. Bottles at the other two stations were changed weekly. Collection times, sample volumes, and meteorologic observations were recorded.

Water. Surface lake water samples were collected by immersing the sample bottle (300-mL Nalgene polyethylene) below the surface of the lake ~5–10 cm, opening the cap, allowing the air to escape by filling, and closing the cap under water. Before sampling, the acid dichromate preservative (6 mL) was added to new bottles that had been rinsed with distilled water. During water sampling the field personnel wore latex gloves to prevent possible skin contact with the lake water sample. Unused bottles were returned to the laboratory, filled with distilled water, and analyzed as reagent and field blanks.

Sediments. Sediment samples were obtained with Hongve (21) and Wildco drop corers. The surface portions (0–6 cm) of the Hongve cores were transferred to zip-lock polyethylene bags that were previously tested and shown to be free of mercury.

Plankton. Plankton samples (primarily zooplankton at >80 μm) were obtained from consecutive vertical tows by using a Wisconsin style net (Wildco Wildlife Supply Co.) and a Minnesota plankton bucket (J. Shapiro, U. of Minnesota, Minneapolis, MN). The first plankton nets used were found to contaminate the samples with mercury. A new net was soaked in dilute acid before use to reduce the leachable mercury content of the mesh. The Minnesota bucket did not leach mercury when tested with dilute acid. This is not the case, however, for newer models. The sampling sequence was started by rinsing the latex
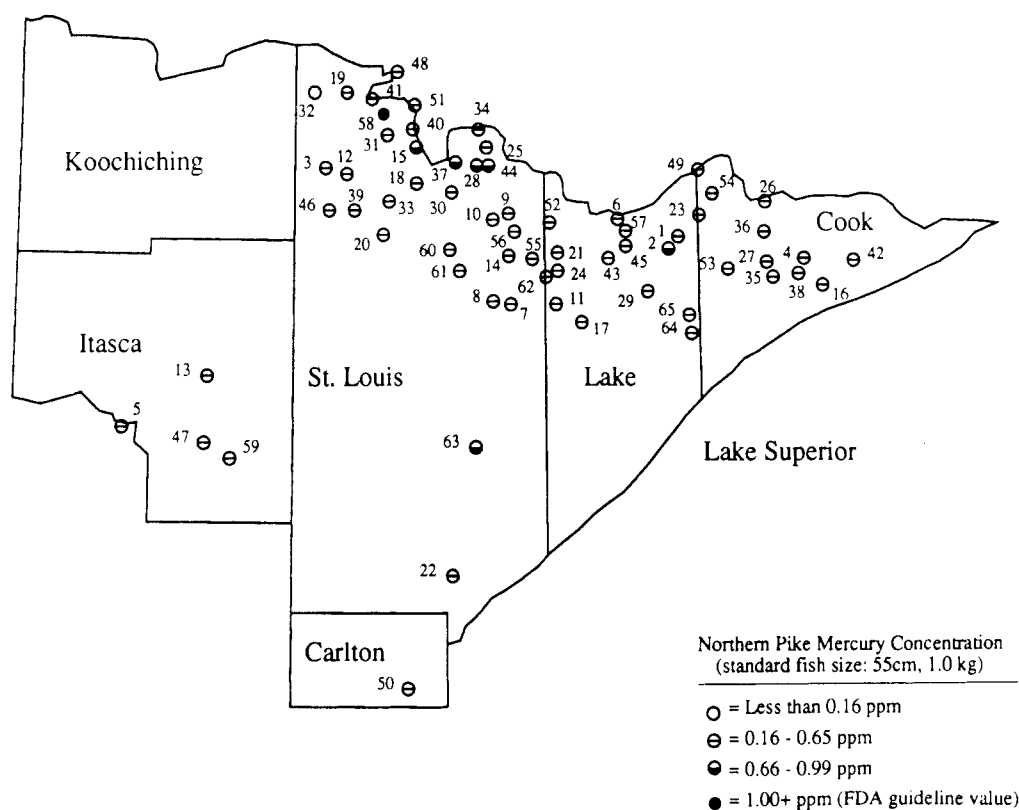
Koochiching

Itasca

St. Louis

Lake

Cook

Lake Superior

Carlton

Northern Pike Mercury Concentration
(standard fish size: 55cm, 1.0 kg)

○ = Less than 0.16 ppm
⊖ = 0.16 - 0.65 ppm
◐ = 0.66 - 0.99 ppm
● = 1.00+ ppm (FDA guideline value)

Figure 1. Map of northern Minnesota showing the locations of the 65 lakes with fish mercury residue data that were used in this study. The mercury levels for the standard size northern pike (55 cm) are indicated by the symbol plotted. The index numbers identify lakes and are listed with location and calculated mercury residue levels for the standard size fish.

gloves and plankton net (with the collection bucket valve open) thoroughly with lake water. The valve was closed and the net and bucket were lowered to within 1 m of the bottom and brought to the surface with moderate speed. After each tow, water was splashed on the net to flush the plankton into the collection bucket. This sequence was repeated until a sufficient sample was obtained. Once the tows were complete, the valve was opened and the plankton concentrate was flushed into a graduated cylinder. The concentrate was diluted to a set volume with lake water to allow for convenient removal of a 20-mL aliquot, which was preserved with formaldehyde for microscopic examination. The remaining portion was poured into a water-sampling bottle containing preservative that was finally filled with lake water. All necessary information (volumes, tow lengths, etc.) was recorded to allow for estimating zooplankton mass density in the water column.

Water, sediment, and zooplankton samples were collected during spring, summer, and fall of 1988. All sampling was done close to the deepest locations at each lake site. For larger lakes, an additional site was chosen. The samples were kept cold until aliquots were taken for mercury analysis.

Analytical Methods

Mercury measurement methodology for precipitation, water, and zooplankton samples utilized cold vapor atomic absorption spectrometry (CVAA) approved by U.S. EPA method 245.1 (22) with modifications (13) for standardizing operating procedures and screening reagents for lowest levels of mercury content to reduce the blank value. Instrumentation and other details are given in Glass et al. (23).

For zooplankton samples, separate aliquots were filtered (0.45 μm) and dried overnight at 105 °C for dry mass determination. All results are reported on a dry weight basis. Microscopic examination was performed by E.

Swain (24) for identification of the major types of plankton and particulate.

Sediment analyses for mercury concentrations were conducted with U.S. EPA method 245.5 (22) with minor modifications. The percentage of moisture in a wet sediment sample was determined by drying overnight at 105 °C. The average dry weight used per sediment analysis was 0.27 g and ranged from 0.033 to 3.2 g.

For 72 samples, we ran the sediment analysis with both wet and dried portions. A regression analysis (no constant) of the pairs indicated a $5.3 \pm 1.0\%$ loss of total mercury on drying. Our results include both wet and dry analyses where the dry samples have been corrected for loss on drying. All results are reported on a dry weight basis.

Tests were conducted to assure the accuracy of the mercury analysis and to check for positive interference by the possible presence of nonmercurial compounds that could absorb UV radiation at 253.7 nm. The gold gauze amalgam accessory was used, as was the deuterium background corrector with the CVAA system to check for these possible interferences. Gold film mercury vapor analyzers (Models 511 and 431), Jerome Instrument Corp., Jerome, AZ 86331, were used as independent checks on the accuracy of the CVAA methods (23). With the various methods, consistent results were obtained with no positive interferences found for the CVAA method.

Database and Data Analysis Methods

Mercury Concentration Survey Database. The detection limit for our analyses was defined as 3 times the standard deviation of the reagent blank values (25). For those samples (mainly water) measuring less than the detection limit, the actual computed value was entered in the database down to a lower limit that corresponded to a 90% confidence interval above the noise level, i.e., blank-corrected signal $> 1.65 \times$ standard deviation of the blanks.

Table I. List of Lake Locations and Computed Fish Mercury Levels[a] at Standard Sizes (Lake Numbers Correspond to Those in Figure 1)

lake no.	lake name	decimal latitude	decimal longitude	Hg, ppm northern pike	Hg, ppm walleye
1	Adams	47.9917	91.1264	0.31	0.25
2	Amber	47.9528	91.1814	0.67	0.62
3	Ash	48.2153	92.9369	0.24	0.21*
4	Ball Club	47.9111	90.4861	0.18	0.20
5	Ball Club	47.3630	93.9500	0.30	0.28*
6	Basswood	48.0522	91.4397	0.50	0.46
7	Bear Island	47.7736	91.9867	0.43	0.41
8	Bearhead	47.7806	92.0833	0.21	0.16
9	Big	48.0728	92.0000	0.36	0.36
10	Big Moose	48.0472	92.0819	0.28	0.26*
11	Birch	47.7708	91.7611	0.29	0.33
12	Black Duck	48.2042	92.8294	0.24*	0.21
13	Black Island	47.5250	93.5260	0.64	0.69*
14	Burntside	47.9264	92.0000	0.31	0.34
15	Crane	48.2861	92.4667	0.88	1.06
16	Devil Track	47.8236	90.4028	0.39	0.39*
17	Dunnigan	47.7075	91.6311	0.49*	0.51
18	Echo	48.1717	92.4653	0.53*	0.56
19	Ek	48.4710	92.8350	0.52	0.55*
20	Elbow	48.0000	92.6444	0.38	0.37*
21	Fall	47.9444	91.7500	0.43	0.36
22	Fish	46.8850	92.2890	0.33	0.21
23	Gabimichigami	48.0625	91.0208	0.33	0.32*
24	Garden	47.9236	91.7500	0.43	0.35
25	Ge-Be-On-Equat	48.2853	92.1083	0.55	0.74
26	Gunflint	48.1000	90.6778	0.32	0.39
27	Homer	47.9042	90.6778	0.32	0.31*
28	Hustler	48.2292	92.1575	0.92	1.03*
29	Isabella	47.8117	91.2867	0.51	0.53*
30	Jeanette	48.1403	92.2861	0.61	0.42
31	Johnson	48.3333	92.6167	0.39	0.30
32	Kabetogama	48.4750	93.0000	0.14	0.13
33	Kjostad	48.1133	92.6119	0.65	0.67
34	Lac La Croix	48.3486	92.1528	0.41	0.35
35	Little Cascade	47.8514	90.6528	0.61	0.65*
36	Loon	48.0764	90.6903	0.23	0.20*
37	Loon	48.2444	92.2667	0.85	0.95*
38	McDonald	47.8625	90.5236	0.26	0.23*
39	Moose	48.0833	92.7897	0.29	0.24
40	Mukooda	48.3450	92.4906	0.31	0.29
41	Namakan	48.4458	92.6958	0.26	0.25
42	Northern Light	47.9047	90.2389	0.23	0.20*
43	One	47.9208	91.4867	0.31	0.31
44	Oyster	48.2278	92.0981	0.88	0.98*
45	Parent	47.9647	91.3958	0.34*	0.33
46	Pelican	48.0750	92.9167	0.29	0.24
47	Prairie	47.3100	93.5430	0.59	0.63
48	Rainy	48.5417	92.5722	0.45	0.38
49	Saganaga	48.2139	91.0208	0.54	0.36
50	Sand	46.5080	92.5080	0.43	0.44*
51	Sand Point	48.4258	92.4806	0.47	0.70
52	Sandpit	48.0394	91.7894	0.65	0.66
53	Sawbill	47.8825	90.8778	0.37	0.36*
54	Sea Gull	48.1250	90.9500	0.18	0.13*
55	Shagawa	47.9153	91.8792	0.16	0.12
56	Slim	48.0125	91.9653	0.39*	0.39
57	Snowbank	48.0097	91.4028	0.31	0.15
58	Tooth	48.3981	92.6422	1.52	1.75*
59	Trout	47.2560	93.4060	0.48	0.63
60	Trout	47.9528	92.2981	0.29	0.30
61	Vermilion	47.8750	92.2500	0.20	0.18
62	White Iron	47.8583	91.8125	0.42	0.50
63	Whiteface	47.3020	92.1700	0.94	1.05*
64	Wilson	47.6750	91.0736	0.17	0.22
65	Windy	47.7347	91.0792	0.64	0.69*

[a] Asterisk indicates value calculated from the other fish species.

Fish Mercury Residue Database. The fish residue data (from fillets, on a wet weight basis) were collected primarily over the period 1980–1987 (6, 16). Data were
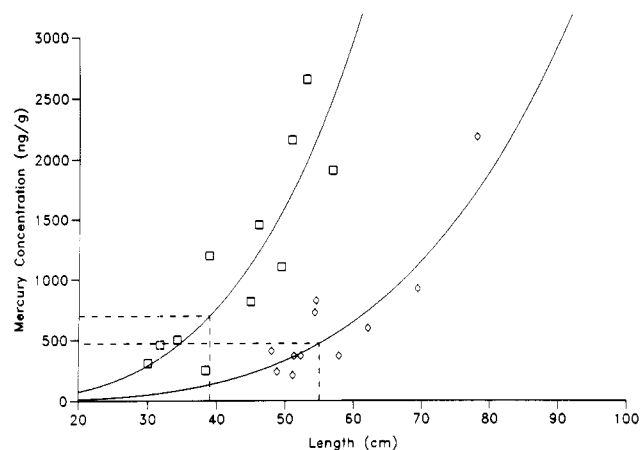

Figure 2. Examples of fish mercury residue level vs length for walleye (□) and northern pike (◇) for Sand Point Lake. The regression function is fish Hg = A(length)^K where A and K are constants. Regression results are as follows. Walleye: $A = 3.34 \times 10^{-3}$, $K = 3.34$, $r^2 = 0.79$, $N = 12$. Northern pike: $A = 1.86 \times 10^{-4}$, $K = 3.68$, $r^2 = 0.70$, $N = 11$. The broken lines show the mercury levels at the standard lengths (39 and 55 cm for walleye and northern pike, respectively).

used to examine length vs weight and mercury concentration vs length relationships for each species in each lake. The two species with the most data were walleye and northern pike, the only species considered in this study. The strongest correlation was obtained for both relationships when log–log transformations of the data were used. An example of the fish residue data vs length with regression lines and their distributions is plotted in Figure 2 for Sand Point Lake.

In order to represent the mercury concentration in fish from a given lake for comparison across all lakes, we selected a standard fish length (and weight) and computed the mercury concentration from the log–log regression equation for each lake. This differs from the approach of Helwig and Heiskary (26), who analyzed fish data by size classes. The choice of standard length was based on two considerations: (1) the need to maximize the accuracy of comparisons between species and (2) standard lengths used by others.

The first consideration is necessary to extend the fish residue database for northern pike. That is, we extended the number of lakes with northern pike residue values from 59 to 65 by calculating the pike residues for six lakes based on the walleye values. The functional relationship (based on 42 Minnesota lakes) between the sizes of the two species and the correlation of calculated mercury residue levels between the species at the various sizes is shown in Figure 3. The best Pearson correlation coefficient of mercury concentrations between walleye and northern pike is 0.88 when their lengths are about 39 and 55 cm (corresponding to 0.59 and 1.0 kg), respectively. The second need is simultaneously met by adopting the standard 1-kg pike used by Hakanson (27). The geometric mean functional relationship equation (28) resulting from use of these standard lengths is northern pike mercury = 0.829 × walleye mercury + 0.067; $r^2 = 0.77$, $N = 42$. Figure 4 shows this relationship for the calculated concentrations of mercury residue levels at the standardized sizes. Because the database for northern pike ($N = 59$) is more complete than that of walleye ($N = 42$), we chose to report all major results involving fish residue in terms of northern pike. The locations of 65 lakes along with the calculated standard fish mercury concentrations are depicted in Figure 1.

Lake Water Chemistry and Watershed Database. Lake water chemistry and watershed variables have been
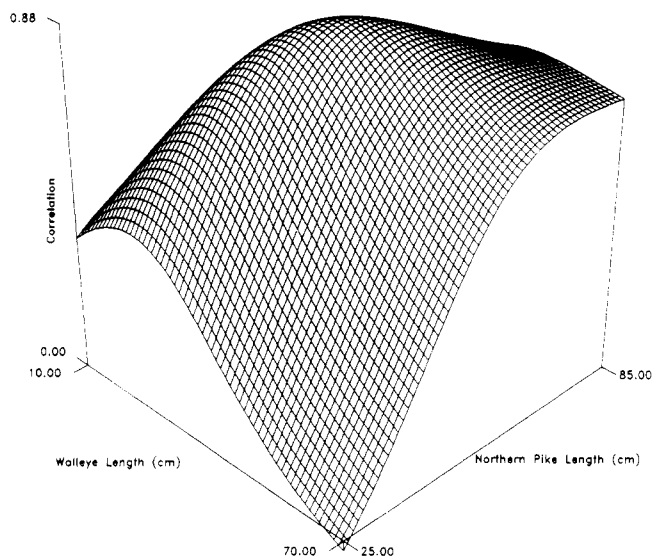
Figure 3. Computed correlation between mercury levels in walleye for various lengths. The maximum is ~0.88 for the pair 39 (walleye) and 55 cm (northern pike).
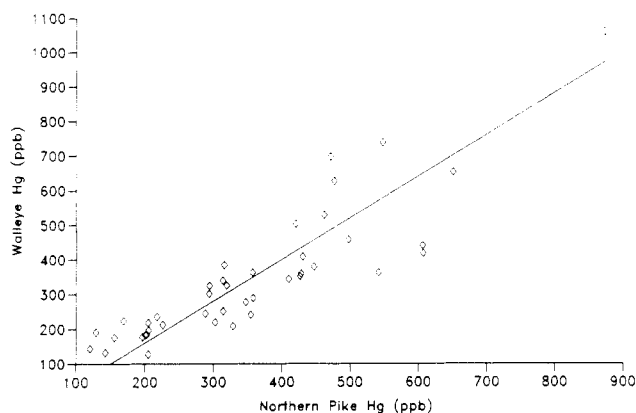

Figure 4. Fish mercury residue levels (standard lengths) for walleye and northern pike for lakes where both species were present. The regression equation is walleye Hg = $-0.81 + 1.21 \times$ northern pike Hg; $r^2 = 0.77$; $N = 42$, where both axes are assumed to have the same precision.

described previously (*15*). The particular subset of 72 watersheds selected from the original 276 is generally representative of most measured parameters. Sixty-three lakes are of the drainage type and should reflect a significant opportunity for geologic influences.

Data Analysis Approach. Statistical evaluations were carried out in three stages. First, the variable distributions were examined to determine if a mathematical transformation was necessary to meet the distribution assumptions required for statistical analysis. This included the evaluation of outliers. Second, a series of correlation matrices was developed to identify the strengths of relationships between variables. Finally, predictor equations were developed for mercury in water, sediment, zooplankton, and fish by use of stepwise and best subsets regression analysis (*29*).

Results

Table II shows a summary of the analytical determinations of mercury. These results indicate that the detection limits for the EPA water method (*22*) can be substantially and routinely improved to a lower limit of ~2 ng/L. The most significant factor in improving the detection limit is the reduction of the reagent blank value (and its variability) by prescreening reagents to select the
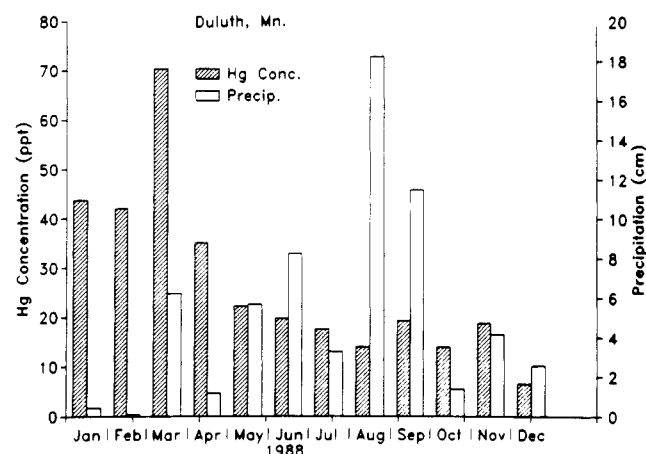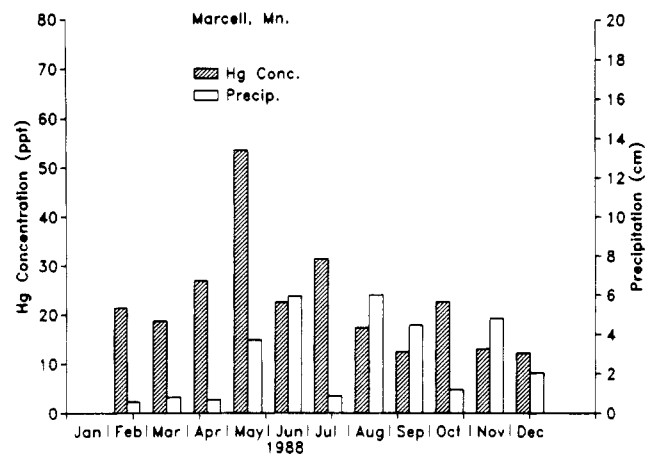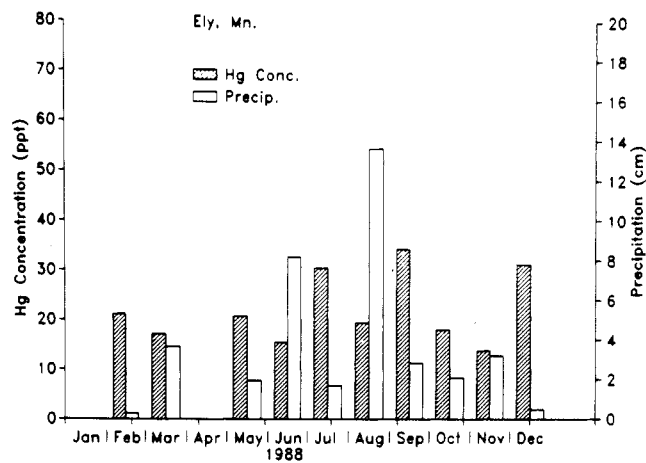

Figure 5. Mercury concentration in precipitation (rain and snow) averages (volume-weighted monthly) along with monthly precipitation depth totals (based on MIC volumes) at Duluth, Marcell, and at Fernberg Road near Ely, MN.

lowest mercury content. Routine blank values of 4 ng/L can be observed.

Table III summarizes the measured values for mercury in precipitation, lake water, sediments, and plankton and calculated mercury residue values for standard sized northern pike. Although data exist for over 100 chemistry and watersheds variables for most of the lakes, we list only those that showed some relationship (Table IV) with the mercury parameters.

Precipitation. The volume-weighted annual mercury concentrations in precipitation averaged 18, 19, and 22 ng of Hg/L, respectively, for Marcell, Ely, and Duluth, MN, and are similar to those reported earlier for Duluth (*13*). The monthly volume-weighted averages along with the precipitation depth data for each monitoring site are shown

Table II. Analytical Characteristics of Mercury Measurements

parameter	no. of runs	detectn limit in flask, ng/L	precision[a] lab	precision[a] field	absolute error,[b] %
precipitation	55	2.2	1	3	−1
lake water	13	2.2	1	1	−2.5
sediment	15	6.6	27	26	−1
zooplankton	18	2.1	22	28	

[a] One standard deviation. Precipitation and lake water values are in nanograms per liter; zooplankton and sediment are in nanograms of Hg per gram. [b] Based on deviation from National Bureau of Standards samples.

in Figure 5. These concentrations compare with estimated yearly averages of 5–30 ng of Hg/L in precipitation over continents around the globe (*30*) and with measured values ranging from 2 to 28 ng of Hg/L at Dorset, Ontario, for 1987–1988 (*31*). By use of mercury concentration and long-term precipitation data, wet annual mercury deposition inputs for each of the study lakes were computed with values ranging from 10.4 to 15.4 μg of Hg/m^2.

Lake Water. Of all the data sets, the lake water samples were closest to the detection limit (averaging 2.2 ng of Hg/L), with all samples from 31 lakes measuring at less than detection. Different samples from 15 lakes measured both above and below detection, whereas the remaining 31 lakes were all above; the highest water value measured was 7 ng of Hg/L. These values are similar to those found by Bloom (*32*) in other U.S. waters and by Hultberg et al. (*11*) in Scandinavian waters, where 0.2–11 and 1–7 ng of Hg/L were measured, respectively.

Sediments. Sediment mercury concentrations (dry weight basis) ranged from 34 to 753 ng of Hg/g and averaged 174 ng of Hg/g for all lakes sampled. It was concluded, however, that the concentrations for two lakes were high outliers apparently because of municipal discharges (*33*) from nearby population centers (Shagawa Lake—Ely and Trout Lake—Bovey and Coleraine). Therefore, we did not include these two sediment values for further analysis. The new range of values was 34–331 ng of Hg/g with an average of 160 ng of Hg/g. These values are similar to those found in Wisconsin and central and northern Sweden where <100–300 (*34*) and 70–400 ng of Hg/g (*12*) were measured, respectively.

Zooplankton. Mercury concentrations in zooplankton (dry weight basis) ranged from about 10 to 210 ng of Hg/g and averaged 90 ng of Hg/g. These values are similar to those listed by Lindqvist (ref 30; 50–200 ng of Hg/g) for Swedish lakes.

Northern Pike. Mercury residue levels in northern pike (wet weight basis) computed for a 55-cm length (1 kg) yielded values ranging from 140 to 1500 ng of Hg/g with an average of ~450 ng of Hg/g. For Swedish lakes, Hakanson (*27*) found larger average levels ranging from 450 to 1200 ng of Hg/g with an overall mean of ~820 ng of Hg/g for 1-kg northern pike grouped by lake pH.

Correlations and Regressions. Table IV shows those variables with correlation coefficients having the strongest relationships ($p < 0.01$) with the mercury concentration variables. For these variables, all correlations at the 95% significance level ($p < 0.05$) are also listed. We chose to list only wet sulfate to represent the atmospheric inputs group because these variables were highly intercorrelated ($r = 0.99$).

The predictor variable candidates were chosen from the significant variables listed in Table IV. Table V lists the best resulting equations with the variables listed in order

of significance. Mercury in northern pike is considered both with and without mercury in zooplankton as a predictor.

In interpreting these multiple regression results we recognize that several resulting significant predictor variables correlate to a high degree with other candidates. This means, for example, that there is a likelihood for a variable such as acid neutralizing capacity (ANC) to be replaced by a variable such as conductivity by choosing a slightly different set of lakes. The list of significant variables from Table V that have strongly associated correlates is shown in Table VI along with those correlates.

In order to test the robustness of our total mercury in water measurements with regard to establishing significant relationships, a column in Table IV was included where lakes with all measurements less than the detection limit were removed from consideration. The results of this test sustained many of the correlations and also revealed the most reliable relationships.

Discussion

Mercury in Lake Surface Water. A comparison between the mercury concentrations in precipitation (~18 ng of Hg/L) and the concentrations in lake surface water (~2 ng of Hg/L) indicates that mercury is removed from water in significant quantities. This is even more evident when one considers the total watershed hydrology. Using evaporative concentration ratio estimates, we computed that the mercury (acting as a nonreactive, conservative substance) in lake water would range from 42 to 117 ng of Hg/L with an average of 70 ng of Hg/L for the study lakes. Therefore, one might expect considerable mercury flux going to such sinks as sediments (*12, 35*) and soils (*36, 37*).

If we assume that (1) the mercury concentration in a lake is nearly homogeneous, (2) the amount of water outflow is the same as the inflow, (3) runoff and precipitation are constant with time, (4) the loss from sedimentation and vaporization is proportional to the concentration in the water multiplied by the lake surface area, and (5) remobilization from the sediment is negligible, then a mass balance equation similar to that of Snodgrass et al. (*38*) can be written:

$$V \, dC/dT = PAC_p + RW(C_i - C) - KAC$$

where V is the volume of the lake, C is the mercury concentration in the lake water, T is time, P is the precipitation depth per unit time, A is the lake area, C_p is the mercury concentration in precipitation, R is the watershed runoff depth per unit time, W is the watershed area, C_i is the concentration of the inflow water, and K is a rate constant.

After solving this differential equation, we can write an expression for K by setting C equal to some equilibrium value as T approaches infinity. That is

$$K = [PAC_p + RW(C_i - C_w)]/(AC_w)$$

where C_w is the equilibrium lake water concentration and is approximated by our measured surface water conditions. Although values would vary for each mercury species, the half-life of all mercury forms, taken as a whole in the water column, may be written as

$$T = V \ln (2)/AK$$

By use of these equations on a subset of drainage lakes that had mercury in water concentrations above the detection limit ($N = 34$), the values for the half-life of mercury in the water column were computed for each. The averages were 0.60 ± 0.54 and 0.21 ± 0.20 years, respectively, for

Table III. Summary of Mercury Concentrations and Watershed Characteristics for the Study Lakes in Northeastern Minnesota

	N	mean	median	SD	min	max
atmospheric annual wet inputs for Hg[a]						
average concn, ng/L	80	18.7	18.6	1.26	16.8	24.2
deposition lake, μg/m^2	80	12.6	12.7	1.15	10.4	15.4
deposition immediate, μg/m^2	72	28.2	24.8	9.90	14.8	58.4
deposition total, μg/m^2	72	1020	126	2870	29	16600
mercury levels and related measurements						
surface water, ng/L	77	2.47	2.30	1.10	0.90	7.00
surface sediment, ng/g	77	174	154	109	34	753
zooplankton, ng/g	53	87.9	86.4	48.8	9.50	209
zooplankton density, mg/m^3	77	148	71.0	237	3.3	1560
northern pike (55 cm), ng/g	65	439	390	236	140	1520
atmospheric wet annual inputs for ions						
sulfate, μequiv/L	72	24.6	24.8	2.51	19.8	28.8
ammonium, μequiv/L	72	14.7	14.8	0.540	13.7	16.3
nitrate, μequiv/L	72	14.1	14.2	1.32	11.6	16.3
hydrogen ion, μequiv/L	72	10.4	10.4	2.96	5.10	15.7
lake water chemistry						
ANC,[b] μequiv/L	72	238	179	172	49.3	923
pH	71	7.05	7.00	0.362	6.10	8.24
conductivity, μS/cm at 25 °C	80	64.3	36.2	98.9	15.4	672
color, Pt–Co units	71	42.2	30.0	28.7	4.20	130
secchi disk depth, m	77	2.47	2.20	1.32	0.40	7.60
chloride, mg/L	67	0.538	0.370	0.411	0.110	1.77
total organic carbon as C, mg/L	67	7.48	6.76	2.53	3.53	14.3
magnesium, mg/L	72	1.53	1.30	0.856	0.500	4.70
calcium, mg/L	72	4.30	3.42	2.40	1.19	13.0
sodium, mg/L	72	1.08	0.958	0.356	0.428	2.41
potassium, mg/L	72	0.510	0.488	0.276	0.156	1.93
aluminum, mg/L	72	0.0990	0.0800	0.0506	0.0220	0.240
iron, mg/L	72	0.184	0.150	0.140	0.0190	0.615
strontium, mg/L	72	0.0168	0.0155	0.00829	0.00700	0.0690
areas						
lake surface, ha	72	2640	328	10700	24	89400
immediate watershed, ha	72	5140	650	20300	55	168000
immediate/lake surface ratio	72	2.24	2.05	0.72	1.30	4.40
relief						
site elevation, m	72	441	432	67.5	338	587
topographic high immediate, m	72	494	476	69.8	378	664
hydrology						
annual precipitation, m/year	80	0.672	0.665	0.048	0.560	0.762
annual evaporation (land), m/year	72	0.476	0.476	0.017	0.446	0.506
annual runoff, m/year	72	0.203	0.196	0.060	0.103	0.315
lake renewal time, year	72	62.4	49.1	46.8	5.85	202
total renewal time, year	72	4.84	2.18	7.58	0.0100	45.4
evaporative concn ratio[c]	72	3.80	3.60	1.01	2.24	6.32
sulfate reduction index	71	0.799	0.780	0.245	0.330	1.28
lake morphometry and location						
latitude north, decimal deg	80	47.974	47.996	0.34	46.508	48.542
longitude west, decimal deg	80	91.793	91.922	0.91	90.067	93.950
maximum depth, m	72	18.8	15.0	17.2	1.50	84.0
mean depth, m	72	7.27	5.70	5.94	1.08	29.0
lake volume, m^3	72	2.33×10^8	0.15×10^8	7.4×10^8	4.35×10^5	5.47×10^9
land cover						
% forest	63	81.7	83.0	9.18	46.2	94.7
% water	63	16.8	16.2	8.25	4.10	38.5

[a] Based on 1988 Hg concentrations along with long-term precipitation data. The deposition parameters are defined as follows: deposition lake, calculated deposition falling directly on lake surface; deposition immediate, calculated deposition falling directly on lake surface plus calculated runoff from immediate watershed (assumes 100% Hg transport to lake); deposition total, calculated deposition falling directly on lake surface plus calculated runoff from total watershed (assumes 100% Hg transport to lake). [b] ANC, acid neutralizing capacity. [c] Calculated from precipitation runoff, and evaporation.

estimated differences between the stream inflow and outflow mercury concentrations ($C_i - C_w$) of 2 and 20 ng of Hg/L. The large deviations could stem from (1) lake to lake variability in mercury inputs and forms, (2) violations of the lake equilibration assumption and the assumption regarding a constant precipitation and runoff with time (i.e., if lake sampling occurred just after a precipitation event, C_w might be anomalously high), and (3) the magnitude of the analytical precision (Table II) relative to the values for the lake water mercury measurements (Table III).

It is interesting to note that the correlations between the mercury in sediment concentrations and computed individual half-life values corresponding to the two estimated differences in stream inflow and outflow concentrations (2 and 20 ng of Hg/L) were −0.41 ($p < 0.05$) and −0.49 ($p < 0.01$), respectively. This is consistent with one of the initial assumptions that sediments act as mercury sinks.

Also, computations of half-life to renewal time ratios, for the same inflow and outflow conditions, yielded values of 0.39 ± 0.35 and 0.08 ± 0.04, respectively. This would

Table IV. List of Variables, and Their Correlations, Which Correlate with a Mercury Variable to a 99% or Greater Significance Level[a]

variable	transform	log (water)[b]		(sediment)$^{1/2}$[c]	zooplankton	log (northern pike)
atmospheric annual wet inputs for mercury						
dep. lake				0.29*		
dep. imm	(log)			0.39		
mercury levels and related measurements						
surface water	(log)			0.35	0.45	0.42
surface sediment[c]	(sqrt)	0.35	0.28*			
zooplankton		0.45	0.44			0.60
zooplankton density	(log)				−0.50	
northern pike	(log)	0.42	0.38*		0.60	
atmosphric annual inputs for ions						
wet sulfate				0.35		
lake water chemistry						
conductivity	(log)	−0.31*			−0.45	−0.36
ANC	(sqrt)	−0.35		−0.27*	−0.51	−0.41
pH		−0.47	−0.37*	−0.32	−0.42	−0.45
color	(sqrt)	0.29*	0.34*	0.43		0.27*
chloride	(log)				−0.36*	
total organic carbon	(log)	0.48	0.51	0.39	0.33*	0.51
magnesium	(log)				−0.45	−0.31*
calcium	(log)	−0.36			−0.48	−0.41
sodium	(log)				−0.31*	
potassium	(log)			−0.33		
aluminum	(sqrt)	0.26*		0.25*		0.30*
iron	(log)	0.53	0.47	0.49	0.41	0.42
strontium	(log)	−0.32		−0.29*		
secchi		−0.24*		−0.29*		
areas						
lake surface	(log)	−0.38		−0.39	−0.39	
immediate wtrshd	(log)	−0.37		−0.35	−0.36*	
imm/lake ratio	(log)			0.32		
relief						
site elevation				0.34		
top. high immed	(log)			0.25*		−0.29*
hydrology						
precipitation				0.32		
runoff				0.34		
evaporation, land				−0.35		
lake renewal time	(sqrt)	−0.27*		−0.55		
total renewal time	(log)			−0.42		
evap. concn ratio	(log)			−0.37		
sulfate red. index				0.34		
lake morphometry and location						
longitude				−0.32		
maximum depth	(sqrt)	−0.32		−0.46		
mean depth	(sqrt)	−0.31		−0.46		
lake volume	(log)	−0.42		−0.45	−0.31*	
land cover						
% forest	(sqrt)		0.39*	0.57		
% water	(sqrt)		−0.39*	−0.56		

[a] Correlations that are at the 95% significance level are also shown for the list and are marked with an asterisk. When transforms were used, the function is indicated in parentheses. [b] Mercury in water is listed two ways: using all values ($N = 77$), and omitting lakes consistently below the detection limit (N used $= 46$). [c] Mercury in sediment values for Trout (Itasca Co.) and Shagawa Lakes were omitted.

suggest that a somewhat significant fraction of mercury inputs to the lake may escape sedimentation, as was concluded by Norton et al. (11).

It is evident from the equations for K and T that lower mercury concentrations in lake water tend to yield lower calculated half-life values. The concentrations of mercury in water corresponding to the subset of lakes used in these calculations averaged 3.0 ± 1.2 ng of Hg/L. If the low concentrations were better known for the 24 lakes (less than detection) that were excluded from this subset of lakes, then their inclusion would result in lower half-life averages.

Although these half-life results are highly variable and slightly overestimate the averages for the entire lake set, the average values are conspicuously higher than the 14-day half-life values obtained by Hesslein et al. (35) using radio tracer techniques on a whole-lake experiment. The mercury additions used in that experiment consisted of mercuric chloride only, while forms normally incident to a lake vary. The presence of even small amounts of long-lived forms can significantly influence the apparent overall half-life.

The positive correlation that occurs between mercury in water and total organic carbon (TOC) suggests an affinity between mercury and natural organic compounds. This binding with dissolved organic material increases the ability of mercury to persist in the water column and resist sedimentation. In fact, humic acid has even been used to preserve mercury in water samples collected in the field for later analysis (39). High TOC values can also indicate

Table V. Multiple Regression Equations Resulting from Stepwise Analyses[a] (Logarithms Are in Base 10)

Hg variable[b]	regression values[b]	N	r^2
log (Hgwat)	= 0.93 (±0.41) + 0.55 (±0.13) × log (TOC) − 0.074 (±0.026) × log (lksrfa) − 0.118 (±0.056) × pH	64	0.43
$(\text{Hgsed})^{1/2}$	= 14.1 (±3.4) + 1.38 (±0.27) × (% forest)$^{1/2}$ − 0.34 (±0.12) × log (lkren) + 4.7 (±2.0) × log (Hgdepim)	59	0.53
Hgzoo	= 170 (±48) − 57 (±15) × log (zdens) + 127 (±40) × log (TOC) − 24 (±8) × log (imwshd)	42	0.45
log (Hgpike)	= 1.69 (±0.18) + 0.0025 (±0.0005) × Hgzoo + 0.57 (±0.20) × log (TOC) + 0.75 (±0.36) × Al	34	0.62
log (Hgpike)[c]	= 3.5 (±0.6) + 0.65 (±0.18) × log (TOC) − 0.21 (±0.07) × pH	53	0.37

[a] Applicable to this study region where annual airborne wet mercury depositions range between 10 and 15 $\mu g/m^2$. [b] Variables in the equations are represented by abbreviations defined as follows: Al, aluminum concentration in water; % forest, percent of watershed that is forest; Hgdepim, mercury loading considering immed wtrshd (see footnotes in Table III); Hgpike, mercury concentration in northern pike; Hgsed, mercury concentration in sediment; Hgwat, mercury concentration in water; Hgzoo, mercury concentration in zooplankton; TOC, total organic carbon concentration in water; imwshd, immediate watershed area; lksrfa, lake surface area; lkren, lake renewal time; zdens, zooplankton density in lake water. [c] Excludes mercury in zooplankton as a predictor.

more contributions from watershed inflows discussed below. Note that TOC is the most significant predictor in the multiple regression (Table V).

Other variables of interest that correlate with mercury in water are pH, calcium, iron, and mercury in zooplankton and northern pike. The reasons for the inverse relationship with pH are unclear in view of the results of Schindler et al. (40), who found that increasing acidity decreased the solubility of mercury. Also, Winfrey and Rudd (11) stated that decreasing pH increased mercury binding to particulates. This could tend to remove mercury from the water through settling. The principal reason that calcium and iron appear as significant may be that they covary strongly with pH (r = 0.82) and TOC (r = 0.73), respectively. Stepwise regressions show that these covarying parameters do not appear simultaneously as significant.

Sources of Mercury Inputs

To investigate the existence of current or recent point sources for lakes located near population centers, we

checked for anomalously high mercury in sediment values. Only two lakes (Shagawa and Trout) appear to have been affected. Two other possible sources stem from the past use of mercury in paper mill operations and gold mining. It was concluded, however, that no available evidence supported mercury contamination influence in the study lakes from these activities.

Mercury from Bedrock and Soils. A Canadian study concluded that mercuriferous belts generally are not found east of the Rocky Mountains (18). Furthermore, it was found that the average mercury content in gabbros and granites (typical rock types along with some glacial deposits found in our study region) were 28 and 62 ng of Hg/g, respectively. To confirm these findings, we analyzed representative bedrocks of four watersheds (Kjostad, Meander, Dunnigan, and Thrush) in the study region and found low mercury concentration levels ranging from 5 to 16 ng of Hg/g for these gabbros and granites.

Jonasson and Boyle (in ref 18) found that soils away from mercury deposits had concentrations ranging from 20 to 150 ng of Hg/g and averaging 70 ng of Hg/g. These values are similar to our measurements of 12–220 ng of Hg/g, for the above four watersheds. The average of these data (87 ng of Hg/g) is about $^1/_2$ that of mercury in sediments. Further details of these bedrock and soil measurements may be found in Smith (41).

Mercury from Atmospheric Deposition. For mercury in sediments there is a significant positive relationship with atmospheric deposition parameters, but there are no significant correlations with our bedrock geology and surficial deposit parameters. Considering this along with low mercury levels in bedrock and high precipitation levels suggests that the source of mercury in these Minnesota lakes is primarily atmospherically derived. On the basis of several other discussions (18, 36, 37), it is thought that any contributions from soils also originate from the atmosphere.

In a companion study using several sediment core sites on each of four lakes (Dunnigan, Kjostad, Meander, and Thrush), Henning et al. (10) studied the stratigraphy and determined accumulation rates in cores as well as on a whole-lake basis. We compared these results with precipitation loadings derived from our work (calculated for each lake) and found that, on average, 60% (range 47–74%) of the mercury in lake sediment can be accounted for by direct wet atmospheric deposition to the lake surface alone. The remaining 40% of the mercury accumulated in the sediments was attributed to inputs from the watershed. These conclusions agree with those by Mierle (31) using other methods and different study lakes.

The most statistically significant variable relating to mercury in sediment is percent forest cover, suggesting a mechanism by which the presence of forest increases the mercury loadings to watersheds and lakes. This is con-

Table VI. Significant Predictor Variables from Table V and Their Most Important Correlates in Order of Correlation Strength

significant variable	variables with indicated absolute correlations		
	$\|r\| \geq 0.90$	$0.90 > \|r\| \geq 0.80$	$0.80 > \|r\| \geq 0.70$
Al			
% forest	(−) % water		color
Hgdepim	imwshd/lake area ratio		
imwshd	lake surface area, lake vol	tot wshd area, lksrfa	
lksrfa	imwshd, lake vol	tot wshd area	
lkren		mean depth, max depth	lake vol
pH		ANC, conductivity, Ca	
TOC	organic anion	color	Fe
Zdens			

sistent with conclusions drawn by Lindberg et al. (42) and Jaworski (in ref 18), who found that direct deposition of metallic mercury from air to vegetation can be a significant source of mercury to aquatic systems.

On the basis of this evidence, we surmise that plant material (such as leaf litter and decomposition products) carried into the lakes constitutes a secondary source of mercury that originates from the atmosphere. Furthermore, note that these processes are somewhat manifested in the TOC composition of lake water.

Several other interesting relationships between mercury in sediments and other variables are shown in Table IV. The fundamental reasons for the significance of many of these are probably similar. For example, color, TOC, iron, and percent forest cover all covary and may reflect increased loadings from the secondary sources, i.e., vegetative sorption. These secondary sources are also implicated by the positive correlation with the immediate watershed area to lake area ratio.

Complexities of Mercury in Watershed Interrelationships and Biotic Accumulation

Morphometric Factors. Those measures dealing with the size of the lake (such as volume, area, depth, and renewal time) all vary inversely ($r \sim -0.5$) with mercury in sediment. Some possible explanations for this observation are as follows: (1) sedimentation rates that depend on lake size may serve to vary the dilution of the sediment mercury accumulations; (2) similar correlations also exist between lake size parameters and the calculated mercury deposition to the lake; and (3) the equation for the half-life of mercury in the water column varies linearly with the average lake depth (volume/area). It is interesting to note the results when the lakes data are divided into two categories, those that are predicted to stratify and those that are not (43). We found for the stratified set ($N = 37$) that the correlations became stronger ($r \sim -0.6$), whereas those for the unstratified set ($N = 35$) became nonsignificant.

Mercury in Zooplankton. Mercury in zooplankton varies positively with mercury in water. In fact, the variables that relate to mercury in zooplankton are generally the same as those relating to mercury in water, with the exception of zooplankton density in the lake, which is most significant. A possible explanation is that high productivity can yield dilution of mercury within the biomass (17). Although the chloride concentration correlates at only $r = 0.5$ with the immediate watershed area, it was found that chloride could also be used as the third predictor variable in the mercury in zooplankton regression.

If we express the mercury in zooplankton on a concentration in lake water basis we find a range of 0.00–0.05 ng of Hg/L (average 0.01 ng of Hg/L). On converting these numbers to those based on the percentage of total mercury in the water we get a range of 0.01–1.8% (average 0.40%).

Mercury in Northern Pike. Table IV shows clearly that mercury in northern pike (henceforth also referred to as fish) is strongly related to total mercury concentrations in water. This shows the importance of mercury methylation and uptake occurring in the water column (20), which are most likely proportional to some exponent of the total mercury concentration (19). Further evidence of the importance of this source of methylmercury is demonstrated by the high correlation of fish mercury with TOC. This variable can relate to the watershed input of mercury as well as the abundance of microorganisms producing methylmercury.

The inverse relationship between fish mercury and pH is consistent with findings showing that methylation rates increase as pH decreases in the water column (44). This is also the case for methylation in the lake sediments (17).

With the exception of aluminum, we think that the other high correlates with fish mercury in the lake water chemistry group are significant because of their high covariance with either pH or TOC. It is interesting to note that in the multiple regression that includes mercury in zooplankton, aluminum is significant but pH is not. This may result from the large degree of variation due to pH already accounted for in the mercury in zooplankton variable.

Our observations regarding either TOC, pH, or their close correlates are similar to results from a number of other lake studies in various regions: Minnesota (26), Wisconsin (8, 34), Ontario (45, 46), and Sweden (27).

The highest correlate with fish mercury is mercury in zooplankton (Table IV), the most significant term in the multiple regression. This observation probably arises from two factors: (1) mercury in zooplankton and fish have a common source(s) of methylmercury; and (2) zooplankton affects fish through the food chain. The food chain and direct accumulation of methylmercury from water through the gills are both important. For northern pike, Jernelov (47) states that the two sources are about equal in contribution to the total amount accumulated, but this could vary depending on the trophic level (48).

It is noteworthy that total mercury in sediment does not seem to significantly correlate with fish mercury (Table IV). Scheider (11) obtained similar results for Ontario lakes, whereas others have observed the opposite (27, 34, 49). One reason that mercury in sediment does not consistently correlate with mercury in fish may be the extreme variability in net methylmercury production in sediment from lake to lake as a result of a variety of factors (other than total mercury concentration). Some of these are as follows: organic content of sediments and the amount of mercury occurring as sulfides (47), aerobic or anaerobic conditions, and the amount of iron present (50). Another reason could be that the water column may be the key site for net methylmercury production.

It was found, however, that the stratified lakes subset yielded a significant correlation between fish mercury and mercury in sediment of 0.40 ($p < 0.05$) whereas the results for the unstratified set remained nonsignificant. The reason for this finding is uncertain.

Summary and Conclusions

Eighty northeastern Minnesota lakes were investigated to study elevated mercury residue levels in fish. Seventy-seven of these were sampled to determine mercury concentrations in water, sediment, and zooplankton, while mercury loadings from precipitation for each were calculated on the basis of results of three monitoring stations. Watershed and chemistry characteristics for 72 lakes had been determined previously and 65 had fish mercury residue data.

The annual average volume-weighted mercury concentrations were measured in precipitation for 1988 at Mercell, Ely, and Duluth, MN, and found to be 18, 19, and 22 ng of Hg/L, respectively. The calculated yearly wet depositional loadings for lakes across the study region ranged from 10 to 15 μg of Hg/m^2.

Mercury levels in surface water ranged from <2 to 7 ng of Hg/L and averaged 2.5 ng of Hg/L with 40% of the lakes being consistently below the detection limit. These values were found to be significantly correlated with TOC, pH (negative), and mercury levels in zooplankton and northern pike. The correlations with TOC and pH probably arise as a result of the influence of these factors on the persistence of mercury in the water column. Moreover, TOC levels indicate possible secondary atmospheric

mercury inputs from the watershed. Calculations regarding mercury lifetimes in the water column compared to lake water renewal times indicated that appreciable fractions of mercury entering a lake may escape sedimentation.

Mercury levels in surface sediment (0–6 cm), on a dry weight basis, ranged from 34 to 331 ng of Hg/g with an average of 160 ng of Hg/g (two outliers removed). Some of the notable correlates with these values were TOC, percent forest cover in the watershed, mercury deposition variables, mercury in surface water, pH (negative), lake size related variables (negative), and calculated values for the half-life of mercury in the water column (negative). The correlations with percent forest cover and TOC indicate the importance of mercury sorption in vegetative materials. The correlations with mercury deposition variables indicate the importance of precipitation as a mercury source.

Mercury levels in zooplankton (>80 μm), on a dry weight basis, ranged from 9 to 200 ng of Hg/g with an average of 88 ng of Hg/g. The total mercury mass in zooplankton represents less than 1% of the total mass in the water column. Some of the notable correlates were mercury in water, mercury in northern pike, zooplankton density in the lake (negative), pH (negative), and TOC. The correlation with mercury in water indicates the direct pathway of bioaccumulation from water. The negative correlation with zooplankton density may be caused by mercury dilution in the biomass.

The mercury levels in a 55-cm (1-kg) northern pike for these Minnesota lakes averaged, on a wet weight basis, 450 ng of Hg/g and ranged from 140 to 1500 ng of Hg/g. The highest correlation of mercury residues between northern pike and walleye occurred for fish lengths of 55 and 39 cm, respectively. Some of the notable correlates were mercury in water and zooplankton, TOC, iron, and pH (negative). These correlations suggest complex pathways of net methylmercury production and the importance of bioaccumulation from both water and the food chain.

The primary source of mercury in these Minnesota lakes was found to be of atmospheric origin. Geologic and point source contributions were not significant. Transport from soils and organic material may also be important, but the mercury from these probably originates from precipitation and direct atmospheric sorption by watershed components.

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Novel Chlorinated Terphenyls in Sediments and Shellfish of an Estuarine Environment

Robert C. Hale, * **John Greaves, Kathryn Gallagher, and George G. Vadas**

School of Marine Science, Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, Virginia 23062

■ Polychlorinated terphenyls (PCTs) are structurally similar to polychlorinated biphenyls (PCBs) and have been used in analogous applications. Aroclor 5432, a PCT formulation whose congeners contain predominantly two to five chlorines, was detected in sediments and oysters from a saltmarsh creek and an adjacent Chesapeake Bay tributary, Back River. Reports of the occurrence of Aroclor 5432 are virtually nonexistent, although sporadic reports of the more highly chlorinated PCT formulation Aroclor 5460 have been published. Capillary gas chromatography with electrolytic conductivity detection was used for quantitation. Identifications were confirmed by both electron ionization and negative chemical ionization mass spectrometry. Sediment concentrations detected were as high as 250 000 $\mu g/kg$ (dry-weight basis). Oysters collected from these areas contained up to 35 000 $\mu g/kg$. This value is equivalent to 6300 $\mu g/kg$, on a wet-weight basis, and exceeds the applicable U.S. limit for PCBs in edible shellfish by more than a factor of 3.

Introduction

Concern over the presence of halogenated anthropogenic compounds in the environment has grown in the last two decades as a result of the persistence, bioaccumulation potential, and health consequences of these chemicals (1–5). Examples of members of this family of xenobiotics are polychlorinated biphenyls (PCBs), whose occurrence has been extensively documented in the scientific literature (6–8). In contrast to the notoriety of PCBs, limited attention has been paid, by either the scientific or regulatory communities, to the environmental distribution and biological consequences of polychlorinated terphenyls (PCTs), despite their structural similarity to PCBs and their extensive manufacture and use. PCTs have been used in sealants, hydraulic fluids, electrical equipment, plasticizers, paints, and investment casting waxes because of their desirable electrical and flame-retardant properties (9). Concern regarding the environmental consequences of PCBs led initially to their restriction to closed systems, such as transformers, and eventually to a prohibition of their commercial production. Similar regulatory attention was not paid to PCTs.

Manufacture of PCTs in the United States is reported to have begun in 1929 and to have ceased in 1972 (9). Production volume has been estimated to have been about 15% that of PCBs during the period 1959–1972 (10). Manufacturing increased steadily from 1959 and peaked in 1971 at approximately 20 million pounds (11). PCTs were also produced in France, Italy, Japan, and the Federal Republic of Germany (9). The last reported importation of PCTs into the United States occurred in 1979 (11). PCT and PCB products were marketed commercially under the trade name Aroclor by the Monsanto Co. and consisted of mixtures of congeners possessing varying degrees of chlorination. Each Aroclor formulation was designated by a four-digit numerical descriptor. The first two digits of each series denote whether the products contain only PCBs (e.g., 12xx and 10xx), PCTs (e.g., 50xx and 54xx), or a combination of PCTs and PCBs (e.g., 25xx and 44xx). The third and fourth digits denote the approximate percent chlorination by weight. For example, Aroclor 5432 consisted of PCTs containing approximately 32% by weight chlorine. Some minor contamination of the "pure" PCT formulations with PCBs was common and it has been argued that their usage is therefore controlled by regulations restricting PCBs (11).

Little information is available documenting the distribution, fate, and effects of PCTs in the environment, particularly for the lower chlorinated formulation, Aroclor 5432. This paper summarizes a study of the distribution of that mixture in sediments in and around Back River, VA, a tributary of the Chesapeake Bay. In addition, the bioavailability of this formulation to aquatic organisms was investigated by examination of indigenous shellfish. The Back River subestuary was deemed to be of particular interest since it not only supports commercial and recreational fishing activity but also is adjacent to a National