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Hypolimnetic methylmercury and its uptake by plankton during fall destratification: A key entry point of mercury into lake food chains?

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Abstract

Seasonal concentration changes in monomethylmercury (MMHg) and total Hg (T-Hg) were determined in Devil's Lake, Wisconsin, a lake with a mercury consumption advisory for walleye. Mercury dynamics were studied in water and several lower food chain fractions during the ice-free seasons in 1994 and 1995, and limited data for Hg in water were collected in 1993. MMHg concentrations increased in hypolimnetic waters before turnover each year, although maximum concentrations declined from 1993 to 1995. As the hypolimnion eroded, MMHg concentrations increased in both particulate matter and *Daphnia*. Maximum concentrations were obtained near the time of complete mixis. The magnitude of this increase correlated with the mass of hypolimnetic MMHg that had built up prior to turnover in 1994 and 1995. Hg concentrations in yearling planktivorous fish exhibited a decline corresponding to the decline in hypolimnetic MMHg from 1993 to 1995. Our results suggest that fall destratification represents an important time period for entry of MMHg to the food chain of lakes exhibiting a hypolimnetic MMHg buildup.

As concern regarding Hg contamination has increased, so has understanding of the mechanisms of monomethylmercury (CH_3HgX or MMHg) production within lake systems and the movement of Hg and MMHg through various compartments of these systems. Atmospheric wet and dry deposition are important sources of Hg to lake systems (Mason et al. 1994), and groundwater can act as a significant source or sink, depending upon hydrological considerations (Hurley et al. 1994a). River and stream inflow can be a source of Hg to lakes as well. The most important sources of MMHg in lake systems that contain a significant amount of this form are currently a source of debate. It has been shown that Hg is methylated by bacteria, and that methylation rates are highest where sulfur-reducing bacteria are present (Gilmour et al. 1992; Matilainen 1994). Mass balances on northern Wisconsin lake systems calculated by Watras et al. (1994) have led to the conclusion that inputs of MMHg are not sufficient to explain in-lake masses; methylation of Hg within the lake must be invoked. A mass balance created for Palette Lake in northern Wisconsin, however, requires very little or no in-lake methylation (Benoit et al. in prep.). What-

ever the principal source of MMHg to a lake may be, it has been observed in many different lakes that concentrations of MMHg in lake water are significantly higher in anoxic hypolimnetic waters than in oxic epilimnetic waters (Verta et al. 1994; Watras et al. 1994; Bloom et al. 1991).

Predators and herbivores in lake systems appear to receive the vast majority of their MMHg body burdens from their food source rather than directly from the water, as indicated by the fact that MMHg bioconcentration factors ($B_f = \log [C_b/C_w]$, where C_b = wet-weight concentration in biota, and C_w = water concentration) are higher in fish than in zooplankton, and in zooplankton than seston (Watras and Bloom 1992; Back and Watras 1995). Concentrations of Hg in aquatic biota can vary seasonally as well as on a species-specific basis. Slotton et al. (1995) observed pronounced increases in Hg body burdens of zooplankton and juvenile bass at the time of thermal destratification of a seasonally anoxic reservoir that is strongly impacted by effects of impoundment and contamination from a nearby abandoned mercury mine.

The observed MMHg buildup in the hypolimnia of lakes, in conjunction with high MMHg bioconcentration factors, creates questions regarding the role of hypolimnetic MMHg in lake food web dynamics. During destratification, hypolimnetic MMHg may transfer a detectable mass of MMHg to phytoplankton or other sestonic particles. Through zooplankton grazing, followed by predation by planktivorous and piscivorous fish and fish-eating birds, this pulse of MMHg could subsequently bioaccumulate at higher trophic levels. A seasonal pattern of increase could lead to strategies for reducing concentrations of Hg in aquatic organisms if hy-

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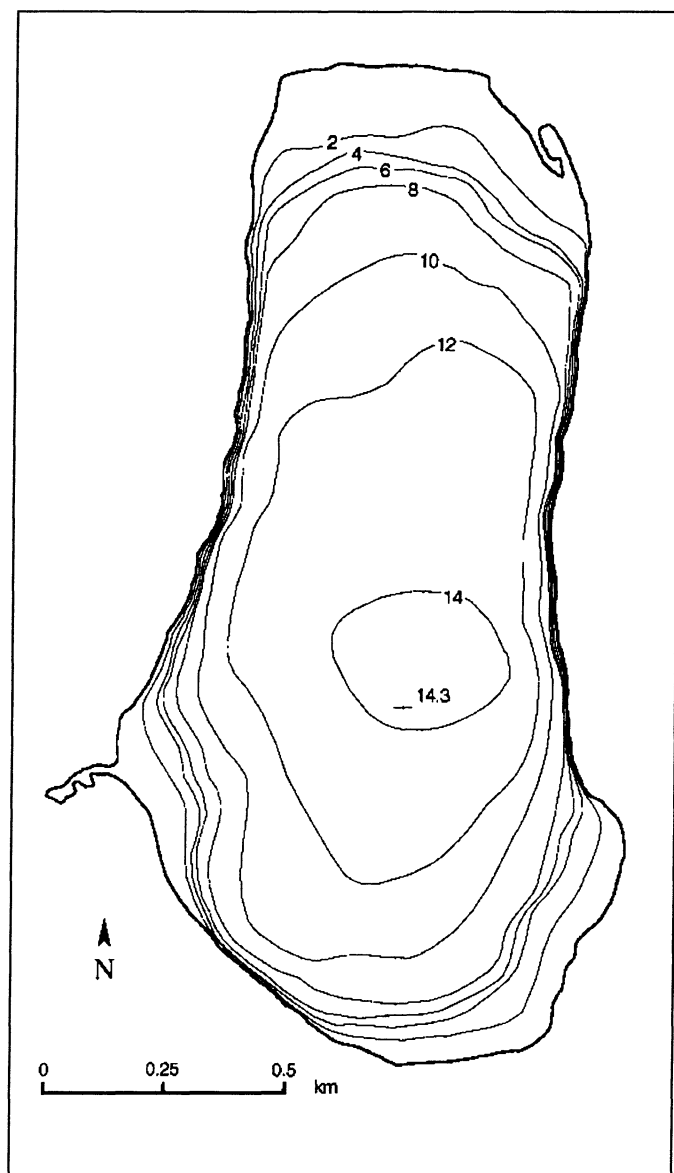


Fig. 1. Bathymetric map of Devil's Lake, Wisconsin. Depth contours are in meters.

polimnetic MMHg buildup can be reduced through techniques such as aeration or early destratification. The goal of this study is to determine if the annual introduction of hypolimnetic MMHg to the mixed zone during fall hypolimnetic erosion and destratification represents an important source of Hg to the lower food chains of lakes.

Materials and methods

Study site—Devil's Lake is located approximately 65 km northwest of Madison, Wisconsin. The lake has a simple bath-tub hydrography (Fig. 1); most of its bottom area is profundal. Its surface area is 149 ha, and its maximum and mean depths are approximately 14 m and 9 m, respectively. Two small springs, one on the east side and one on the west

side of the lake, represent the only surface inputs, and no surface outflows exist. The west-side spring flows through a small wetland before entering the lake. The lake is dimictic, with fall turnover usually occurring in mid-October. From 1986 to 1995, epilimnetic chlorophyll *a* (Chl *a*) concentrations were less than $7 \mu\text{g liter}^{-1}$ between April and August and peaked in September or October at $4\text{--}25 \mu\text{g liter}^{-1}$ (Wisconsin Department of Natural Resources unpubl. data). For this study, depths at which the dissolved oxygen concentration was $>1.0 \text{ mg liter}^{-1}$ were considered to be epilimnetic, and those at concentrations $<1.0 \text{ mg liter}^{-1}$ were considered to be hypolimnetic. At peak stratification in 1994 this division was approximately 4.5 m above the bottom of the deep hole, and in 1995 it was approximately 3 m above the bottom. In 1994 and 1995, epilimnetic temperature in the summer varied between 21 and 27°C , and hypolimnetic temperature varied between 10 and 13°C . Directly after turnover, water temperature was between 13 and 14°C both years. Because of its location in a quartzite outcropping, the geochemistry of the lake is more similar to lakes in northern Wisconsin than to southern Wisconsin's calcareous lakes. Its relatively low acid neutralizing capacity (ANC) (approximately $450 \mu\text{eq/liter}$) results in epilimnetic pH values between 7 and 8 and a hypolimnetic pH near 6 (Lathrop et al. 1989), values substantially lower than other southern Wisconsin lakes. An inverse correlation between ANC and walleye Hg concentration has been observed for walleye in Wisconsin lakes (Lathrop et al. 1991). Devil's Lake has a consumption advisory for walleyes (*Stizostedion vitreum vitreum* Mitchell) (Lathrop et al. 1989), based on the fact that Devil's Lake Walleyes greater than 25 cm in length have been found to contain 0.5–1.0 ppm Hg (wet-weight basis) (Wisconsin Department of Natural Resources 1994). These concentrations are similar to those found in many northern Wisconsin lakes with similar or lower ANCs (Lathrop et al. 1991).

Sample collection—Samples for Hg analysis were collected from June 1994 through November 1995, excluding the winter months. In addition, whole-water MMHg and whole-water total Hg (T-Hg) samples were collected on 30 September 1993. Most sample types except for fish were collected at approximately 6-week intervals in the spring and early summer and on approximately 3-week intervals in the late summer and early fall. Temperature and dissolved oxygen concentration profiles were taken more frequently; these profiles were used to determine the date of lake destratification. Mercury samples were collected within 4 d of complete destratification in both years.

Five types of samples were collected for total Hg and MMHg analysis: whole-water samples, particulate matter greater than $2.2 \mu\text{m}$ in diameter, particulate matter between 2.2 and $35 \mu\text{m}$, particulate matter between 35 and $243 \mu\text{m}$, and *Daphnia*. Mercury samples were collected at various depths from a station at the deepest location in Devil's Lake (see Fig. 1). All samples collected for MMHg or total mercury analysis were collected using ultraclean techniques (Patterson and Settle 1976; Hurley et al. 1996) including thorough acid cleaning of all sample containers, minimiza-

tion of metal sampling equipment, and clean hands—dirty hands sampling protocols.

Whole-water and particulate samples were collected at different depths to create a water-column concentration profile. One to three epilimnetic depths were sampled, as it was found that Hg concentrations varied little in the mixed zone. When the lake was stratified, however, four to five depths were sampled in the hypolimnion to determine concentration profiles for T-Hg and MMHg. A lake map was used to calculate volumes at different depth intervals; these volumes, in conjunction with MMHg determinations, were used to calculate masses of MMHg associated with water and particles at different depths. These calculations provided a means for assessing the movement of MMHg between particulate and filterable fractions and between the hypolimnion and mixed zone.

Samples of unfiltered water were collected in Teflon[®] bottles that had been cleaned in hot, concentrated nitric acid. Particulate matter was collected on Whatman Scientific QM-A quartz fiber filters rated by the manufacturer to retain particles larger than 2.2 μm in diameter when liquid is the filtered medium. The filters are rated at 0.8 μm for retention of dry airborne particles. These filters were housed in acid-cleaned Teflon filter cartridges. Prior to sampling, quartz fiber filters were ashed at 450°C to volatilize any Hg associated with them. Filters that capture particles less than 2.2 μm in diameter (e.g., 0.45 μm) are usually used for separation of particulate and dissolved components; quartz fiber filters, however, are the only variety that can be ashed to remove Hg. Thus, material that passes through these quartz fiber filters will be referred to as filterable and that which is retained will be called particulate.

Samples containing particulate matter in the 2.2–35- μm and the 35–243- μm size fractions were obtained from lake water pumped through a 243- μm sieve and a 35- μm sieve in series. Sieves were constructed from acrylic tubes and nylon mesh netting. Periodically, the water passing through both of these sieves was captured in a clean vessel and a measured volume was vacuum aspirated through a quartz fiber filter. The 35- μm sieve retentate was then washed onto a separate quartz fiber filter using lake water. Additional filtrations of these two fractions were performed to determine mass of these particles per liter of lake water. Size-fractionated samples were collected either at different discrete depths between 1 and 7 m or were composites of water collected from 1 m and 7 m depth.

Collection of particles greater than 35 μm and less than 35 μm was performed based on a published relationship between body length of zooplankton and maximum size of particle ingested (Burns 1968). *Daphnia pulicaria*, the principal *Daphnia* species present in Devil's Lake, can ingest particles smaller than approximately 35 μm but cannot ingest significantly larger particles. Henceforward, particles in the 2.2–35- μm range will be referred to as edible, while those in the 35–243- μm range will be referred to as inedible. Particles larger than 243 μm were assumed to be composed principally of zooplankton and were discarded. It should be emphasized that the term edible will be used to refer to particles of a small enough size to be consumed by *D. pulicaria*.

Whether all particle types in this size range were in fact consumed by this species was not determined.

Zooplankton were collected in a nonmetallic plankton tow net that had been leached in ultrapure water. The net was pulled through the water column from a depth of 8 m (near but never below the thermocline), and the contents were transferred to a clean Teflon jar filled with lake water. Jars were double bagged, put on ice, and returned to the laboratory, where they were stored at 4°C. Within 24 h of collection, individual live *Daphnia* were picked from the jars using acid-cleaned glass pipets and transferred to Teflon vials. The transfer process was performed in a clean room using clean hands—dirty hands techniques. This procedure is similar to that used by Back and Watras (1995). Twenty to 30 of the largest possible individuals were placed in each vial. Triplicate samples of this type were created for both MMHg and T-Hg analyses. A drop of water from the sample jar was used as a blank. *Daphnia* samples were stored double bagged and frozen. For 1994 samples, average dry mass of *Daphnia* was determined by averaging the lengths of 30 individuals and determining dry weight using a body weight-to-length ratio determined by Lynch et al. (1986). For 1995 samples, three subsamples of 20–30 individuals each were collected, placed on a filter, dried, and weighed to determine dry weight. The two methods gave comparable values for dry mass of individual *Daphnia*. Mass of individual *Daphnia* ranged from 0.03 to 0.14 mg, with an average mass of 0.06 mg.

Yearling mimic shiners (*Notropis volucellus*) and bluegills (*Lepomis macrochirus*) were collected for Hg analysis during late April or early May of 1995 and 1996, and bluegills were collected in the same time frame in 1993. Bluegills were collected by electroshocking, and shiners were collected using a shoreline seine. Whole fish from a given collection date were divided into three separate samples of 22–80 shiners or 9–12 bluegills each; these samples were placed in clean plastic bags and stored frozen until analysis. Shiners collected for analysis ranged in length from 28 to 42 mm, with an average length of 34 mm. Bluegills collected for analysis ranged in length from 45 to 80 mm, with an average length of 60 mm.

Sample analysis—Analysis for total Hg concentration was performed using a two-stage gold amalgamation technique with a cold vapor atomic fluorescence detection system (CVAFS) (Gill and Fitzgerald 1987; Hurley et al. 1995). Organic matter was oxidized using BrCl before analysis.

All samples analyzed for MMHg concentration (with the exception of fish tissue) first underwent treatment with sulfuric acid and KCl to convert all forms of MMHg to MMHg-chloride. They were distilled to remove MMHg from associated organic matter (Horvat et al. 1994). MMHg was then chromatographically separated from other Hg forms, pyrolyzed to Hg⁰, and detected by CVAFS (Bloom 1989; Hurley et al. 1995). T-Hg and MMHg samples collected in 1993 were analyzed by Frontier Geosciences.

Fish samples for MMHg analysis were homogenized in a stainless steel blender and digested in a 25% (weight-to-volume) solution of KOH in methanol. Between 0.5 and 1 g of fish tissue was placed in 20 ml of digestate solution,

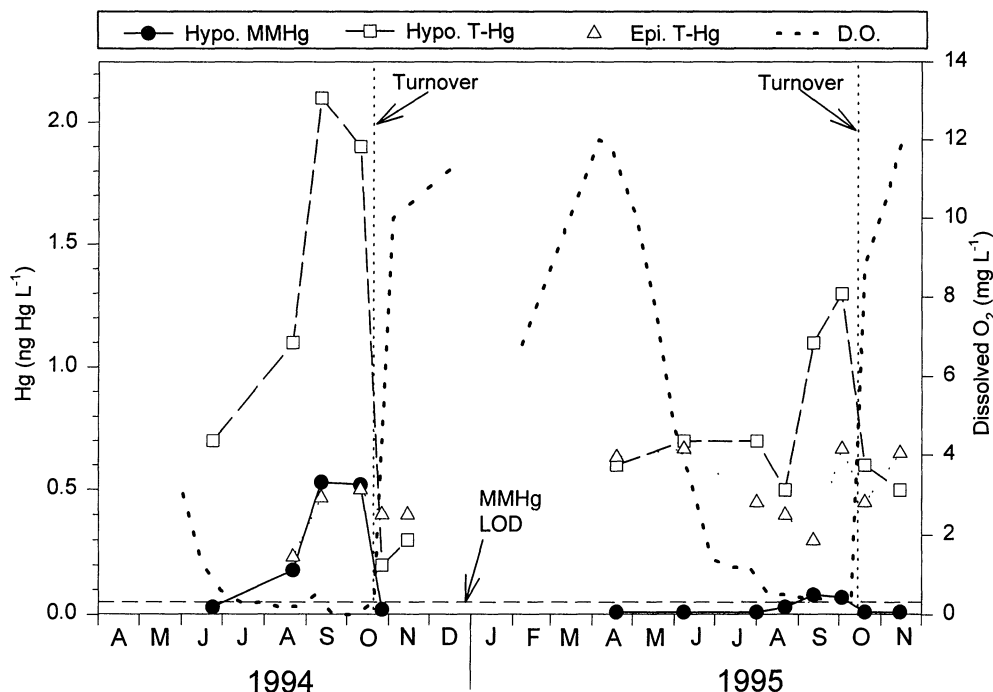


Fig. 2. Concentrations of T-Hg, MMHg, and dissolved O_2 1 m above the lake bottom and T-Hg concentrations in the epilimnion. MMHg sampling points that are less than detection limits are shown to indicate that samples were taken.

sonicated for 1 h, and placed in an oven at 50°C for at least 24 h. A 0.023-ml aliquot of this solution was neutralized with 2 M acetic acid and analyzed by the same procedure as described for all other MMHg samples. This procedure is similar to that described by Bloom (1992). Fish samples for T-Hg analysis were run by the State of Wisconsin Laboratory of Hygiene by a procedure similar to that described by Bloom (1992). All fish samples were analyzed under clean-room conditions.

For total Hg analysis, triplicates were run on a few representative aqueous samples and on all *Daphnia* samples. Particulate samples for total Hg analysis often provided higher Hg concentration values than whole-water samples from the same depth; i.e., a higher mass of T-Hg was associated with the filters than would have been expected even if they had retained all of the Hg associated with the water passed through them. Total Hg concentrations were all above limits of detection, so accurate determinations could be made. Filters were therefore assumed to be contaminated with Hg and results of filter T-Hg analyses will not be presented. Filters did not show evidence, however, of contamination with MMHg, so results of particulate MMHg analyses are presented. Sample collection on filters was sufficiently time intensive as to make it impossible to collect replicates for analysis on a regular basis, so particulate MMHg concentration values in most cases represent one determination only. In the few cases where replicate analyses were collected, however, samples showed fair agreement when analyzed for MMHg. For replicate filter samples available, the absolute value of differences between measured

concentrations and the mean concentration was on average 18% (median = 11%) of the measured value.

Analysis of variation in whole-water MMHg samples was difficult to quantify, as many duplicates collected were below detection limits. Because determination of whole-water concentration does not include the potential uncertainty added by the filtration step, whole-water MMHg determinations should be somewhat more precise. Spikes of MMHg standard were added to some whole-water and *Daphnia* samples to determine recovery from distillation. On average, 89% of spikes added to whole-water samples were recovered (standard error = 2%; $n = 29$), and on average 104% of spikes added to *Daphnia* were recovered (standard error = 13%; $n = 7$). Values reported herein are not corrected for these average recoveries nor are they corrected for recoveries from individual analyses. Error bars shown in figures represent 95% confidence intervals for multiple analyses, approximated using a Z-statistic. Standard errors were calculated using a first-order error approximation (Reckhow and Chapra 1983).

Fish samples collected on each date and for each species were analyzed in triplicate for MMHg, total Hg, and percent water. Tissue samples spiked with the appropriate dissolved standard before digestion were also analyzed for total Hg and methyl-Hg analysis. Recoveries greater than 95% were calculated for all spiked fish samples.

All MMHg samples were analyzed on the basis of mass Hg as MMHg. MMHg concentrations are reported as the corresponding mass of Hg throughout this text.

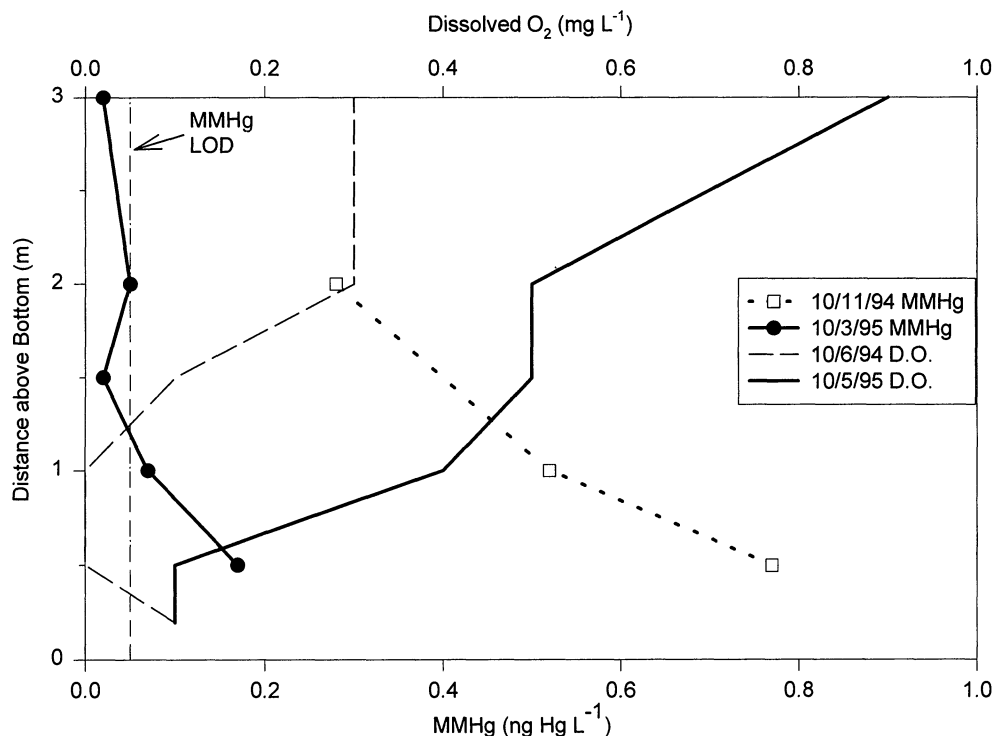


Fig. 3. Dissolved O₂ and unfiltered MMHg concentrations in hypolimnetic waters. MMHg sampling points that are less than detection limits are shown to indicate that samples were taken.

Results and discussion

Hg concentration in water—Whole-water (unfiltered) T-Hg concentrations generally varied between 0.1 and 1.0 ng liter⁻¹ in the epilimnion, but hypolimnetic waters were elevated in Hg concentration during 1994 and 1995 (Fig. 2). MMHg concentrations in the unfiltered epilimnetic water were almost without exception less than the method limit of detection (LOD), which was 0.05 ng liter⁻¹ for water samples. As with total Hg, however, MMHg concentrations were elevated in the hypolimnion (Fig. 2). In addition, the enrichment of Hg is concurrent with depletion of dissolved oxygen in the hypolimnion. Increases in Hg concentrations (particularly MMHg concentrations) in anoxic hypolimnetic lake volumes have been observed by other researchers (Slotton et al. 1995; Watras and Bloom 1994).

Dissolved oxygen concentrations 1 m above the bottom of the deep hole were lower in 1994 than in 1995. The lower dissolved oxygen concentrations in 1994 were accompanied by higher hypolimnetic T-Hg and MMHg concentrations for that year. Most of the difference in T-Hg concentration between years is attributable to the higher MMHg concentrations observed in 1994, indicating that it is concentration of the methylated form of Hg that is most strongly affected by conditions present in the hypolimnion. The inverse correlation between MMHg and dissolved oxygen concentration is spatially evident as well; as oxygen concentrations decreased with depth in the hypolimnion, MMHg concentrations increased (Fig. 3). It is not clear from these results whether dissolved oxygen concentration itself affects hypolimnetic MMHg concentration, but these results indicate that decrease

in hypolimnetic oxygen concentrations coincide spatially and temporally with MMHg buildup, and that these two values may change in proportion to one another.

An analysis of particulate and filterable MMHg in hypolimnetic water shows that the large difference between concentrations in 1994 and 1995 is almost exclusively due to filterable MMHg. For the two sampling dates in each year directly before turnover, the average hypolimnetic concentration of MMHg associated with particulate matter was approximately the same in 1994 (0.07 ng liter⁻¹) as in 1995 (0.05 ng liter⁻¹). Average filterable MMHg concentration for these two dates, however, was as much as 25 times higher than concentration associated with particles in 1994 (0.46 ng liter⁻¹), while in 1995 concentration of filterable MMHg (0.02 ng liter⁻¹) was not as high as the corresponding particulate concentration.

Seasonal dynamics of Hg in biota fractions: Edible and inedible particles—MMHg concentrations in edible and inedible size fractions of particles showed marked seasonal trends (Fig. 4). In both 1994 and 1995, MMHg concentrations in the two fractions more than tripled during erosion of the hypolimnion in September and October. Concentrations in the edible fraction peaked and then dropped to near prestratification levels soon after, though concentrations in the edible fraction remained elevated for a longer period in 1994 than in 1995. Concentrations around turnover in the inedible fraction did not show the sharp decrease seen in the edible fraction, possibly because inedible particles are not as readily consumed by zooplankton. Particle aggregation might also contribute to this pattern. MMHg concentrations

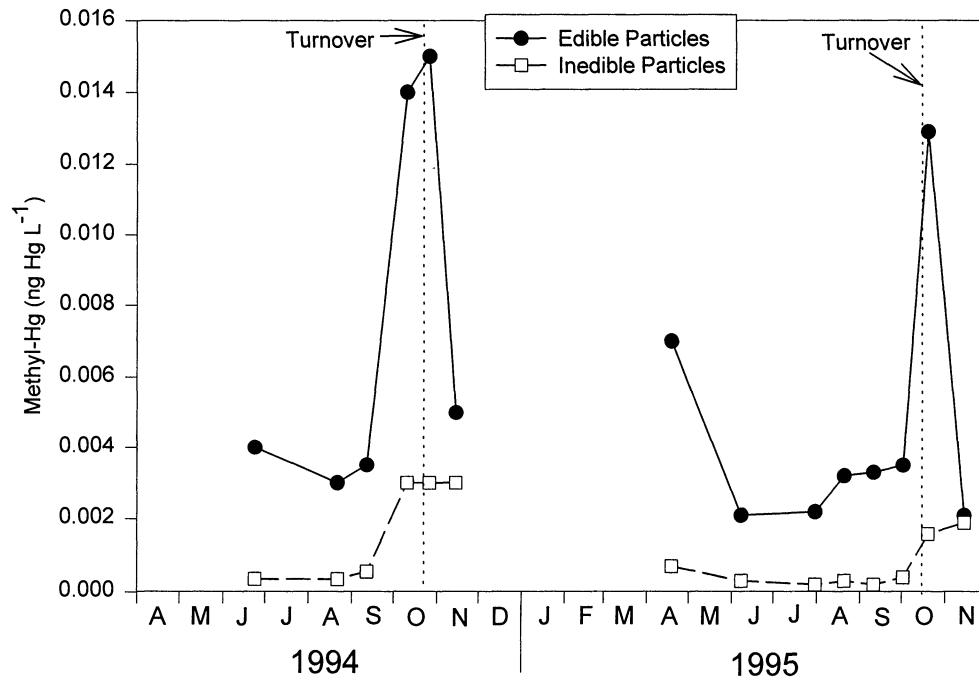


Fig. 4. MMHg concentrations per liter lake water associated with edible (2.2–35 μm) and inedible (35–243 μm) particles in the epilimnion of Devil's Lake.

in the edible fraction were elevated in the spring as well, although spring concentrations were not as high as peak concentrations near turnover.

MMHg concentrations of edible and inedible particles, when expressed on a per liter lakewater basis (Fig. 4), had seasonal patterns similar to concentrations expressed on a

per mass particles basis (Fig. 5), with some exceptions. Peaks in MMHg concentration were again evident during erosion of the hypolimnion. On an Hg-per-mass basis, however, concentration in the edible fraction peaked at a slightly lower value in 1994 than in 1995, though the 1994 peak again appeared to last longer. On a per-mass basis, concen-

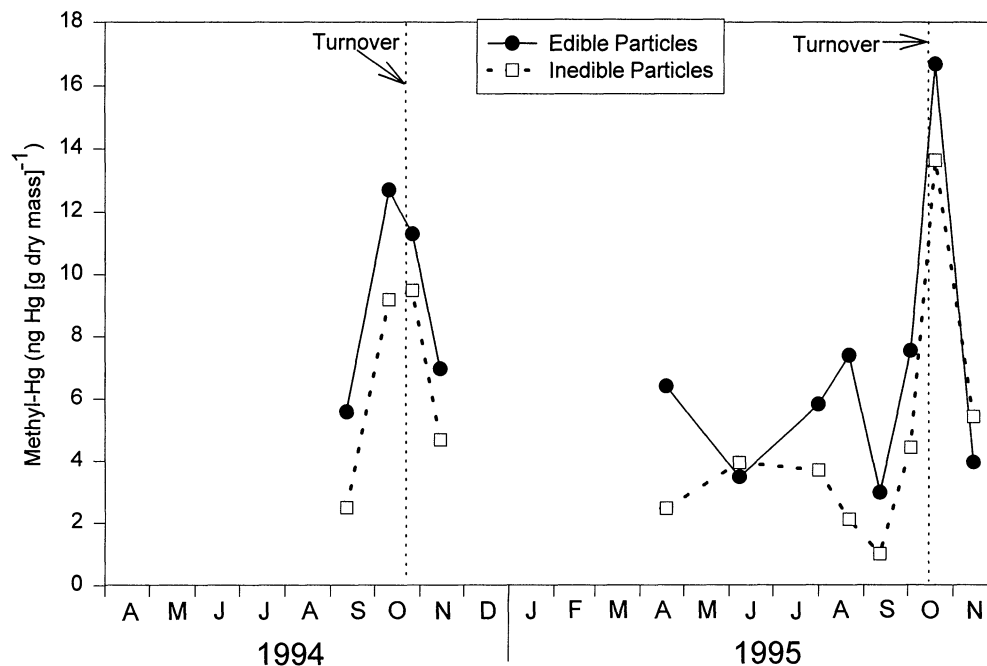


Fig. 5. MMHg concentrations per dry mass in edible (2.2–35 μm) and inedible (35–243 μm) particles in the epilimnion of Devil's Lake.

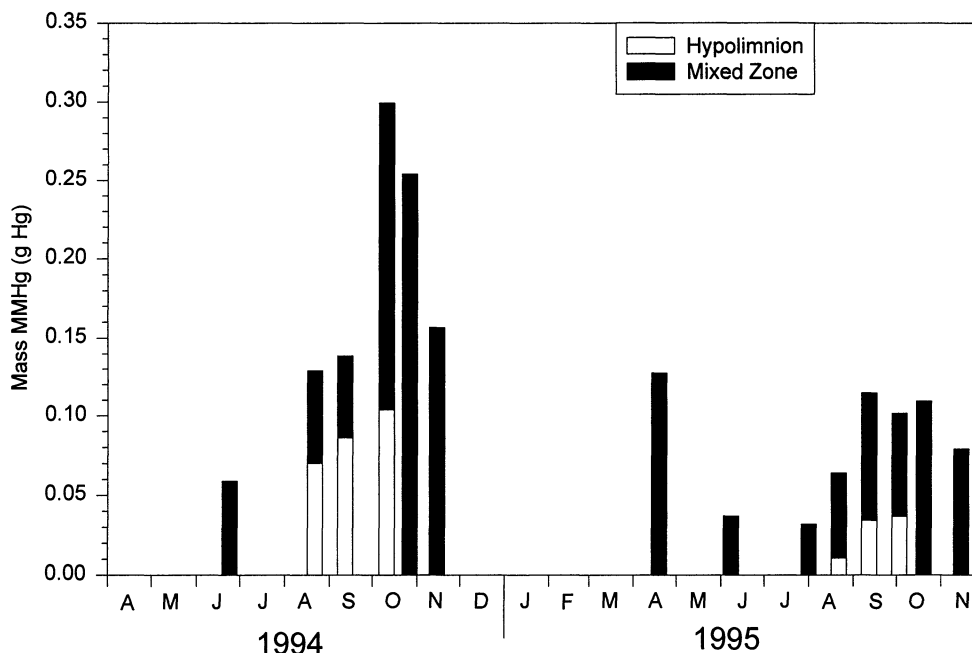


Fig. 6. Mass of MMHg associated with particles $>2.2 \mu\text{m}$ in diameter.

trations associated with inedible particles again peaked near turnover, but in this case they reached nearly the same concentrations as edible particles and quickly fell off in concentration after turnover. These differences indicate that individual particles in both size ranges behave in similar fashion with respect to association with MMHg, and that the differences exhibited in Fig. 4 are in large part the results of changes in the concentration of particles themselves. Such changes in particle concentration may result in part from dynamics in the populations of various species of phytoplankton. Grazing of edible particles, for example, may have caused the sharp drop in per-liter MMHg concentrations in this fraction, while a lack of grazing kept inedible particles at higher levels.

The more pronounced increase in MMHg associated with particles during fall destratification in 1994 can be seen more clearly in whole-lake estimates of particle-bound MMHg mass for the 2 yr (Fig. 6). The degree to which particulate MMHg masses increased near turnover provides further evidence that much of the MMHg built up in the hypolimnion is taken up by particles at this time. In addition, calculation of changes in mass of whole-water and particle-associated MMHg with time and depth allowed for estimation of the degree to which hypolimnetic MMHg was transferred to mixed-zone particles after turnover. The increase in MMHg mass in the hypolimnion during the stratified period was estimated and compared to the increase in particle-associated MMHg masses between prestratification sampling and the sampling following lake mixing. Because whole-water MMHg concentrations outside of the anoxic hypolimnion were generally below detection limits, a worst-case concentration just below the detection limit was used to estimate the concentration of MMHg in bottom waters before stratification; because this represents a maximum concentration

of MMHg in the prestratification bottom waters, it leads to a minimum calculated increase in MMHg in the hypolimnion. In 1994, the mass of MMHg in the hypolimnion increased by approximately 220 mg during the stratified period. Oxygen profiles indicate that the hypolimnion started to erode in late September 1994, and the thermocline was 1 m deeper than its minimum depth by early October. Around this time, concentration of MMHg in mixed-zone particulate matter increased by approximately 200 mg. The sharp increase early in the hypolimnetic erosion process may have been due to a plankton layer near the oxic-anoxic interface, as detected by Watras and Bloom (1994) in a northern Wisconsin lake, or it may have been due to elevated MMHg concentrations very close to the sediment-water interface throughout the hypolimnion (i.e., a continuation of the increase in MMHg concentration with depth seen in Fig. 3). We did not detect such layers, but our sampling resolution may not have been adequate to do so. The apparent correlation was not so clear in 1995; buildup in the hypolimnion was calculated at approximately 12 mg, and change in MMHg in mixed-zone particulate matter was calculated at approximately 70 mg. This difference may be due to the worst-case assumption that would have had a more pronounced effect in 1995, when MMHg masses were much lower. Elevated concentrations near the sediment-water interface may also have contributed. Allowing for some error due to smaller concentrations in 1995, these values indicate that MMHg stored in the hypolimnion is quickly taken up by mixed-zone particulate matter during erosion of the hypolimnion.

The enrichment of MMHg in the two particle fractions during erosion of the hypolimnion strongly suggests that hypolimnetic MMHg is quickly taken up by particles when it enters the mixed zone. Inspection of particulate matter sam-

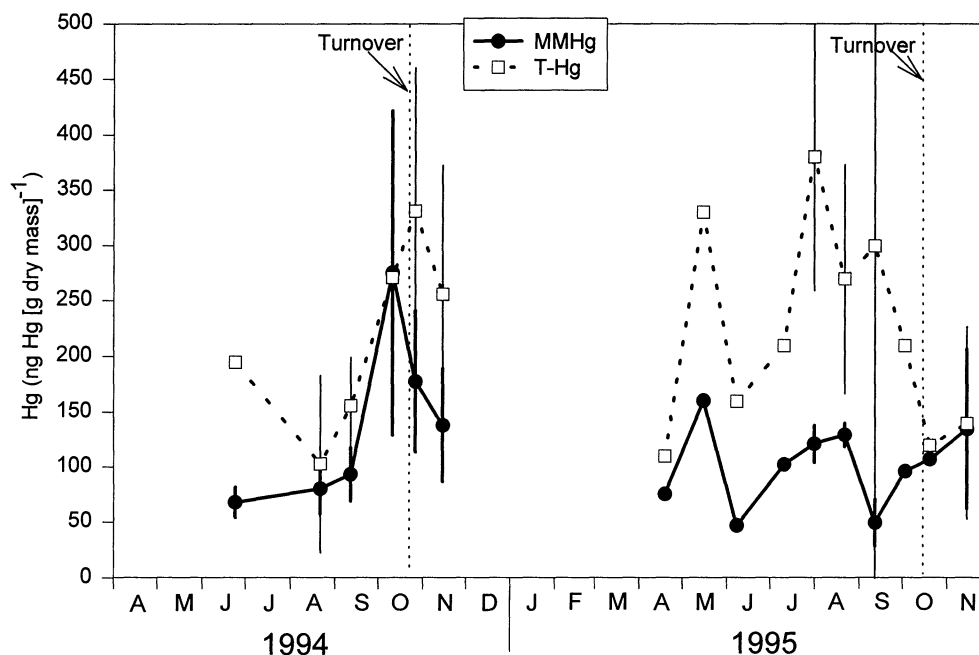


Fig. 7. Total Hg and MMHg concentrations per dry mass in *Daphnia*. Error bars represent 95% confidence intervals estimated using a Z-statistic and a first-order approximation of standard error.

ples indicated that the majority of particulate matter collected in both size fractions consisted of phytoplankton. Epilimnetic water samples were taken before and after turnover in 1995 and inspected under a microscope. The majority of particles observed were phytoplankton, principally *Chroomonas* (9–16 μm in length) and *Cryptomonas* (25–35 μm in length). In addition, the similarity of MMHg concentrations in edible and inedible particle fractions on a per-mass basis (Fig. 5) suggests that MMHg diffuses into particles (e.g., it enters the cell cytoplasm of phytoplankton) as opposed to sorbing to their surfaces. If surface sorption was the principal mode of MMHg association with particles, concentration of MMHg per mass particle should be much lower in the inedible fraction because the surface-area-to-mass ratio decreases as particle size increases. The relatively small difference between the two size fractions is a pattern more consistent with a mechanism in which MMHg diffuses through the entire particle. Mason et al. (1996) have shown that the majority of MMHg associated with the diatom *Thalassiosira weissflogii* is found in the cell cytoplasm, rather than attached to the cell membrane, indicating that diffusion through the membrane is a more significant process than sorption to it.

This evidence does not rule out the possibility that MMHg was associated with bacteria or inorganic particles rather than with phytoplankton. In a California reservoir contaminated with Hg, Slotton et al. (1995) found a positive correlation between peaks in zooplankton T-Hg concentrations and concentration of Mn particles formed as a result of turnover-related changes in redox conditions. Hurley et al. (1994b) found that MMHg flux to sediment traps in a northern Wisconsin lake was correlated almost as strongly with Fe flux as with flux of major Chl *a* derivatives. MMHg may

be associated with particles other than phytoplankton in Devil's Lake, as well. This does not, however, rule out the possibility that *Daphnia* are consuming this particle-associated MMHg. *Daphnia* may consume particles other than phytoplankton if those particles are in an appropriate size range; for example Burns (1968) determined the range of food sizes that *Daphnia* would eat by observing their consumption of plastic beads.

Daphnia—Temporal trends in *Daphnia* MMHg concentrations on a per-gram basis (Fig. 7) were similar to trends in edible-particle MMHg concentrations and particle-associated MMHg masses throughout 1994 and 1995. Masses of individual *Daphnia* varied little between sampling dates, so trends in *Daphnia* MMHg on a per-gram basis were also similar to mass MMHg per individual *Daphnia*. An increase in *Daphnia* MMHg concentrations occurred near turnover in 1994, concurrent with the increases in edible-particle and total particulate matter MMHg concentrations. The increase in *Daphnia* MMHg concentrations that occurred near turnover in 1995 is not as large as that in 1994, a behavior that seems to correspond with the longer-lasting period of elevated edible-particle MMHg concentrations and the increased whole-lake mass of particle-associated MMHg in 1994.

The large variability in mass MMHg per biomass *Daphnia* (Fig. 7) for the last three sampling dates in 1994 indicates that a more quantitative analysis is required to determine if the mean concentration during the period before destratification begins is significantly different from the mean concentration after it has begun. For this analysis, the period before destratification begins was defined as the first sampling in June of a given year through the first instance in

Table 1. Mercury concentrations in different fractions, Devil's Lake, Wisconsin.

	Whole-water Hg concentration 1 m from bottom, ng Hg liter ⁻¹ *		MMHg in all lake particles, g†	MMHg in edible particles, ng Hg g ⁻¹ dry weight†	MMHg in <i>Daphnia</i> , ng Hg g ⁻¹ dry weight†	Hg in bluegill, ng Hg g ⁻¹ dry weight (ng Hg g ⁻¹ wet weight)‡		Hg in shiners, ng Hg g ⁻¹ dry weight (ng Hg g ⁻¹ wet weight)‡	
	Hg as methyl-Hg	Total Hg				Hg as methyl-Hg	Total Hg	Hg as methyl-Hg	Total Hg
1993	1.2	3.0	—	—	—	837 (185)	814 (180)	—	—
1994	0.52	2.0	0.23	9.6	186	509 (115)	575 (129)	483 (115)	506 (120)
1995	0.07	1.2	0.10	9.1	100	265 (58)	324 (70)	287 (70)	336 (82)

* Based on a running daily average of concentration between 7–12 September and 3–11 October. Total and MMHg data from 1993 are based on one sampling only, on 30 September 1993.

† Based on a running daily average of Hg concentrations between 12 September and 15 November of the given year.

‡ Concentrations for fish born in the year listed and sampled the following spring.

which the dissolved oxygen concentration at the top of the hypolimnion was determined to have increased to a value greater than 1 mg liter⁻¹ (i.e., the first evidence that the hypolimnion was eroding). In both 1994 and 1995, this occurred in early October. All samplings later than this date in a given year were included in the postdestratification period.

Mann-Whitney tests were performed on individual Hg analyses of *Daphnia* (two to four per sampling trip) divided by the mean dry biomass per *Daphnia* determined for that date. Mean dry biomass was used because more variability was observed in the MMHg determinations than in the biomass determinations. The Mann-Whitney test was used because the group of samples from each period was small ($n = 8$ to $n = 13$), so it was difficult to determine if the samples were from a normal distribution. In 1994, MMHg concentration in *Daphnia* during the period before erosion began was significantly different ($P = 0.0003$) from the concentration in the period after it had begun. In 1995, though, the difference between the two groups was not significant ($P = 0.365$). This test indicates that, in spite of the large variability in 1994 analyses, the mean MMHg concentration in *Daphnia* was in fact higher after destratification commenced. The same cannot be said for 1995.

The concentrations of MMHg in *Daphnia* collected before destratification were similar in 1994 and 1995 (see Fig. 7). During destratification, however, concentrations were higher in 1994 than in 1995, similar to the differences in hypolimnetic MMHg mass (see Fig. 6). MMHg concentrations in *Daphnia*, like those in particles, indicate that buildup of MMHg in the hypolimnion manifests itself as an important source of MMHg to the lake food chain during destratification. Thus, there is strong evidence that introduction of MMHg to the oxic zone during destratification has important effects on the lower food chain of Devil's Lake, and that the extent to which lake destratification affects *Daphnia* MMHg concentration is dependent upon the degree to which MMHg builds up in the hypolimnion. Slotton et al. (1995) and Regnell (1995) have also seen increases in, respectively, T-Hg and MMHg concentrations in zooplankton during destratification. Furthermore, Regnell (1995) determined that not all of the MMHg stored in hypolimnetic waters was accounted for in postturnover surficial sediments, indicating that only

a fraction of the MMHg mixed into the water column during destratification was quickly incorporated into the sediment. Thus, much of this large quantity of MMHg has a different fate. Although demethylation is another potential fate for this MMHg, *Daphnia* MMHg concentration dynamics indicate that a large fraction is incorporated into lower-food-chain organisms.

T-Hg concentrations in *Daphnia* exhibit a less consistent behavior in relation to lake turnover (Fig. 7). In 1994 T-Hg concentration in *Daphnia* increased as turnover approached and decreased sharply thereafter, but in 1995 *Daphnia* T-Hg concentrations decreased as turnover approached. Reasons for these temporal responses of T-Hg concentrations in *Daphnia* are not clear.

Planktivorous fish—Hg concentrations measured in yearling bluegill and shiners represent an annual index of Hg concentrations in lower food-chain organisms. In their first year of life, the diet of both fish species consists primarily of zooplankton (Becker 1983). Our own analyses of the stomach contents of Devil's Lake shiners show that at almost all times, their stomach contents consist of at least 15% zooplankton. In May and October at least 85% of their stomach contents consisted of *Daphnia* (Gorski et al. in prep.). Concentrations of MMHg in fish were remarkably similar between species in a given year. As is the case for particles, *Daphnia*, and hypolimnetic water, fish MMHg concentrations declined from 1993 to 1995 (Table 1). Running average concentrations in Table 1 were calculated by determining the area under the appropriate concentration plot (see Fig. 2) between the dates listed and dividing this value by the number of days between sampling dates. This provides average whole-water concentrations 1 m above the bottom of the deep hole for the period of peak stratification and average particle and *Daphnia* concentrations for the period of hypolimnetic erosion and turnover.

Analysis results indicate that, within 1 standard error, the MMHg and T-Hg concentrations are not significantly different in the 1993 bluegill and 1994 shiners. For all samples analyzed, the Hg in fish was almost exclusively in the form of MMHg (Table 1). Bloom (1992) saw a similar abundance of MMHg in several saltwater and freshwater fish and shell-

Table 2. Biomagnification factors between different compartments of the food web. Edible particle and *Daphnia* concentrations used are running daily averages for dates between 12 September and 15 November of the given year. Fish concentrations used are from fish born during the given year and sampled in spring of the following year.

	Edible particles to <i>Daphnia</i>	<i>Daphnia</i> to mimic shiners	<i>Daphnia</i> to bluegill
1994	19	2.6	2.7
1995	11	2.9	2.7

fish, though only muscle tissue of the various species was analyzed in that study.

Bioconcentration factors, which compare biota Hg concentration on a wet-weight basis to Hg concentration in water were not calculated for MMHg concentrations due to the facts that epilimnetic MMHg concentrations in whole-water samples were below detection limits and that all particle and *Daphnia* mass determinations were performed on a dry-weight basis. Assuming, however, that the operationally defined edible particles adequately represent the diet of *Daphnia*, and that adult *Daphnia* adequately represent the diet of the two species of fish, biomagnification factors (BMF) from edible particles to *Daphnia* and from *Daphnia* to fish can be calculated using Eq. 1:

$$\text{BMF} = \frac{\text{mass Hg/dry mass predator}}{\text{mass Hg/dry mass prey}}. \quad (1)$$

Defined in this manner, BMF comprises a method for determining the number of times Hg concentration increases as it moves up the food chain. BMF values for MMHg from edible particles to *Daphnia* and from *Daphnia* to the two species of fish studied are based on the concentration data in Table 1 and are shown in Table 2. Values for edible particles and *Daphnia* represent concentrations during erosion of the hypolimnion. Average BMFs from edible particles to *Daphnia* are over 7.5 times those for *Daphnia* to fish.

The particle-to-*Daphnia* BMF values in Table 2 are within an order of magnitude of the highest particle-to-zooplankton values determined by Back and Watras (1995). They are three to six times higher than those determined from the results of Watras and Bloom (1992). These differences may be in part due to the fact that in both of these studies the presumed zooplankton food source was separated for analysis by a different technique than the edible-inedible separation used here.

Multiyear Hg dynamics—Notable changes in Devil's Lake Hg concentrations occurred between the years covered in this study as well as within them. Mercury concentrations for each fraction shown in Table 1 without exception decreased as the study progressed from 1993 to 1995. The rate of decrease in Hg concentrations was greatest in whole-water, hypolimnetic MMHg concentrations. The fact that this decrease extends to planktivorous fish suggests that the relative extent of hypolimnetic MMHg buildup in a given year directly affects the food chain at least up to the level of planktivorous fish.

A question remains regarding the reason for the steady decrease in MMHg concentrations from 1993 to 1995. One possible explanation relates to the extremely heavy rainstorms that occurred in 1993. It is likely that runoff introduced large amounts of inorganic Hg to the lake, and that additional Hg was introduced from newly flooded shoreline areas. Studies of newly impounded reservoirs indicate that flooding formerly dry land adds inorganic Hg and organic nutrients to the associated water body (Johnston et al. 1991). In addition, measurable levels of MMHg have been found in precipitation and in runoff (Rudd 1995), so rain events can be a source of MMHg as well as inorganic Hg to water bodies. Increased inorganic Hg concentrations add to the pool of Hg available for methylation, and increased organic nutrient concentration can increase rates of primary production that can in turn lead to increased stratified periods.

The decline in hypolimnetic MMHg between 1994 and 1995 corresponds to an increase in hypolimnetic dissolved oxygen concentrations between those years, though further research is needed to determine if hypolimnetic dissolved oxygen concentration and MMHg buildup are indeed related. If this linkage exists, then more traditional lake management techniques that improve hypolimnetic oxygen concentrations (i.e., that reduce the extent of stratification) may have some benefit for reducing Hg levels at all levels of the lake food chain.

Conclusions

Results from 2 yr of intensive sampling of lake water and biota indicate that MMHg stored in the anoxic hypolimnion during the summer stratified period is likely to represent an important source of MMHg to the food chains of lakes with anoxic hypolimnia. This stored MMHg begins to become available to lake biota during erosion of the hypolimnion in the fall and remains available until a short time after complete turnover. The concentration of MMHg in both zooplankton and algae can increase several times between peak stratification and complete mixing; two- to fourfold increases were observed in this study. Results from planktivorous fish, zooplankton, and particles of different sizes indicate that the mass of MMHg stored in the hypolimnion is directly related to the degree to which particle and biota concentrations change. It appears that the body burden of MMHg in zooplankton and planktivorous fish is a result primarily of transfer from ingestion of lower-food-chain organisms and particles. This biomagnification occurs to the greatest degree between edible-sized particles and zooplankton.

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