Episodes of Elevated Methylmercury Concentrations in Prairie Streams

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Methylmercury (MeHg) and total mercury (THg) concentrations were determined weekly from late March through mid-December 2000 in unfiltered water samples from two prairie streams in south-central Minnesota. The Little Cobb River and County Ditch 86 drain predominantly agricultural watersheds, but riparian areas along much of the Little Cobb River are forested, whereas County Ditch 86 is a utilitarian drainage waterway with grassed riparian areas. Episodes of elevated MeHg concentration (1.3 ng/L) were observed in both streams in early May during a period of algal bloom. Between late May and late September, MeHg concentrations varied between 0.05 and 0.39 ng/L in the Little Cobb River and between 0.03 and 0.29 ng/L in County Ditch 86. Precipitation was well below average in August and September, and discharge in both streams ceased by late September. MeHg concentrations in the Little Cobb River increased dramatically in early October after autumnal leaf fall, increasing from 0.44 to 4.90 ng/L over a 5-week period. In contrast, MeHg concentrations in County Ditch 86 varied between 0.22 and 0.48 ng/L over the same time frame. The observed differences are thought to reflect differences in the amounts of litterfall entering the two streams. These results show that algal bloom and leaf fall events can result in elevated MeHg concentrations in surface waters, potentially leading to increased MeHg accumulation in fish.

Introduction

The bioaccumulation of mercury (Hg) in aquatic food chains has resulted in widespread fish contamination, leading to health concerns for fish-eating populations. Methylmercury (MeHg) is the primary bioaccumulative species, accounting for over 95% of the Hg found in fish (*1*). Fish accumulate MeHg through their diet (*2*), but MeHg uptake mechanisms at the base of the food chain are still uncertain. Concentrations of MeHg in macrozooplankton from lakes in Ontario (Canada) were found to correlate positively with percent wetland in the catchments, indicating that terrestrial sources of MeHg contribute significantly to biotic uptake (*3*). Other evidence has suggested that the composition of fine particulate substrate consumed by zooplankton has a significant influence on the amount of MeHg accumulated (*4*). Waters in which the particulate fraction contained a higher proportion of autochthonous carbon (in the form of algae and

bacteria) relative to terrestrially derived carbon had higher MeHg concentrations in both the particulate fraction and the consumers.

The major sources of MeHg in surface waters are (i) terrestrial runoff, (ii) atmospheric deposition, and (iii) internal production (*5*). MeHg can enter surface waters via runoff from terrestrial sources (*6*–*9*) and by fluvial transport from upstream source areas such as wetlands (*10*–*13*). Major influences on MeHg concentrations and yields include watershed characteristics, particularly the proportion of wetlands, and the timing and intensity of precipitation and snowmelt events (*14*–*17*). MeHg in watershed soils may originally have been deposited directly from the atmosphere or indirectly via throughfall and litterfall (see below) in forested catchments. MeHg can also be produced in watershed soils (*18*), particularly if those soils are subjected to periods of saturation (*9*) or flooding (*19*, *20*). Direct atmospheric inputs of MeHg to water bodies may be significant in some situations (*5*). Production of MeHg in situ may be important in many aquatic systems, particularly where anoxic and/or anaerobic conditions prevail and the methylation of Hg by sulfate-reducing bacteria is significant (*21*–*23*). Biologically mediated and abiotic demethylation reactions also influence MeHg concentrations in surface waters, and net MeHg concentrations represent a balance of all inflow, outflow, production, and degradation processes.

Recent studies on forested catchments have shown leaf litter to be a significant input of MeHg to forest soils (*24*–*29*). Tree foliage collects both total Hg (THg) and MeHg from the atmosphere by deposition and perhaps adsorption. On-leaf methylation processes may also take place. Nagase et al. (*30*) observed that fulvic acids extracted from leaf mold were capable of abiotic methylation of Hg in laboratory tests. Leaf litter decomposing on forest floors contains anaerobic pockets, especially when moistened by rainfall, where biological methylation reactions may produce MeHg. Precipitation runoff can transport this MeHg from fallen leaf litter to surface waters. Direct litterfall into water bodies may also deliver significant amounts of MeHg to waters and may stimulate in situ methylation processes. The processes involved when leaf litter falls directly into surface waters may be similar to those operating in newly flooded areas. Methylmercury may be transferred from vegetation into the overlying water, or created in place as a result of enhanced biological activity, or both (*31*, *32*). Vegetation decomposing under anoxic conditions was found to stimulate the methylation of Hg (*33*), while MeHg was released under both oxic and anoxic conditions from branches and leaves of alder and black spruce immersed in river water (*34*).

We report here on two distinct episodes of high MeHg concentrations in prairie streams draining largely cultivated watersheds. One episode corresponded with a period of high algal production in the streams, whereas the other was associated with leaf inputs to one of the streams. Such episodes may represent important MeHg exposure scenarios for resident fish populations and may have long-term consequences for fish Hg concentrations.

Methods

Environmental Setting. The Minnesota River drains 44 000 km² in the southwestern and south-central portions of the state of Minnesota and parts of Iowa and South Dakota. The climate is subhumid continental featuring cold, dry winters and warm, moist summers. Average annual precipitation increases from 56 to 79 cm, and runoff increases from 3 to 15 cm from west to east across the watershed (*35*). The fine-

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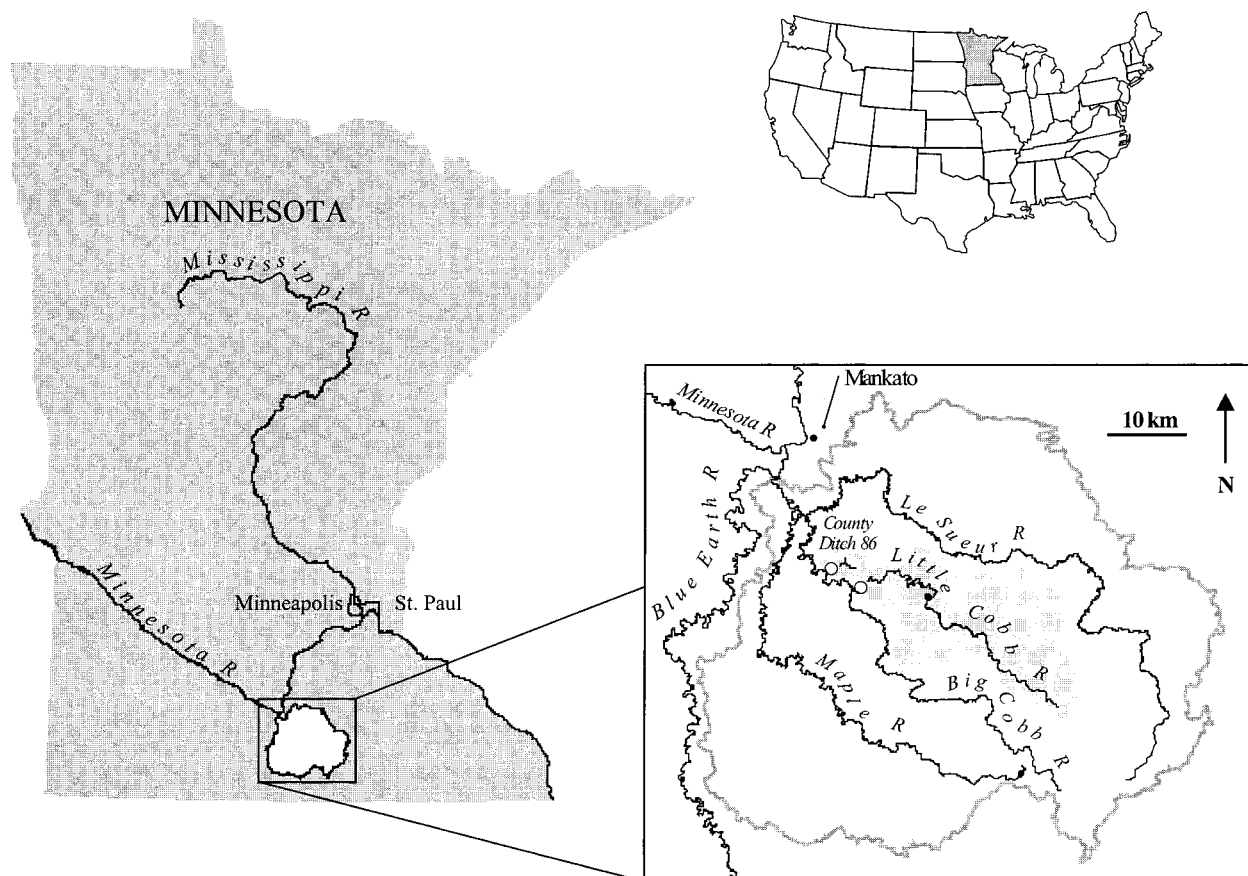
FIGURE 1. Location of the sampling sites (○). The Le Sueur River Watershed is shown in outline; watersheds of the Little Cobb River and County Ditch 86 are shaded.

grained calcareous mollisol soils of the region are highly productive, and land use is dominated by corn and soybean agriculture (36). Artificial surface and subsurface drainage systems extend throughout the Minnesota River Basin to quickly remove excess water in support of agricultural production. Stream and river water quality is strongly influenced by runoff inputs from precipitation events. Soil materials eroded from farm fields and riverbanks result in elevated concentrations of suspended solids, nutrients, and other pollutants in local waterways during runoff events.

The work described here was carried out on the Little Cobb River and County Ditch 86 in the Le Sueur River Watershed in the eastern portion of the Minnesota River Basin (Figure 1). The Le Sueur River is tributary to the Blue Earth River, which accounts for 46% of the discharge of the Minnesota River at Mankato, MN (35), making it the largest tributary of that river. The Little Cobb River and County Ditch 86 are tributaries of the Big Cobb River, which enters the Le Sueur River near Rapidan, MN. The Little Cobb River is a third-order stream draining 343 km² in the central portion of the Le Sueur River Watershed. Land use in the Little Cobb subbasin is predominantly row-crop agriculture, but mature deciduous forest covers much of the riparian area, and the stream channel follows a natural course. On the basis of the limited historical record (1997−1999) and our observations in 2000, discharge in the Little Cobb River can cease under late summer−early fall conditions, depending on precipitation timing. The much smaller watershed of County Ditch 86 (22.4 km²) is also given over largely to row-crop agriculture, but the banks of this utilitarian, first-order waterway are generally grassed and devoid of trees. While a historical record is lacking, discharge in County Ditch 86 stopped in the early fall of 2000, and cessation of flow may be a common occurrence on this stream as well.

Sample Collection and Analysis. Whole-water grab samples were collected at sites on these two streams on a weekly basis from late March through mid-December 2000 using appropriate clean sampling techniques (37); some weeks were missed, and some weeks included multiple sample collections. All mercury samples were collected in 250- or 500-mL acid-cleaned Teflon bottles, which were transported to and from the sampling site in double zip-lock bags (see Supporting Information). Samples for total suspended solids (TSS) and volatile suspended solids (VSS) analysis were obtained at the same frequency as those for mercury analysis. Samples for dissolved organic carbon (DOC), dissolved reactive phosphorus (DRP), total Kjeldahl nitrogen (TKN, representing organic and ammonium nitrogen), and chlorophyll a were collected less frequently or during targeted event sampling. Samples for DOC analysis were collected in clean amber glass jars; samples for all other analyses were collected in plastic bottles.

All samples for Hg analysis were returned to the clean analytical lab on ice, within 6 h of collection. Subsamples (50 mL) for MeHg analysis were immediately poured into acid-cleaned 60-mL Teflon vials and stored at 4 °C in the dark. Next, the remainder of the sample was prepared for THg analysis using an acid−permanganate digestion at 95 °C for 2 h (38). The following day, samples for MeHg analysis were distilled in an acid-cleaned all-Teflon apparatus to remove matrix interferences to the analytical procedure (39; see Supporting Information).

Total Hg was determined by cold vapor atomic fluorescence with single gold trap amalgamation (40). All samples were analyzed in duplicate; the mean relative standard error for the duplicate determinations was 1% (n = 71). Analysis of THg in the Certified Reference Material NIST 1641d Mercury in Water gave a mean value of 1.61 mg/kg with a
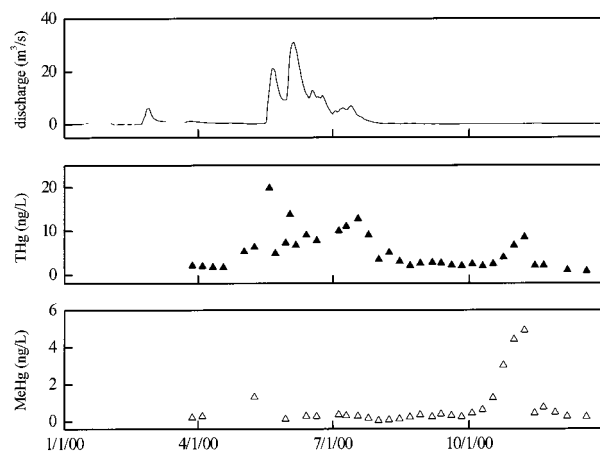
FIGURE 2. Stream discharge and concentrations of THg and MeHg in the Little Cobb River.
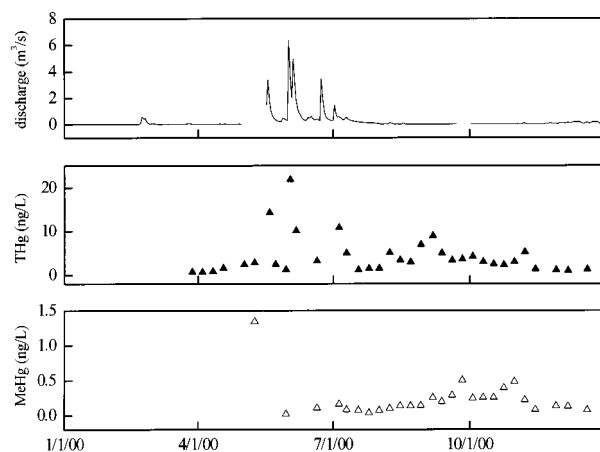

FIGURE 3. Stream discharge and concentrations of THg and MeHg in County Ditch 86.

CV of 0.6%, $n = 16$ (certified value = 1.590 mg/kg $\pm$ 0.018 mg/kg). The method detection limit for THg was 0.06 ng/L (based on 3 times the standard deviation of the blank values). MeHg was determined by aqueous-phase ethylation/gas chromatography with atomic fluorescence detection (*41*, *42*). Analysis of MeHg in the Certified Reference Material DORM-2 Dogfish Muscle gave a mean value of 4.64 mg/kg with a CV of 10%, $n = 16$ (certified value = 4.47 mg/kg $\pm$ 0.32 mg/kg). Analysis of duplicate samples yielded a mean relative standard error of 9% ($n = 19$). The mean matrix spike recovery of MeHg was 101% with a CV of 13% ($n = 25$). The method detection limit for MeHg was 0.03 ng/L. Concentrations of TSS, VSS, DRP, DOC, TKN, and chlorophyll *a* were determined by standard methods (*43*). Method detection limits were as follow: TSS, 2 mg/L; VSS, 2 mg/L; DRP, 0.005 mg/L; DOC, 1 mg/L; TKN, 0.2 mg/L; and chlorophyll *a*, 1 μg/L.

Results and Discussion

Several precipitation events resulted in periods of elevated discharge on both Little Cobb River (Figure 2) and County Ditch 86 (Figure 3) during the spring and summer of 2000. The timing of the hydrological events in the two adjacent watersheds was similar, with periods of high flow following precipitation events in May and June. The smaller County Ditch 86 responded rapidly to precipitation events, and the discharge returned quickly to base levels afterward. The subsurface tile-drainage system that feeds County Ditch 86 delivers water rapidly and efficiently with little lag time and little hydrological resistance. The hydrograph for the Little Cobb River shows a slower response to precipitation events

and a slower return to base flow conditions. The watershed of the Little Cobb River is much larger than that of County Ditch 86 (337 vs 18.8 km^2), and the drainage process is more drawn out. Very limited rainfall and greater evapotranspiration in mid- to late-summer resulted in the cessation of flow in County Ditch 86 by mid-August and in the Little Cobb River by mid-September.

Mercury concentrations and speciation in these two streams varied over the course of the summer, responding to varying hydrological and climatic conditions (Figures 2 and 3; Table 1 in Supporting Information). Soil inputs from surface erosion and bank sloughing during hydrological events resulted in elevated TSS levels in both streams (Table 1 in Supporting Information). Total Hg concentrations were highly correlated with TSS concentrations during these events, indicating that sources of suspended solids are also sources of THg. A similar conclusion was drawn from a study of THg and TSS concentrations and loadings in the mainstem Minnesota River (*36*, *38*). For the Little Cobb River, the regression equation for THg and TSS data from May 19 through September 26 was THg (in ng/L) = 0.065 × TSS (in mg/L) + 1.42 ($r^2 = 0.96$, $n = 20$). For County Ditch 86, the corresponding equation was THg = 0.068 × TSS + 0.91 ($r^2 = 0.97$, $n = 19$). The slope of the regression line gives an estimate of the concentration of THg per unit mass of suspended solids (65 ng/g for the Little Cobb River and 68 ng/g for County Ditch 86). These values are considerably higher than a corresponding value presented previously for Fort Snelling on the Minnesota River (46 ng/g; *36*). The reason for this difference is uncertain; however, it may involve the organic content of the particulate matter in these streams. The VSS/TSS ratio is a measure of the organic fraction of the suspended sediments. The mean VSS/TSS ratio observed in the Little Cobb River from May 19 through September 26 was 0.21; that for County Ditch 86 was 0.17. The VSS/TSS ratio on the Minnesota River at Fort Snelling during 1995 and 1996 was 0.10. Mercury is probably associated with particulate-bound organic matter in these streams, and suspended sediments having a higher organic content may also have a higher concentration of THg.

Methylmercury concentrations in the two streams were not correlated with TSS concentrations and showed little response to variations in discharge (Figures 2 and 3). Between late May and late September, MeHg concentrations varied between 0.05 and 0.39 ng/L in the Little Cobb River and between 0.03 and 0.29 ng/L in County Ditch 86. The MeHg/THg ratio ranged from 1 to 6% in County Ditch 86 between late May and September 12 and then increased to 8% on September 19 and 14% on September 26. In the Little Cobb River, the MeHg/THg ratio varied from 1 to 4% between mid-May and August 15 and then was higher (9−15%) over the following 6 weeks. Factors influencing MeHg concentrations during this time were not clearly defined, although informal observations suggested that higher algal content in the streams appeared to result in higher MeHg levels. An algal bloom event in both streams in early May provided an extreme example of how algal growth in these streams could affect MeHg concentrations. At that time, under conditions of little precipitation and high temperatures, the Little Cobb River turned green and turbid. Total and volatile suspended solids concentrations were quite high (111 and 32 mg/L, respectively, on May 2 and 123 and 31 mg/L, respectively, on May 9) for a non-hydrologic event, reflecting substantial in-stream biological production. High chlorophyll *a* (450 μg/L) and TKN (12 mg/L, NH$_3$ < 0.02 mg/L) concentrations observed on May 2 give an indication of the bloom conditions; the mean values of samples collected between June and November were much lower at 30 μg/L ($n = 8$) and 1.6 mg/L ($n = 8$), respectively (Table 2 in Supporting Information).

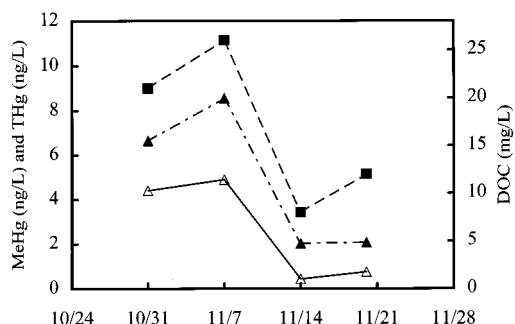**FIGURE 4.** MeHg (△), THg (▲), and DOC (■) concentrations in the Little Cobb River before and after the flushing event.

FIGURE 5. Results of incubating leaves in water: variation of MeHg concentrations in DDW (◇) and Le Sueur River water (◆) with time.

Total Hg concentrations were elevated during the bloom event (5.28 and 6.31 ng/L on May 2 and 9, respectively); the apparent THg concentration per unit mass of suspended sediment was lower than ordinarily seen when soil particles are mobilized (48 (May 2) and 51 (May 9) ng/g as compared with 65 ng/g). More significantly, the MeHg concentration was 1.31 ng/L on May 9, representing 20% of the THg concentration (unfortunately we have no data for the MeHg concentration on May 2). Similar conditions were observed in County Ditch 86 at this time, where an even higher MeHg/THg ratio of 48% was observed. The algal bloom in this stream was characterized by elevated concentrations of MeHg (1.34 ng/L) and THg (2.82 ng/L) on May 9. These conditions may result in increased uptake of MeHg by resident fish populations, particularly if the MeHg is primarily associated with the algae. It is likely that the MeHg we measured during this event was mostly associated with the biotic material in the water column; unfortunately, we did not characterize the partitioning of MeHg between the seston and the water phases in order to examine this possibility.

As described above, levels and trends of THg and MeHg concentrations were generally similar in the two streams from March through September. In October and November, however, a second event characterized by very high MeHg concentrations was observed in the Little Cobb River, while MeHg concentrations in County Ditch 86 were higher than previous levels but not extremely high. The concentration of MeHg in the Little Cobb River increased from 0.44 ng/L on October 3 to 4.90 ng/L on November 7 under the conditions of essentially zero discharge. This increase in MeHg concentration was accompanied by a change in water color (from clear to dark brown) and an increase in the DRP concentration, from 0.18 mg/L on October 2 to 0.47 mg/L on October 31 (Table 2 in Supporting Information). The concentration of THg also increased at this time, from 2.38 ng/L on October 3 to 8.55 ng/L on November 7. The MeHg/THg ratio was unusually high during this event, increasing from 18% on October 3 to 66% on October 31 and then decreasing slightly to 57% on November 7. Gentle rains falling on November 6 and 12 resulted in the resumption of flow in the stream and the flushing of the brown, MeHg-rich water from the system. The concentrations of MeHg, THg, and DOC all dropped precipitously with the resumption of discharge (Figure 4), as did the DRP concentration (0.17 mg/L on November 14).

Discharge was also negligible on County Ditch 86 throughout October, but this stream did not exhibit the extremely high MeHg concentrations observed in the Little Cobb River. Concentrations of MeHg in County Ditch 86 increased from 0.24 ng/L on October 3 to 0.48 ng/L on October 31; rain on November 6 flushed the stream and reduced the MeHg concentration to 0.22 ng/L on November 7. The MeHg/THg ratio was 17% on October 24 and 16% on October 31 and then decreased to 4% on November 7 as runoff brought higher THg concentrations and flushed the MeHg-rich water. Water in this stream was not colored like that in the Little Cobb
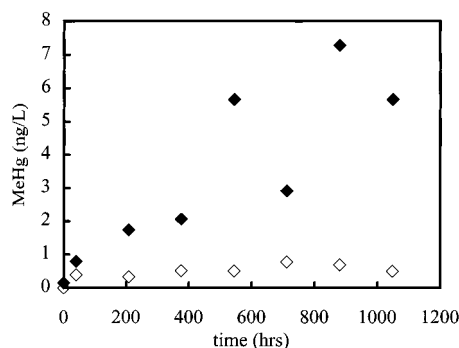
River during this time; the DOC concentration in the ditch was only 12 mg/L on October 31 as compared to 21 mg/L in the river. The concentration of DRP in County Ditch 86 increased from 0.07 mg/L on October 2 to 0.12 mg/L on October 31 (Table 3 in Supporting Information) but did not reach the high levels observed in the Little Cobb River.

We observed a significant quantity of newly fallen leaf litter in and beside the Little Cobb River beginning in early October as the maple, oak, cottonwood, and other deciduous trees shed their leaves. In the absence of stream discharge, leaf litter falling into the stream sat in stagnant water for several weeks. Physical, chemical, and biological decomposition processes resulted in the leaching of colored organic materials from the leaves into the water, leaving the water dark brown in color and high in DOC. The elevated DRP concentration at this time suggests that anoxic conditions were established and iron oxyhydroxides (Fe(III)OOH) were reduced, releasing hydroxide-bound orthophosphate. Leaves contain MeHg and other Hg species both surficially and constituitively, and the elevated MeHg concentrations observed probably reflect at least in part the addition of MeHg to the water directly from the leaves. The addition of leaves to the stream may also have stimulated biological activity directed toward decomposition of the leaves. The enhanced biological activity under anoxic conditions may have increased Hg methylation rates and in-stream MeHg concentrations in a way similar to what occurs when terrestrial areas are flooded to create reservoirs (31, 32).

Land cover on the riparian areas of County Ditch 86 is mostly grass with few trees, and leaf litter does not enter the stream in large quantities. Water in County Ditch 86 did not turn brown after leaf fall because leaf litter inputs were not significant. MeHg concentrations were elevated above typical summertime concentrations, but the conditions leading to extremely high MeHg concentrations in the Little Cobb River were not duplicated in County Ditch 86.

We performed several laboratory experiments to examine the hypothesis that leaf litter inputs resulted in elevated MeHg concentrations in the Little Cobb River. In one experiment, a mixture of cottonwood, maple, oak, and elm leaves collected from beside the Little Cobb River was placed in water in a Teflon bottle, and 50-mL aliquots of the water were analyzed for MeHg periodically over several weeks. Two bottles were prepared: one containing deionized, distilled laboratory water (DDW), and the other containing relatively low-MeHg water (0.15 ng/L) taken from the Le Sueur River. The mass of leaves in the bottle containing DDW was 12 g, and that in the other bottle was 21 g. The mass of water in each bottle was 450 g at the start of the experiment; as aliquots were withdrawn over time, the water was not replenished. The bottles were kept at room temperature (21 °C), capped tightly except for sampling. Samples taken from both bottles showed increased MeHg concentrations within 40 h of the start of the experiment (Figure 5). Throughout the experiment, MeHg

concentrations were higher in the river water than in the DDW. MeHg concentrations in the DDW never exceeded 1 ng/L, but those in the river water increased to over 7 ng/L after about 5 weeks. The color of the water in both bottles darkened over the course of the experiment, with the river water reaching a darker hue. In addition, the river water developed a strong sulfurous (H_2S) odor over time, but the DDW maintained a sweet, "decaying leaf litter" smell throughout. We interpreted these results to indicate that Hg methylation under anaerobic, sulfate-reducing conditions was taking place in the river water bottle, whereas MeHg in the DDW came from the washing off or leaching of MeHg from the leaves. Microorganisms may have utilized available sulfate in the river water for respiration, but the absence of appreciable sulfate prohibited similar activity in the DDW. The microorganisms acting in the river water may have originated in the water and/or they may have been attached to the leaf surfaces. Biologically mediated methylation of Hg under sulfate-reducing conditions is known to be a prevailing route to MeHg production in the environment (21−23). Elevated MeHg concentrations in the Little Cobb River may have resulted from enhanced methylation of Hg under anoxic conditions promoted by leaf litter decomposition and zero discharge.

In another experiment, a mixture of maple, oak, and cottonwood leaves (mass ratio 1.2:1:1) was rinsed with DDW (5.0 g of leaves in approximately 100 mL of DDW) for 20 min. Two 50-mL water samples were then distilled and analyzed for MeHg. Both samples showed elevated MeHg concentrations (0.94 and 0.78 ng/L), indicating that some MeHg is immediately transferable to water when leaves are immersed. This process probably also contributed to the elevated MeHg concentrations observed in the Little Cobb River.

Further studies involving long-term sampling and the addition of sampling sites on other streams would be necessary to determine how representative these results are. As presented here, the results suggest that direct leaf litter inputs to water bodies can have both immediate and longer term effects on MeHg concentrations. MeHg on leaves falling into water can be transferred rapidly into the water phase, and biological degradation may release MeHg held constitutively in the leaves. In addition, biological activity stimulated by organic leaf litter inputs can increase Hg methylation in surface waters, especially under anoxic conditions, again resulting in elevated MeHg concentrations. These findings add further credence to the important role of litter fall as a transport vector for MeHg in forested watersheds. Leaf litter in forested riparian areas strongly influences MeHg concentrations in underlying soils and in runoff waters that drain those soils.

Acknowledgments

Supporting Information Available

Details of sampling procedure and distillation method; Table 1 containing THg, MeHg, TSS, VSS, and DOC data for both sampling sites; Table 2 containing DRP, TKN, and chlorophyll *a* data for the Little Cobb River; Table 3 containing DRP, TKN, and chlorophyll *a* data for County Ditch 86. This material is available free of charge via the Internet at http://pubs.acs.org.

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