Environmental Pollution **50** (1988) 285–294

Modelling the Effect of Acidity on Mercury Uptake by Walleye in Acidic and Circumneutral Lakes

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(Received 17 March 1987; revised version received 18 June 1987;
accepted 27 August 1987)

ABSTRACT

An association between acidification of lakes and high mercury concentrations in fishes has been reported. In northern Wisconsin (USA), for example, walleye (Stizostedion vitreum) *in naturally acidic lakes have higher mercury concentrations than walleye in circumneutral lakes (Weiner, 1983). In this study a bioenergetic based model for mercury uptake is applied to identify potential causes of higher mercury concentrations in fishes living in acidic lakes. Application of the model to walleye populations in northern Wisconsin indicates that higher mercury concentrations in acidic lakes are most likely a result of both increased concentrations in the water and increased efficiencies of uptake from water. Higher concentrations in the water would result in higher concentrations in the food.*

INTRODUCTION

High concentrations of mercury in fish are associated with an increase in acidity. In Sweden, 10 000 lakes have northern pike (*Esox lucius*) with mercury concentrations greater than 1 mg kg^{-1}, and high mercury concentrations are associated with high acidity (Lindqvist *et al.*, 1984). In northern Wisconsin, walleye (*Stizostedion vitreum*) in naturally acidic lakes have higher mercury concentrations than walleye in circumneutral lakes (Wiener, 1983). Schneider *et al.* (1979) compared mercury concentrations in walleye from 59 Ontario lakes and found fish from low alkalinity lakes had higher mercury concentrations. Suns *et al.* (1980) found that mercury concentrations in yellow perch (*Perca flavescens*) from 14 lakes from Ontario were correlated with pH.

Environ. Pollut. 0269-7491/88/$03·50

Fish are exposed to methyl-mercury in their water and food. Wobeser (1975) found methyl-mercury concentrations in fish muscle were directly proportional to the concentrations in their food. McKim *et al.* (1976) observed a rapid uptake of methyl-mercury from water and no elimination. Lock (1975) used a stable isotope of mercury to show that rainbow trout obtained most of their methyl-mercury body burdens from their food rather than from the water. Huckabee *et al.* (1979) concluded that food and water were about of equal importance as sources of mercury for brook trout. Rodgers & Qadri (1982) estimated that yearling yellow perch in the Ottawa River, Ontario, obtained 62% of their mercury from food and 38% from the water. Elimination of methyl-mercury by fishes has been studied by McKim *et al.* (1976), Weisbart (1973) and Massaro & Giblin (1972); the rate of elimination is very slow.

If the higher concentrations of mercury in fish from acidic environments are caused by an increased rate of uptake, then either concentrations of mercury available to fish must increase with acidification or mercury must become more readily available with acidification. There are few laboratory data relating mercury uptake with acidity, but a study by Drummond *et al.* (1974) suggests that methyl-mercury uptake increased with a lowering of pH. Methyl-mercury is the major form of mercury in fishes, and while an increase in acidity apparently decreases formation of methyl-mercury, it increases the fraction of methyl-mercury in the aqueous phase (McDonald, 1985). Haines (1981) concluded that, with acidification, concentrations of heavy metals may increase both from direct input and from dissolution from the watershed or sediments.

The present study used the bioenergetic based model of Norstrom *et al.* (1976) to identify possible causes of elevated mercury residues in fish from low pH waters. Norstrom *et al.* (1976) and Jensen *et al.* (1982) applied the bioenergetics based model to describe contaminant uptake and Jensen *et al.* (1982) showed that the model could be applied to describe uptake of PCBs in different environments. Jensen *et al.* (1982) did a sensitivity analysis for model parameters.

MODELLING UPTAKE OF MERCURY

The bioenergetic model developed by Norstrom *et al.* (1976) and applied by Jensen *et al.* (1982) is given by the equation:

$$\mathrm{d}P/\mathrm{d}t = \frac{e_{\mathrm{PF}}C_{\mathrm{PF}}}{q_{\mathrm{F}}e_{\mathrm{F}}}[\alpha W^{\gamma} + (1+\beta)\,\mathrm{d}W/\mathrm{d}t] + \frac{e_{\mathrm{PW}}C_{\mathrm{W}}}{e_{\mathrm{ox}}C_{\mathrm{ox}}q_{\mathrm{ox}}}[\alpha W^{\gamma} + q_{\mathrm{A}}\,\mathrm{d}W/\mathrm{d}t] - kPW^{V}$$

where P = body burden of mercury (g); e_{PF} = efficiency of uptake of contaminant from food; e_{PW} = efficiency of uptake of contaminant from water; q_f = energy equivalent of organism's food (C g^{-1}); q = energy equivalent of organism (C g^{-1}); C_{PF} = concentration of contaminant in food of fish (g g^{-1}); C_{PW} = concentration of contaminant in water (g g^{-1}); e_f = efficiency of utilisation of food by fish; W = weight of fish (g); α = low routine metabolism (C week^{-1} g^{-1}); β = coefficient relating growth rate to energy associated with growth; γ = exponent of body weight for metabolism; v = exponent of body weight in clearance term; k = clearance coefficient (g^{-v} week^{-1}); e_{ox} = efficiency of oxygen uptake; q_{ox} = energy equivalent of oxygen (C g^{-1}); C_{ox} = concentration of oxygen in water (g g^{-1}); V = rate of water flow past the gills (g week^{-1}).

Norstrom *et al.* (1976) applied annual growth rates and Jensen *et al.* (1982) applied von Bertalanffy's growth equation:

$$W = W_{\mathrm{inf}}(1 - e^{-Kx})^b$$

which describes growth in terms of three species specific growth parameters—the asymptotic weight, W_{inf} (g), the growth coefficient, K (per year), and the exponent in the length–weight relation b.

RESULTS AND DISCUSSION

Wiener (1983) reported mercury concentrations in axial muscle tissue of walleye from naturally acidic and circumneutral lakes in northern Wisconsin (Tables 1 and 2). Mercury concentrations were higher in acidic lakes (Fig. 1). In the acidic lakes 8 of 22 fish examined contained mercury concentrations higher than the United States Food and Drug Administration 'action level' of 1 mg kg^{-1}. In the circumneutral lakes none of the 17 walleye examined exceeded the 'action level'. The bioenergetics based uptake model was applied to describe mercury uptake by walleye in these lakes.

Parameter estimates were obtained from the literature or from data published in the literature (Table 3). Growth parameters were estimated using data for Wisconsin lakes given by Eschmeyer (1950). Metabolic parameters were estimated using information in Nordstrom *et al.* (1976) and Jensen *et al.* (1982). Parameters for mercury uptake were reported by Norstrom *et al.* (1976). As a base for calculations, mercury concentrations in food and water reported for yellow perch (*Perca flavescens*) in the Ottawa River by Norstrom *et al.* (1976) were applied.

The model identifies each pathway that might result in an increase in mercury concentration: 1, an increase in efficiency of uptake from either food or water; 2, an increase in the concentration of methyl-mercury in the

TABLE 1
Total Mercury Concentrations in Axial Muscle Tissue of Walleye in Acidic Northern Wisconsin Lakes (from Wiener, 1983)

Age	*Total length (mm)*	*Wet weight (g)*	*Mercury concentration* ($mg\,kg^{-1}$)
5	401	822	0·80
7	484	1 304	0·82
5	426	736	1·41
4	426	708	1·10
7	442	877	1·11
5	391	737	0·41
4	384	481	0·72
7	478	934	1·07
7	500	1 075	1·43
4	372	481	0·50
5	466	1 134	1·65
4	401	652	0·58
4	404	709	0·68
4	399	822	0·49
4	415	879	0·51
4	426	765	0·57
5	459	934	0·69
7	531	1 673	0·89
7	540	1 472	1·39
5	458	1 077	0·76
5	467	1 304	0·59
7	521	1 389	1·74

aqueous phase; 3, an increase in the concentration of methyl-mercury in food; 4, a change in the clearance coefficient; or 5, a change in the growth parameters.

The model was applied to examine effects of increases in food and water concentrations of mercury, decreases in efficiency of uptake, decreases in growth, and decreases in elimination of mercury. Using the concentrations of mercury observed in the food and water of yellow perch in the Ottawa River gives mercury concentrations in walleye higher than those observed in the circumneutral lakes of northern Wisconsin, but lower than those observed in acidic lakes (Figs 1 and 2). Decreasing mercury concentration in the food by about a third gives simulated mercury concentrations in walleye close to those observed in circumneutral lakes (Fig. 1). To obtain mercury concentrations in walleye similar to those observed in the acidic lakes the concentration in the food must be increased by a factor of from 2- to 3-fold

TABLE 2
Total Mercury Concentrations in Axial Muscle Tissue of Walleye in Circumneutral Northern Wisconsin Lakes (from Wiener, 1983)

Age	*Total length (mm)*	*Wet weight (g)*	*Mercury concentration* ($mg\,kg^{-1}$)
4	392	566	0·12
5	401	566	0·24
5	444	906	0·23
4	375	538	0·17
5	400	594	0·18
5	469	934	0·21
5	423	679	0·22
4	383	509	0·27
4	366	396	0·22
4	370	453	0·22
7	477	1 047	0·35
5	391	566	0·31
4	380	453	0·27
7	419	623	0·32
4	359	255	0·22
7	426	708	0·57
7	412	623	0·36
5	320	371	0·38

above that found in the yellow perch of the Ottawa River (Fig. 1). The food of walleye, which is generally on a higher trophic level than that of yellow perch, would be expected to have a higher mercury concentration than the food of yellow perch. The observed increase in mercury concentration in acidic lakes cannot be explained in terms of an increase in efficiency of uptake from food because the efficiency is already high at 80%.

The mercury concentration in the water needs to be increased about 3-fold above that found in the Ottawa River to obtain concentrations similar to those observed in walleye in the acidic lakes (Fig. 2). The high mercury concentrations in walleye from acidic lakes also could result from an increase in the efficiency of uptake from water. The efficiency of uptake of mercury from water is only 12% (Norstrom *et al.*, 1976), and doubling the efficiency of uptake from 12% to 24% is equivalent to doubling the concentration in the water. The efficiency of direct uptake across the gills increases in waters with low pH and calcium content because of an increased gill membrane permeability (Rodgers & Beamish, 1983).

Tomlinson *et al.* (1980) suggested that the higher mercury concentrations

TABLE 3
Parameter Estimates for Uptake of Mercury by Walleye

Concentration in food	3·3 × 10^{-8} (g g^{-1})
Concentration in water	4·0 × 10^{-12} (g g^{-1})
Efficiency of uptake of mercury from the water	0·12
α	12·48 (C year^{-1} g^{-1})
γ	0·92
Efficiency of oxygen uptake	0·75
Oxygen concentration	9·32 × 10^{-6} (g g^{-1})
Caloric equivalent of oxygen	3·42 (C g^{-1})
β	1·0
Efficiency of uptake of mercury from food	0·80
Efficiency of utilisation of food	0·82
Clearance coefficient	10·504 (g^{-v} year^{-1})
Loss exponent of weight	0·58
Initial weight	35·81 (g)
Initial concentration	5·00 × 10^{-6} (g g^{-1})
Initial age	1·0 (year)
Exponent in length–weight relation	3·25
Asymptotic weight	3 687·00 (g)
Growth coefficient	0·24 (year^{-1})

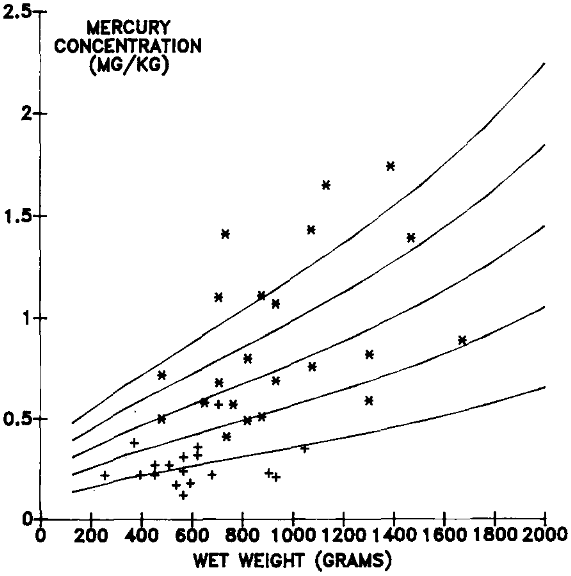

Fig. 1. Observed mercury concentrations (mg kg^{-1}) in walleye in acidic (*) and circumneutral (+) lakes, and simulated concentrations with food concentrations, from the bottom up, of 0, 1, 3·3, 6, and 9 × 10^{-8} (g g^{-1}).

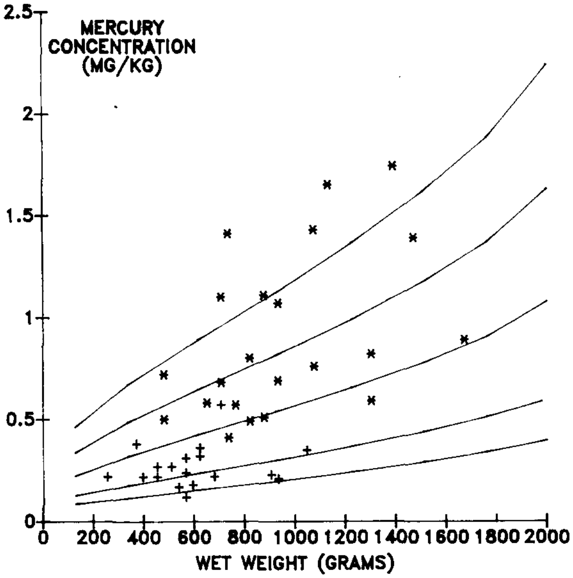

Fig. 2. Observed mercury concentrations ($mg\,kg^{-1}$) in walleye in acidic (*) and circumneutral (+) lakes, and simulated concentrations with water concentrations, from the bottom up, of 0, 4, 8, 12, and 16×10^{-12} ($g\,g^{-1}$).

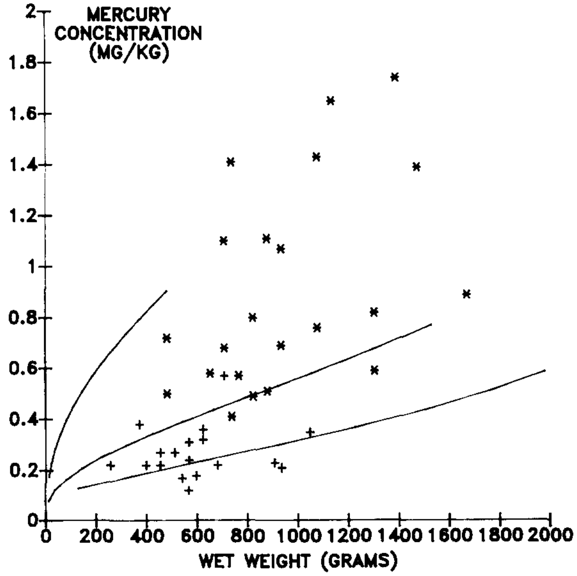

Fig. 3. Observed mercury concentrations ($mg\,kg^{-1}$) in walleye in acidic (*) and circumneutral (+) lakes, and simulated concentrations with growth coefficients, from the top down, of 0·05, 0·10, and 0·24 (per year).

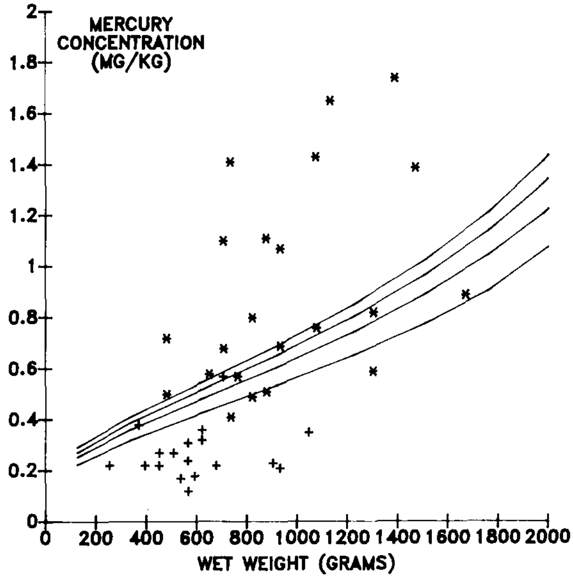

Fig. 4. Observed mercury concentrations (mg kg^{-1}) in walleye in acidic (*) and circumneutral (+) lakes, and simulated concentrations with elimination coefficients, from the top down, of 10·504, 5, 2, and 0 (g^{-v} year).

in fishes from acidic lakes were caused by a decrease in growth, but the simulations indicate that the difference in mercury concentrations between circumneutral and acidic lakes cannot result from a difference in the growth rate. An increase in pH may decrease the growth of walleye, but a large decrease in growth is necessary to obtain the observed increase in mercury concentrations (Fig. 3), and then in simulations walleye do not grow to the observed size (Fig. 3). Weiner (1983) also reported that the growth rate of walleye was not lower in the acidic lakes.

The increase in mercury concentrations in walleye in acidic lakes cannot be caused by a decrease in the coefficient of elimination. If the coefficient of elimination is decreased to zero, the observed mercury concentrations are still well below those observed in the acidic lakes (Fig. 4).

The above simulations indicate that the most likely causes of higher mercury concentrations in fishes from acidic lakes are increases in concentrations in the water and an increase in the efficiency of uptake from the water. An increase in the water concentration would result in an increase in the food concentration, so the necessary increases in the food and water concentrations are about one-half those necessary for increases in food or water concentrations alone.

REFERENCES

Drummond, R. A., Olson, G. F. & Batterman, A. R. (1974). Cough response and uptake of mercury by brook trout, *Salvelinus fontinalis*, exposed to mercuric compounds at different hydrogen-ion concentrations, *Trans. Am. Fish. Soc.*, **103**, 244–9.

Eschmeyer, P. (1950). The life history of the walleye in Michigan. *Bull. Inst. Fish. Res. No. 3.* Michigan Department of Conservation. Lansing, Michigan. 99 pp.

Haines, T. A. (1981). Acidic precipitation and its consequences for aquatic ecosystems: A review, *Trans. Am. Fish. Soc.*, **110**, 669–707.

Huckabee, J. W., Elwood, J. W. & Hildebrand, S. G. (1979). Accumulation of mercury in freshwater biota. In: *The biogeochemistry of mercury in the environment.* Ed. by J. O. Nriagu, Elsevier/North-Holland Biomedical Press. New York, 277–302.

Jensen, A. L., Spigarelli, S. & Thommes, M. M. (1982). PCB uptake by five species of fish in Lake Michigan, Green Bay of Lake Michigan, and Cayuga Lake New York, *Can. J. Fish. Aquat. Sci.*, **39**, 700–9.

Lindqvist, O., Jernelov, A., Johansson, K. & Rodhe, H. (1984). *Methyl mercury in the Swedish environment: Global and local sources.* National Swedish Envir. Protection Board Rept. SNV PM 1816, Solna, Sweden. 105 pp.

Lock, R. A. C. (1975). Uptake of methylmercury by aquatic organisms from water and food. In: *Sublethal effects of toxic chemicals on aquatic animals*, ed. by J. W. Roeman and J. J. Strik, Elsevier, New York.

Massaro, E. J. & Giblin, F. J. (1972). Uptake, distribution and concentration of methyl mercury by rainbow trout (*Salmo gairdneri*) tissues. In: *Proc. 6th Ann. Conf. Trace Sus. in Env. Health. Univ. Mo., Columbia, Mo.*, ed. by D. D. Hemphill, 124–9.

McDonald, M. E. (1985). Acid deposition and drinking water, *Environmental Science and Technology*, **19**, 772–6.

McKim, J. M., Olson, G. F., Holcomb, G. W. & Hunt, E. P. (1976). Long term effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): Toxicity, accumulation, distribution, and elimination, *J. Fish. Res. Board Can.*, **33**, 2726–39.

Norstrom, R. J., McKinnon, A. E. & DeFreitas, A. S. W. (1976). A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*), *J. Fish. Res. Board Can.*, **3**, 248–67.

Rodgers, D. W. & Beamish, F. W. H. (1983). Water quality modifies uptake of waterborne methylmercury by rainbow trout, *Salmo gairdneri*, *Can. J. Fish. Aquat. Sci.*, **40**, 824–8.

Rodgers, D. W. & Qadri, S. U. (1982). Growth and mercury accumulation in yearling yellow perch, *Perca flavescens*, in the Ottawa River, Ontario, *Environ. Biol. Fish.*, **7**, 377–83.

Scheider, W. A., Jeffries, D. S. & Dillon, P. J. (1979). Effects of acidic precipitation on Precambrian freshwaters in southern Ontario, *J. Great Lakes Res.*, **5**, 45–51.

Suns, K., Curry, C. & Russell, D. (1980). The effects of water quality and morphometric parameters on mercury uptake by yearling yellow perch.

Ontario Ministry of the Environment, Technical Report LTS 80-1, Rexdale, Ontario, Canada.

Tomlinson, G. H., Brouzes, R. J. P., McLean, R. A. N. & Kadlecek, J. (1980). The role of clouds in atmospheric transport of mercury and other pollutants. 1. The link between acid precipitation, poorly buffered waters, mercury and fish. In: *Ecological impact of acid precipitation*, ed. by D. Drablos and A. Tellar, SNSF Project, Aas-NLH, Norway.

Weisbart, M. (1973). The distribution and tissue retention of mercury-203 in the goldfish (*Carassius auratus*), *Can. J. Zool.*, **51**, 143–50.

Wiener, J. G. (1983). Comparative analyses of fish populations in naturally acidic and circumneutral lakes in northern Wisconsin, US Fish and Wildlife Service, Eastern Energy and Land Use Team. FWS/OBS/-80/40.16. 107 pp.

Wobeser, G. (1975). Prolonged oral administration of methyl mercury chloride to rainbow trout (*Salmo gairdneri*) fingerlings, *J. Fish. Res. Board Can.*, **32**, 2105–23.