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Distribution and Transport of Total Mercury and Methylmercury in Mercury-Contaminated Sediments in Reservoirs and Wetlands of the Sudbury River, East-Central Massachusetts

Water-Resources Investigations Report 99-4060



U.S. Department of the Interior
U.S. Geological Survey

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By JOHN A. COLMAN, MARCUS C. WALDRON,
ROBERT F. BREAUULT, and ROBERT M. LENT

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Northborough, Massachusetts
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For additional information write to:

Chief, Massachusetts–Rhode Island District
U.S. Geological Survey
Water Resources Division
10 Bearfoot Road
Northborough, MA 01532

Copies of this report can be purchased from:

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Denver, CO 80225-0286

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CONVERSION FACTORS AND OTHER ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	2.540	inch
degrees Celsius (°C)	$^{\circ}\text{F} = 1.8 \times ^{\circ}\text{C} + 32$	degree Fahrenheit
gram (g)	0.03527	ounce
kilometers (km)	0.6214	mile
meter (m)	0.3048	foot

OTHER ABBREVIATIONS

cm/s	centimeters per second
cm ² /s	centimeters squared per second
mg/L	milligrams per liter
mL	milliliters
ng/g	nanograms per gram
ng/L	nanograms per liter
ng/L/cm	nanograms per liter per centimeter
μg/g	micrograms per gram
μg/m ² /yr	micrograms per square meter per year
μm	micrometers
μS/cm	microsiemens per centimeter at 25° Celsius

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Abstract

Total mercury and methylmercury were measured in 4 reservoir cores and 12 wetland cores from Sudbury River. The distribution of total mercury and methylmercury in these cores was evaluated to determine the potential for total mercury and methylmercury transport from reservoir and wetlands sediments to the water column. Concentrations of methylmercury were corrected for an analytical artifact introduced during the separation distillation used in the analysis procedure. Corrected methylmercury concentrations correlated with total mercury concentrations in bulk sediment from below the top layers of reservoir and wetland cores; methylmercury concentrations at the top layers of cores were relatively high, however, and were not correlated with total mercury concentrations. Concentrations of methylmercury in pore water were positively correlated with methylmercury concentrations in the bulk sediment. High concentrations of total mercury and methylmercury in sediment (73 and 0.047 micrograms per gram dry-weight basis, respectively) contributed less to the water column in the reservoir than in the wetlands probably because of burial by low concentration sediment

and differences in the processes available to transport mercury from the sediments to the water in the reservoirs, as compared to the wetlands.

INTRODUCTION

The Sudbury River comprises a system of flowing reaches, impounded reaches, and riparian wetlands in east-central Massachusetts that was contaminated over a 60-year period with mercury (Hg) from the Nyanza Chemical Waste Dump Site (the Nyanza site) in the town of Ashland, Massachusetts (Wiener and Shields, in press). In the investigation described here, the potential for the transport of total mercury (ΣHg) and methylmercury (MeHg) from reservoir and wetland sediments to the water column was evaluated using (1) distribution of MeHg and ΣHg in Sudbury River sediments in relation to a Hg point source (the Nyanza Site); (2) partitioning of ΣHg and MeHg between pore water and reservoir and wetland bulk sediment; and (3) association of ΣHg -contaminated Sudbury River sediments with net MeHg generation in river reaches, as determined from measurements of the distribution and correlation of ΣHg and MeHg in bed sediments. Net MeHg generation in this investigation means the difference between release of MeHg from the sediment and methylation of Hg in the water column, and sedimentation and demethylation of MeHg in the water column.

In a surface-water investigation of the Sudbury River, Waldron and others (in press) measured Hg mass-balance budgets for reaches of the Sudbury River using transport data of ΣHg and MeHg. Waldron and coworkers determined that net generation of MeHg in the contaminated reservoir was similar to yield measured in a lake with no point-source contamination (Watras and others, 1994). However, yield of ΣHg and net generation of MeHg per area of wetland sediments in a Hg contaminated riparian wetland reach was 60 and 15 times greater, respectively, than at a wetland site uncontaminated by point source Hg (Krabbenhoft and others, 1995).

Net generation of MeHg is important in investigations of the environmental effects of Hg contamination, because MeHg is the form of Hg that is concentrated by fish and aquatic food chains (Bloom, 1992). Conditions that cause a difference in the response of net MeHg generation to ΣHg concentrations in the reservoir and wetland reaches in the Sudbury River could be associated with differences in the sediments of the two reaches. Previous investigations of Hg methylation indicate that sulfate-reducing bacteria in lake sediment are associated with the methylation process (Gilmour and Henry, 1991). Hg deposition/export budget comparisons of upland and wetland drainages have indicated that wetlands are sites of Hg conversion to MeHg (Rudd, 1995). Because of the importance of sediments in Hg methylation, investigation of the Sudbury River sediment environments could contribute significant information regarding the relative impact of Hg contamination on MeHg presence in reservoir and wetland environments (Waldron and others, in press).

The significance of the results of investigation of ΣHg and MeHg in the Sudbury River sediments may extend beyond the local issue regarding determination of environmental impact of Hg contamination from the Nyanza site. Connections between ΣHg concentration and MeHg generation in aquatic environments are not well established (Kelly and others, 1995). Without the establishment of an association between ΣHg and MeHg in the environment, the efficacy of Hg emission control as a management strategy to control environmental impact of Hg may be questioned (Kelly and others, 1995), because Hg released to the environment from major sources, like coal combustion, is not in the methyl form (Prestbo and Bloom, 1995).

An investigation of ΣHg and MeHg in sediments of the Sudbury River may establish a relation between the large range of ΣHg concentrations in the river sediments and concentrations of MeHg in the sediments.

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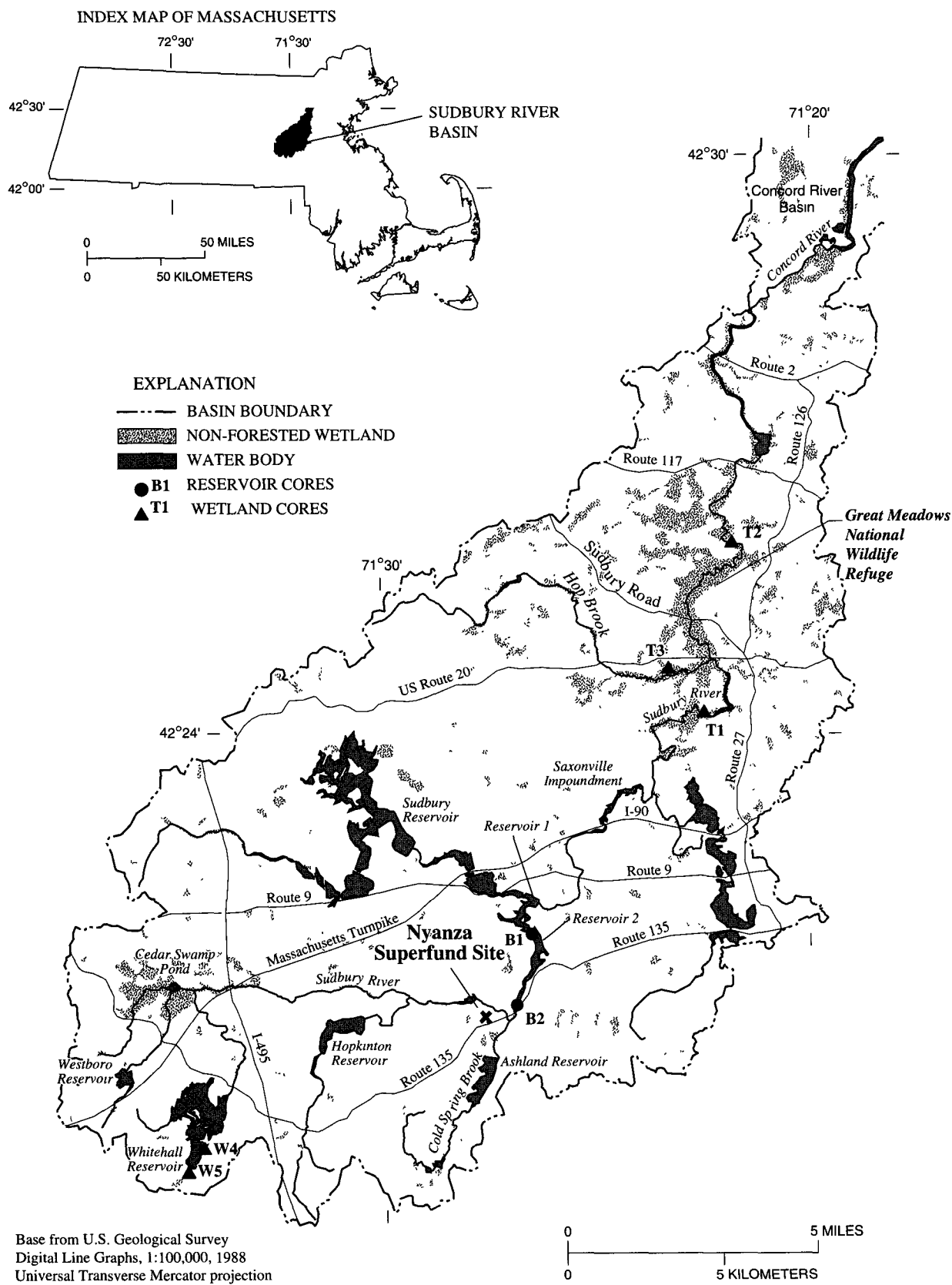
DESCRIPTION OF STUDY AREA AND CORING LOCATIONS

Sediment cores were obtained from two reservoirs and at three transects in the wetlands. Background and contaminated cores were obtained for each sediment type.

Study Area

The Sudbury River begins in Cedar Swamp Pond, flows east 17 km past the Nyanza Site, and then northeast through three impoundments, in downstream order, Reservoir 2, Reservoir 1, and the Saxonville Impoundment (fig. 1). Downstream from the Saxonville Impoundment, the river enters a 19-km reach bordered by palustrine scrub-shrub and emergent (wet-meadow) wetlands that are part of the Great Meadows National Wildlife Refuge.

There is little potential for resuspension of sediments in the reservoirs downstream from the Nyanza Site (David Abraham, U.S. Army Corps of Engineers, written commun., 1998). Downstream from the reservoirs in the wetland reach, the stream channel continues to be low gradient, and water velocities are not sufficient to resuspend sediments except at channel constrictions near road bridges.



Base from U.S. Geological Survey
Digital Line Graphs, 1:100,000, 1988
Universal Transverse Mercator projection

Figure 1. Locations of reservoir cores, wetland cores, and the Nyanza Site in the Sudbury River Basin in east-central Massachusetts.

Soils in the Sudbury River Basin are developed from weathering of glacial drift derived from the crystalline metamorphic rock underlying the region. The ground water and stream water in contact with the relatively insoluble rock and soil is low in hardness (annual mean 38 mg/L as CaCO₃) and low in conductance (annual mean 220 µS/cm). Wiener and Shields (in press) provide a more detailed description of the study area.

Coring Locations

Reservoir sediment cores were collected from Whitehall Reservoir, upstream from the Nyanza Site, and from Reservoir 2, the first reservoir downstream (about 1 km) from the Nyanza Site (fig. 1 and table 1). These cores were collected from the deep-hole (greatest water depth) and a littoral site in each reservoir. The sampled sites in Whitehall Reservoir were within 300 m of each other. Sites sampled in Reservoir 2, which is long and narrow, were 2 km apart.

Wetland sediment cores were collected downstream from the Saxonville Impoundment in the reach of the Sudbury River that flows through the Great Meadows National Wildlife Refuge. Twelve wetland cores were collected—four cores each along two transects (T1 and T2, fig. 1) orthogonal to the direction of river flow and a single reference core from a third transect (T3, fig. 1). Three additional, time-series cores were collected at one of the T1 sampling sites.

Transects T1 and T2 were located 21 and 31 km, respectively, downstream from the Nyanza Site. Cores from transects T1 and T2 were collected in the river channel, at the riverbank, and 30 and 60 m from the riverbank. The reference wetland core (at T3) was collected in floodplain soils on Hop Brook, 10 m from the brook's bank and far enough upstream from the Sudbury River (about 2 km) to be uncontaminated by the Nyanza Site. Each coring site is identified by transect number and distance from the stream channel (table 2).

The wetland cores were collected from submerged locations, except for the three time-series cores. The time-series cores were collected in August and September 1995 to determine changes in Hg species during the summer dry period. During the

summer, water levels declined more than 0.5 m in the Sudbury River channel and in temporary flood-plain monitoring wells. The unsaturated cores were obtained at transect T1, 30 m from the riverbank.

Table 1. Sampling sites, collection dates, and core length for sediment cores collected in selected reservoirs of the Sudbury River, east-central Massachusetts

[No., number; cm, centimeter; m, meter]

Core site No.	Sampling site	Date collected	Core length (cm)	Depth of water (m)
W4	Whitehall Reservoir, deep hole	August 26, 1994	72	7.9
W5	Whitehall Reservoir, littoral	August 26, 1994	44	3.5
B1	Reservoir 2, deep hole	August 25, 1994	24	4.6
B2	Reservoir 2, littoral	May 12, 1995	70	2.7

Table 2. Sampling sites, collection dates, and core length for sediment cores collected in riparian wetlands of the Sudbury River, east-central Massachusetts

[No., number; cm, centimeter]

Transect No.	Sampling site	Date collected	Core length (cm)
T1	Stream channel	August 10, 1995	54
T1	At stream bank	May 9, 1995	78
T1	30 meters from stream bank	May 8, 1995	68
T1	30 meters from stream bank	August 8, 1995	74
T1	30 meters from stream bank	August 31, 1995	69
T1	30 meters from stream bank	September 9, 1995	63
T1	60 meters from stream bank	May 5, 1995	60
T2	Stream channel	September 7, 1995	55
T2	At stream bank	May 18, 1995	70
T2	30 meters from stream bank	May 16, 1995	58
T2	60 meters from stream bank	May 10, 1995	60
T3	Hop Brook reference site	May 25, 1995	55

STUDY METHODS

Data-collection efforts consisted of sediment coring operations and chemical analysis of the sectional core samples.

Coring and Sampling Procedures

Cores were collected using a piston corer with an 8-cm inside diameter acrylic-core barrel. Core barrels were cleaned with 10 percent hydrochloric acid (HCl) and tap water between uses. For the reservoir cores, the piston was fixed over the sediment by a cable attached to a boat. The core barrel was pushed past the piston using push rods from the surface. For the wetland cores, the piston also was fixed over the sediment. A slide hammer drove the barrel past the piston into the sediment.

Upon retrieval, cores were transported upright to the laboratory, refrigerated at 4°C, and extruded the next day. Cores were extruded into an N₂ atmosphere in a disposable plastic glove bag and sectioned at intervals ranging from 2 to 10 cm; the intervals increased in thickness with depth in the core. Subsamples spanning the thickness of each section were, separated with a clean plastic spoon for ΣHg and MeHg analyses of the bulk sediment. Subsamples of sediment for pore-water separation were placed into pre-cleaned, preassembled, polycarbonate, disposable Nalgene filtration units with a cellulose nitrate filter (0.2-μm pore size). The filtration units were transferred to a second glove bag with a N₂ atmosphere and pore water was extracted by vacuum application.

Analytical Procedures

The dry fraction and loss on ignition (at 550°C) of sediment samples were measured by standard methods (American Public Health Association and others, 1975). All Hg results reported for bulk sediment are in terms of Hg concentrations per gram dry weight of sediment.

Samples intended for Hg analysis were packed on ice and sent by overnight courier to Frontier Geosciences, Inc., in Seattle, Wash. Samples for ΣHg analysis in bulk sediments were prepared by hot

HN₃/H₂SO₄ digestion of a 1-g sample (Bloom and Crecelius, 1987), dilution to 25.6 mL in a Teflon vial with 0.001 N BrCl, SnCl₂ reduction of 0.01 to 1.0 mL sub aliquots, and purging onto dual gold-coated sand traps. Hg was detected by cold-vapor atomic fluorescence spectrometry (CVAFS) (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988). MeHg was separated from the bulk sediments by distillation from the HCl acidified sample, amended with ammonium pyrrolidine dithiocarbamate matrix modifier (Bloom and von der Geest, 1995). MeHg concentrations were determined, after aqueous phase ethylation, pretrapping on Carbotrap, and isothermal GC separation, by CVAFS detection (Horvat and others, 1993a). ΣHg in pore water was analyzed after BrCl oxidation (5 to 10 mL subsamples) by the procedures used in the sediment analysis. MeHg in pore water was determined after distillation (Horvat and others, 1993b) using the same procedures used in the bulk sediment analysis.

Quality controls applied to the Hg analyses included use of standard reference materials (NRCC and PACS-1, certified for ΣHg, and DORM-2, certified for ΣHg and MeHg), and split-sample analyses. Means of three analyses of each standard, determined with each core analyzed, were within the standard's certified range. Differences between split samples for 11 sample pairs of ΣHg in bulk sediment averaged 10 percent of the mean.

During the present investigation, analytical comparisons of samples spiked with inorganic Hg and unspiked samples indicated that an analytical artifact in the MeHg distillation procedure and in other commonly used methods of MeHg extraction from natural samples caused higher concentrations of MeHg to be measured than were actually present in the original sample (Bloom and others, 1997). The artifact is caused by conversion of a small amount of the ΣHg to MeHg during the analysis extraction procedure and is significant in water and sediment samples that have ratios of MeHg:ΣHg that are less than 1 percent (Bloom and others, 1997). MeHg:ΣHg ratios in pore-water samples of the present investigation were large enough to obviate the need for correction. MeHg:ΣHg ratios in some sediment samples were less than 1 percent and required correction.

Bloom and others (1997) measured the conversion (methylation) of Hg(II) spikes that were added to a variety of natural materials including three composite wetland samples from sediments collected in the present investigation. The percentage of added Hg(II) that was methylated in these wetland samples did not vary greatly—0.010, 0.015, and 0.019. The percentage of Hg(II) methylated from a fourth wetland sample from the Florida Everglades was 0.019. Four conversion rates measured for the present investigation on discrete wetland core samples from the Sudbury River decreased with depth in the sediment core from 0.02 percent at 2 to 4 cm below the top of the core to 0.01 percent at a depth of 18 to 20 cm depth. Conversion factors were not calculated for fine-grained reservoir sediments; conversion factors for reservoir and river sands were higher (0.05 to 0.09 percent) than the wetland samples.

In the present investigation, the conversion value of 0.019 percent was used to correct all MeHg analyses in bulk sediment. Use of the highest conversion value of the range measured in fine-grained samples means that MeHg may be over corrected (too low) in some samples. Over correction might obscure a correlation between MeHg and ΣHg in the sediment but avoids the problem of false correlation.

DISTRIBUTION OF TOTAL MERCURY AND METHYLMERCURY IN SEDIMENTS

Data were obtained on sediment loss on ignition, and on ΣHg and MeHg in bulk sediment and in pore water. These parameters were measured in both reservoir and wetland sediment.

Sediment Loss on Ignition

Sediment loss on ignition (LOI) was greater for the Whitehall Reservoir cores (median 33, range 30 to 42 percent) than for the Reservoir 2 cores (median 13, range 5 to 20 percent) and was variable among the

wetland cores (median 25, range 1 to 57 percent). Despite the low minimum value for the wetlands, LOI was greater than 15 percent in the top 15 cm of all wetland cores. LOI evidence of substantial organic carbon in the Sudbury River sediments (LOI equals about two times organic carbon) indicates that post-depositional migration of Hg in sediments would be minimal (Rasmussen, 1994).

Total Mercury in Bulk Sediment of Reservoir Cores

The maximum concentrations of ΣHg in sediment were much less (0.4 μg/g) in the cores from Whitehall Reservoir than in the cores from Reservoir 2 (maximum ΣHg = 73 μg/g) (fig. 2). ΣHg concentrations in Whitehall Reservoir decreased continuously with depth, from 0.3 to 0.4 μg/g at the top layer of the core to about one-tenth those values at a depth of 50 cm, a pattern noted in many lakes for which the Hg source is atmospheric deposition (Swain and others, 1992). ΣHg concentrations in the near surface (0 to 4 cm) at Whitehall Reservoir (300 to 400 ng/g) were 1.5 to 2 times greater than was measured in a Wisconsin seepage lake in which point sources of Hg were not a factor (Hurley and others, 1994). ΣHg concentrations at 40 to 70 cm depth in the Whitehall Reservoir cores (30 to 70 ng/g) were similar to those reported below the sediment surface for the seepage lake. By contrast, ΣHg concentrations in Reservoir 2 cores increased with depth, from 6 μg/g at the top of the core to midcore concentrations as great as 73 μg/g. The thick deposit of above-background ΣHg concentration in core B2 indicates that deposition of ΣHg was greatest at this site. Farther downstream in Reservoir 2, a mid-core peak was measured in core B1 with a lower concentration and decreased thickness indicating less ΣHg deposition. The reservoir results were consistent with data from cores collected by Frazier and others (in press), who described the variation of Hg sedimentation rates with time and distance from the Nyanza Site on the basis of analysis of age-dated cores.

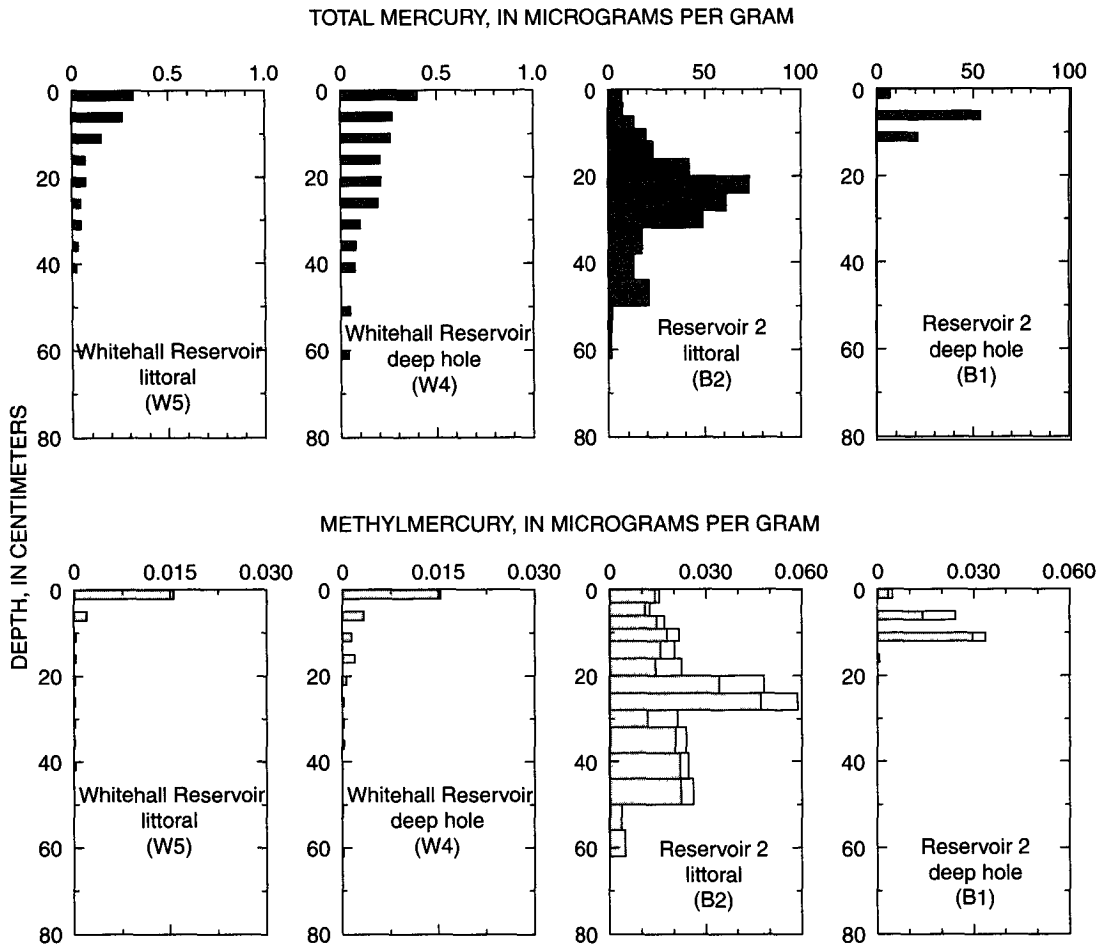


Figure 2. Total mercury and methylmercury concentrations (dry-weight basis) in sediment cores from Whitehall Reservoir and Reservoir 2. Core site number is given in parentheses. Bar thickness, represents sediment-section thickness subsampled for analysis. Length of shaded bar in methylmercury figures represents corrected results. Total length of the stacked bars represents uncorrected results. (Note difference between reservoirs in scale for mercury concentrations.)

Methylmercury in Bulk Sediment of Reservoir Cores

Concentrations of MeHg in bulk sediment required corrections for methylation of Hg during analysis, as discussed in the Analytical Procedures section. Only the corrections associated with the relatively high concentrations of ΣHg present in the Reservoir 2 cores were large enough to be visible in figure 2.

Cores from Whitehall Reservoir and Reservoir 2 contained similar concentrations of corrected MeHg (hereafter MeHg refers to corrected concentrations) at the top of the cores (about $0.015 \mu\text{g/g}$), but different concentrations deeper in the sediments (fig. 2). MeHg concentrations in the cores from Whitehall Reservoir decreased tenfold in the first 10 cm of core depth and reached a constant value of about $0.0001 \mu\text{g/g}$ at depths below about 20 cm. On a percentage basis, the MeHg concentration decrease was more pronounced than the

decrease of ΣHg , so that the ratio of MeHg to ΣHg decreased with depth in the Whitehall Reservoir sediments, from 4 to 5 percent at the top of the cores to 0.1 to 0.5 percent at depths below 10 cm.

The depth profiles for MeHg and ΣHg in cores from Reservoir 2 were similar in the same core. Thus, the greatest MeHg concentration in bulk sediment, 0.047 $\mu\text{g/g}$, was measured at depths of 24 to 28 cm in core B2 from Reservoir 2, coinciding with the greatest ΣHg concentration. MeHg concentrations in Reservoir 2 cores decreased to the below-surface concentrations of the Whitehall Reservoir cores deeper in the sediment, below the level at which large ΣHg concentrations were measured. The MeHg: ΣHg ratios in cores from Reservoir 2 ranged from 0.1 to 0.2 percent, which are similar to the ratios measured below the top layer of the Whitehall Reservoir cores.

Total Mercury in Bulk Sediment of Wetland Cores

The depositional pattern of ΣHg is more complex in the flood-plain riparian wetlands than in the reservoirs. Flow through the wetlands could resuspend or deposit ΣHg , depending on stream-stage changes and local microtopography, such as hummocks and deposited sediment bars. Sediment deposition in the wetlands is limited to periods when overbank flow takes place—late autumn, winter, and early spring—whereas sediment deposition in the reservoirs can take place at all stream stages, year-round.

ΣHg depth profiles of the overbank wetland cores collected 21 km downstream from the Nyanza Site (transect T1, 30 and 60 m from the channel, figs. 3A and 4) were of lower concentration but of similar shape (mid-core maximum) as the cores from Reservoir 2. ΣHg concentrations generally were higher in the T1 wetland cores than in the T2 wetland cores (fig. 3A and 3B), which were obtained 10 km farther downstream. ΣHg concentrations were similar at a given depth in the unsaturated time-series cores (T1, 30 m, fig. 4). Concentrations in the time-series cores indicate that a consistent depositional pattern can extend over an area of several square meters in the wetlands but concentrations in the transect cores

(fig. 3A and 3B) indicate one pattern does not extend over an interval as large as 30 m. The channel and bank cores contained lower ΣHg concentrations than the 30 and 60 m cores for T1, but channel and bank cores were similar to the overbank cores in T2. Maximum ΣHg concentrations measured in the T2 cores were at or near the surface. ΣHg concentrations were lowest in the Hop Creek reference core (T3, fig. 3B), with a pattern of slight increase from the top of the core to 10 cm, then a decrease with depth.

Core coverage was not sufficient to determine the total amount of ΣHg deposited in the wetlands, but comparison of the four cores from the flood plain away from the channel (fig. 3) indicated that more ΣHg was deposited in the sediments closer to the Nyanza Site (T1 transect, fig. 1) than in the sediments farther downstream (T2). Concentrations of ΣHg in the T2 transect, however, continued to be greater than ΣHg concentrations measured at the reference wetland site, T3 (fig. 3).

Similarity of the ΣHg concentration-depth profiles at T1 to those from Reservoir 2 (mid-core maximums) indicated that deposition in the T1 wetland core may have been in response to the same Hg source as that recorded in the reservoir sediments. The downstream wetland pattern of surficial maximum may have resulted from different processes, such as ΣHg leaching or erosion from the upstream deposits and redeposition downstream.

ΣHg concentrations in the Hop Brook reference wetland core (240 ng/g at the top layer and 60 ng/g at depth) were similar to the top layer and deep Hg concentrations of North American and Northern European cores from wetlands reviewed by Zillioux and others (1993), which were selected to represent atmospheric input sources. The low ΣHg concentrations in sediment and in water samples from Hop Brook (Waldron and others, in press) confirm that Hop Brook did not carry point-source ΣHg to the wetland reference site.

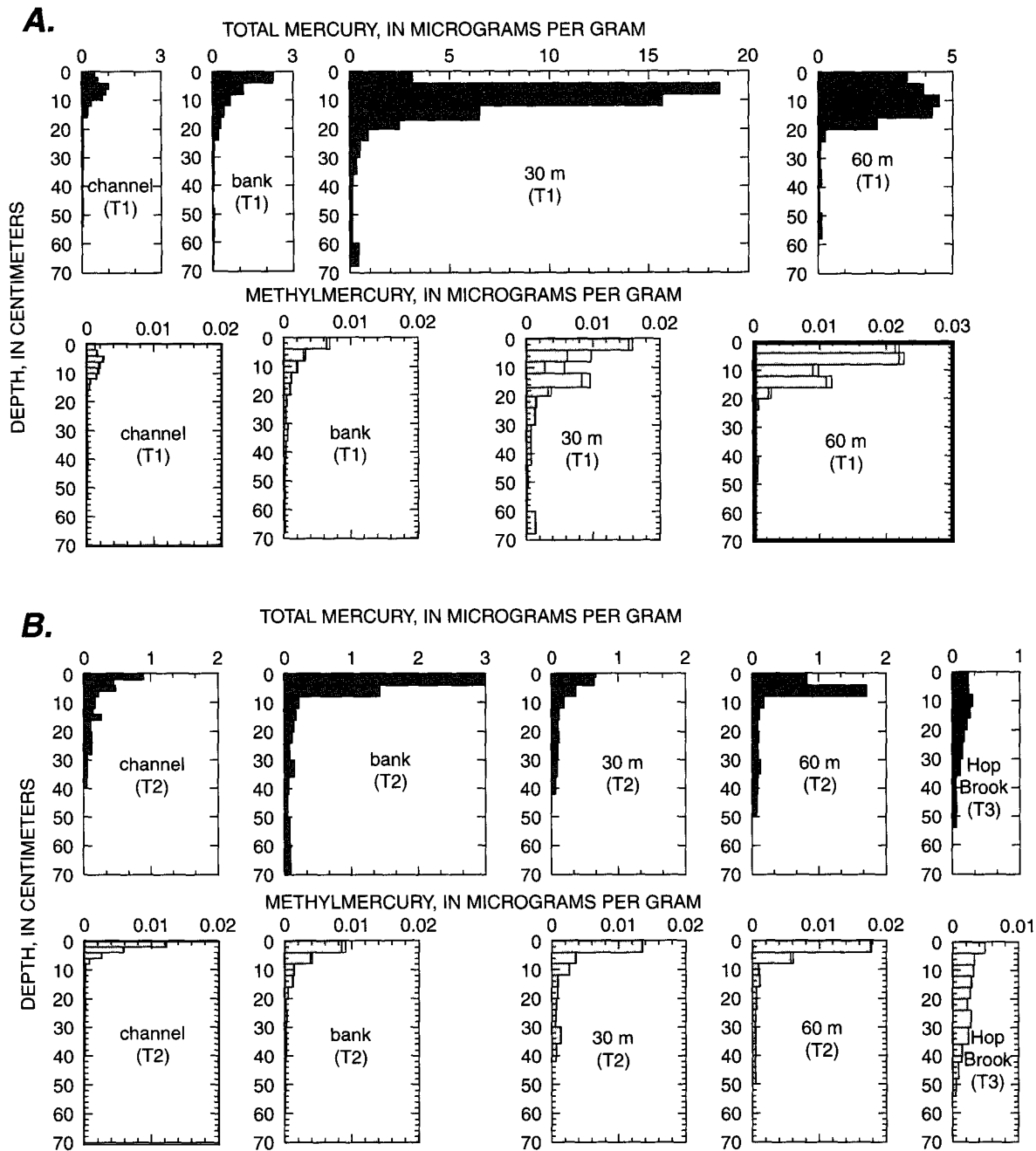


Figure 3. Total mercury and methylmercury concentrations (dry-weight basis) in water-saturated, sediment cores from wetlands. Panel A cores are from transect T1, 21 kilometers downstream from the Nyanza Site. Panel B cores are from transect T2, 31 kilometers downstream from the Nyanza Site, and from transect T3, the reference site. Distance along the transects from the stream channel is indicated in meters, and transect numbers are given in parentheses. Bar thickness represents sediment-section thickness subsampled for analysis. Length of shaded bar in methylmercury figures represents corrected results (see text). Total length of the stacked bars represents uncorrected results.

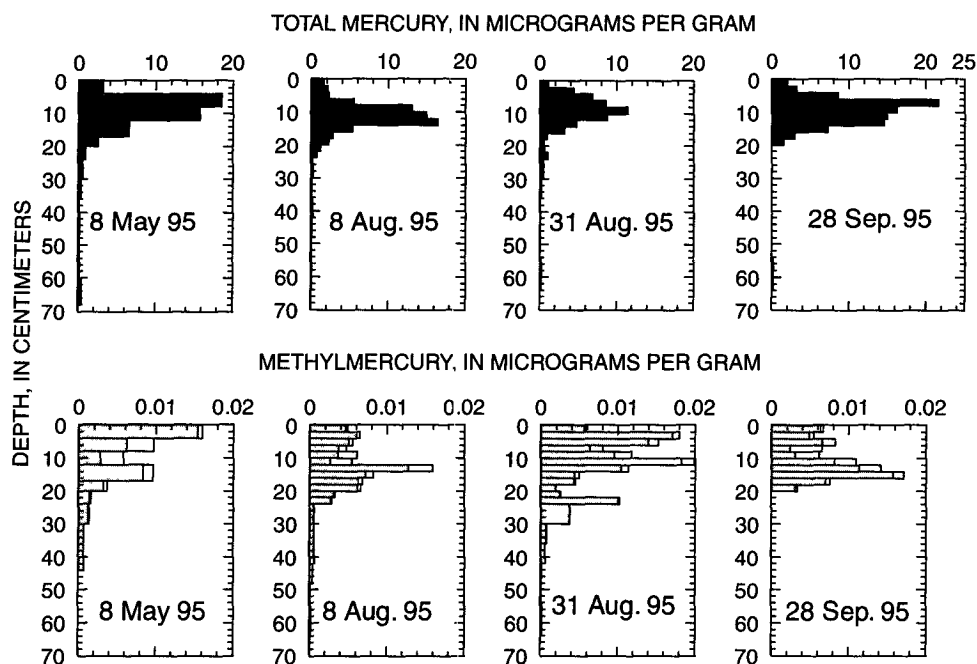


Figure 4. Total mercury and methylmercury concentrations (dry-weight basis) in time-series cores from a wetland floodplain of the Sudbury River, transect T1, 30 meters from the stream bank. The August and September cores were unsaturated. Bar thickness represents sediment-section thickness subsampled for analysis. Length of shaded bar in methylmercury figures represents corrected results. Total length of the stacked bars represents uncorrected results.

Methylmercury in Bulk Sediment of Wetland Cores

Corrections for artifact MeHg in analyses of wetland sediment were small except in the cores at T1, 30 m, where ΣHg concentrations were highest (fig. 3). As was the case for the reservoir cores, relatively high concentrations of MeHg (0.01 to 0.02 $\mu\text{g/g}$) were measured at the top of most of the wetland cores. Exceptions were the Hop Brook reference core (0.005 $\mu\text{g/g}$, 0–4 cm) and the 3 unsaturated cores obtained at T1, 30 m in August and September 1995 (0.005 to 0.007 $\mu\text{g/g}$, 0–2 cm, fig. 4). Relatively high MeHg concentrations also were measured as deep as 15 cm below the top of the cores with below-surface ΣHg concentration maximums. In the cores at T1, 30 m and T1, 60 m, this resulted in 2 MeHg peaks—at the top of the cores, and in the 10- to 20-cm depth interval of the ΣHg concentration maximum.

Although concentrations of MeHg in the unsaturated wetland cores (fig. 4) were slightly lower at the surface than in the saturated cores, the subsurface peaks of MeHg in the unsaturated cores were similar to those of the saturated cores. Below the first few centimeters, MeHg persisted in the cores throughout the summer, despite a decline in the water table in the wetland areas.

The MeHg: ΣHg concentration ratio below the surface in most of the wetland cores was similar to that of the reservoir cores. The ratio at the top layers ranged from 0.3 to 2 percent. At depths of 4 cm and greater, the ratio generally ranged from 0.1 to 0.5 percent, although some layers in cores at T1, bank; T1, 60 m; and in T2, 30 m approached 1 percent.

MeHg concentrations measured at the top of the reservoir cores (about 15 ng/g) were seven times greater than those determined at the top of a Wisconsin seepage-lake core (Benoit and others, 1994) and four times greater than the maximum measured in 11 surface samples from Quabbin Reservoir (Massachusetts)

(Gilmour and others, 1992: in conversion from reported wet weights for the latter, 0.2 dry-weight fraction was assumed). MeHg concentrations in bulk sediment at the top of wetland cores also were two to seven times higher than those measured elsewhere in wetlands (Kelly and others, 1997). The reason for high MeHg concentrations in bulk sediment from the Sudbury River, even at reference locations, compared to those reported elsewhere, is unknown.

Correlation of Total Mercury and Methylmercury in Bulk Sediment

Plots of ΣHg compared to MeHg concentration in bulk sediment samples (fig. 5A for depths 0 to 4 cm, fig. 5B for depths greater than 4 cm) summarize the relation between these parameters in the reservoir and wetland sediment cores. Virtually no correlation is evident between the parameters at the top of the cores (log-linear regression r^2 of 0.03), but a correlation is indicated below the top layers (log-linear regression r^2 of 0.68).

The top-layer data (0 to 4 cm, fig. 5A) comprise relatively constant MeHg concentrations from core to core but variable ΣHg concentrations. This top layer represents about one-twentieth of the total depth over which high MeHg concentrations were measured in the Reservoir cores, and about one-third of the wetland cores. Thus, the total amount of MeHg on a depth-integrated basis varied between the Whitehall and Reservoir 2 cores by a factor of 63, but varied only by a factor of 2.5 among the wetland cores, including the Hop Brook reference core.

Total Mercury and Methylmercury in Pore Water

Measurements of ΣHg in pore water were restricted to core B2 from Reservoir 2 and to the 0- to 30-cm depths of the saturated wetland cores (selected profiles in fig. 6). If the volume of

pore-water sample available was insufficient to complete the ΣHg and MeHg analyses, MeHg was given priority. Concentrations of ΣHg in pore water were not measured for the unsaturated time-series cores. ΣHg concentrations were more variable and much higher in the reservoir core (23 to 3,400 ng/L) than in the wetland cores, where values ranged from 1.2 to 420 ng/L, with most sample concentrations from 12 to 65 ng/L. ΣHg concentrations in bulk sediment and pore water for reservoir and wetland cores were positively correlated (log-linear regression r^2 of 0.43, fig. 7).

MeHg concentrations in pore water from the Reservoir 2 core ranged from 1 to 2 ng/L (fig. 6) except for a concentration of 5.1 ng/L in the 28- to 32-cm interval. MeHg concentrations in pore water of the wetland cores generally were highest at the top of the core and decreased with depth (selected cores, fig. 6). MeHg concentrations in the pore water decreased less rapidly with depth in the T1 cores, which contained higher MeHg concentration in bulk sediment than the T2 cores. This reflects a general correlation between MeHg in bulk sediment and pore water in wetland cores (fig. 8, log-linear regression r^2 of 0.59). The relation in core B2 was not as strong (fig. 8, log-linear regression r^2 of 0.26).

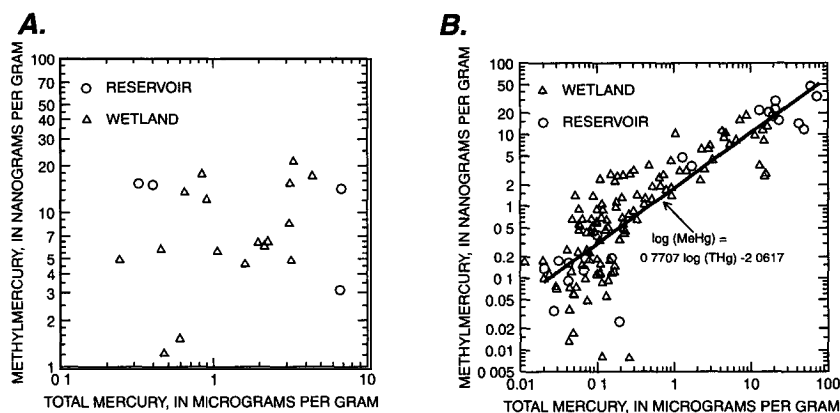


Figure 5. Relation of total mercury to methylmercury concentrations (dry-weight basis) in bulk sediment in upper sections (panel A, 0-4 centimeter depth, log-linear regression r^2 of 0.03) and lower sections (panel B, greater than 4 centimeters depth, log-linear regression r^2 of 0.68) for reservoir and wetland cores.

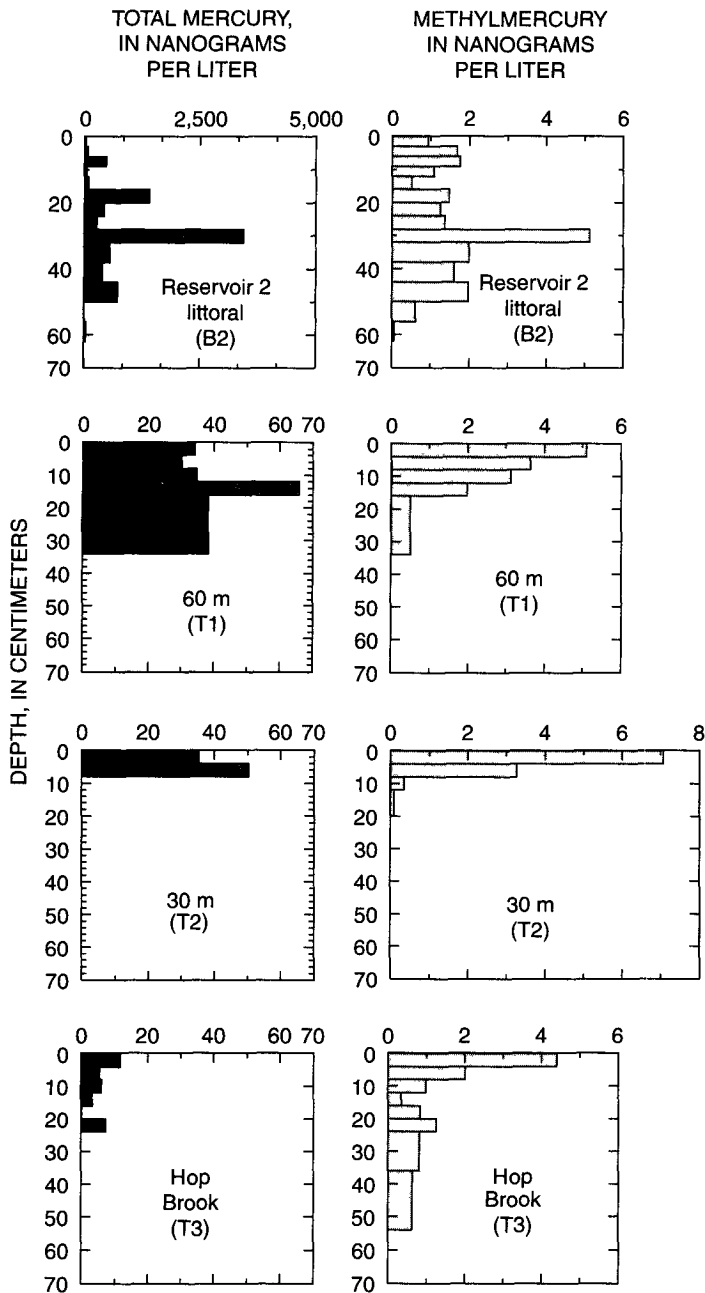


Figure 6. Total mercury (left side) and methylmercury (right side) concentrations in pore water of cores from wetland and reservoir sediments of the Sudbury River. Distance along the transects from the stream channel is indicated in meters, and transect numbers are given in parentheses.

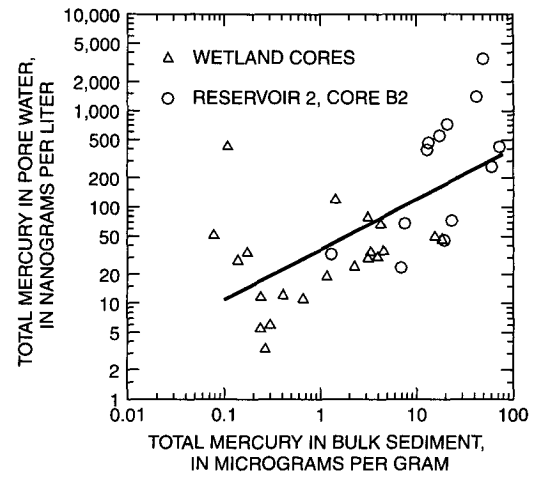


Figure 7. Relation of total mercury concentration in bulk sediment to total mercury concentration in pore water for Reservoir 2 core B2 and wetland cores, log-linear regression r^2 of 0.43.

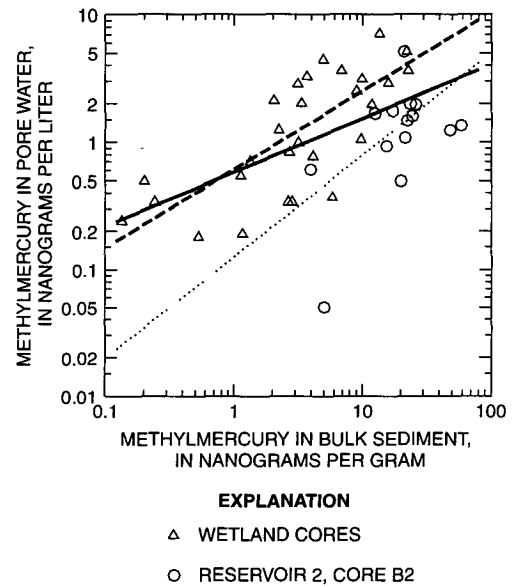


Figure 8. Relation of methylmercury concentration in bulk sediment to methylmercury concentration in pore water for Reservoir 2 core B2 and wetland cores. The log-linear regression r^2 is 0.31 (solid line) using all data, 0.59 (dashed line) using only wetland data, and 0.26 (dotted line) using only reservoir data.

TRANSPORT OF TOTAL MERCURY AND METHYLMERCURY

Mass-balance budget differences in ΣHg and MeHg transport for stream-reaches of the Sudbury River were measured by Waldron and others (in press) and described in the introduction of the present paper. ΣHg and MeHg increases in the riparian wetlands are of particular interest because they occurred primarily beyond the distance to which Hg is currently being transported from the Nyanza Site (Waldron and others, in press) and because the increases may indicate a link between ΣHg presence and MeHg generation in a wetland. ΣHg and MeHg increases within a reach may come from the sediment, although there are alternative sources. For example, the net generation of MeHg in the wetland reach could result from wetland plant growth above wetland sediment or from algal mats growing in the river channel. The extent to which the budget differences in the Hg budgets of the reservoir and the wetlands can be verified by sediment core analyses as resulting from sediment processes is examined here.

Transport of Mercury Species Between Reservoir Sediment and Water Column

The large downward net flux of ΣHg ($323 \mu\text{g}/\text{m}^2/\text{yr}$) measured by Waldron and others (in press) for the sediments of Reservoir 2 was consistent with the 6-times-background load of ΣHg contributed by the Sudbury River to the reservoir, with higher-than-background concentrations of ΣHg measured at the top of the reservoir's cores, and with greater-than-background sedimentation rates of ΣHg at the surface of Reservoir 2 cores computed by Frazier and others (in press). The net flux is the result of one-way fluxes into and out of the sediment—the latter driven by diffusion in the pore water. Although substantial pore-water concentrations of ΣHg were measured below the sediment surface in core B2 (fig. 6), the ΣHg pore-water gradient between reservoir water and the sediment surface is not large ($13 \text{ ng}/\text{L}/\text{cm}$) and would

support a flux of only about $22 \mu\text{g}/\text{m}^2/\text{yr}$, assumed porosity of 0.8 and diffusivity of $10^{-5} \text{ cm}^2/\text{s}$ (Berner, 1980). An upward diffusive flux of this magnitude could plausibly be overcome by sedimentation of the ΣHg transported in by the Sudbury River and so does not contradict the results of Waldron and others (in press).

Net generation of MeHg ($3.8 \mu\text{g}/\text{m}^2/\text{yr}$) in Reservoir 2 was not greater than that found in an uncontaminated lake (Waldron and others, in press), which indicates that Hg contaminating the sediments in Reservoir 2 and the associated high MeHg concentrations measured in the bulk sediment there did not result in substantial release of MeHg from the sediments. Actually, MeHg concentrations in bulk sediment at the surface of the Reservoir 2 cores were similar to those of the reference cores from the Whitehall Reservoir. MeHg concentrations were high only at depth in cores from Reservoir 2. The MeHg pore-water gradient between reservoir water and the core surface ($0.8 \text{ ng}/\text{L}/\text{cm}$) would support a one-way flux of only $1.3 \mu\text{g}/\text{m}^2/\text{yr}$, with assumed porosity 0.8, and diffusivity of $10^{-5} \text{ cm}^2/\text{s}$ (Berner 1980). Thus, the high MeHg concentrations measured at depth in sediment in Reservoir 2 and the high MeHg concentrations in pore water that would be expected with them (fig. 8 for correlation) may not have entered into the diffusive flux at the surface where the sediment-water exchange takes place. Lack of diffusive flux at the sediment surface would support the reservoir observations of Waldron and others (in press).

Transport of Mercury Species Between Wetland Sediment and Water Column

Net increases in ΣHg measured in the riparian wetland reaches ($175 \mu\text{g}/\text{m}^2/\text{yr}$) were as much as 60 times greater than increases measured in an uncontaminated wetland (Waldron and others, in press). Leaching of the historical ΣHg deposits in the wetland sediment could be the source of the net increases in the water column that was computed for the wetland reaches. Although present-day ΣHg

transport into the wetland reach is at approximately background rates, the wetland ΣHg core profiles (figs. 3 and 4) indicate that above-background amounts of ΣHg were transported into the wetland in the past. Leaching of the deposits in the wetland was relatively efficient, compared to $22 \mu\text{g}/\text{m}^2/\text{yr}$ one-way sediment flux for the more highly contaminated Reservoir 2, as might be expected because transport in periodically flooded wetlands would be by diffusion and advection (Kelly and others, 1997), rather than by diffusion alone.

ΣHg concentration in the most contaminated Sudbury wetland core (T1, 30 m) was only about 12 times greater on a depth-integrated basis than in the reference core from Hop Brook; ΣHg concentrations in pore water (if the outlier $500 \text{ ng}/\text{L}$ value in fig. 7 is excluded) are as much as 10 times greater ($100 \text{ ng}/\text{L}$) than that measured in pore water of the reference Hop Brook core. These maximum measured values appear to be too small to account for the 60-fold difference between net ΣHg increases in contaminated and uncontaminated wetlands. Causes of the discrepancy may be that high concentrations of ΣHg in the Sudbury River wetland were not detected by the sparse sampling coverage or that substantially different hydrologic processes operated in the two wetlands so that a comparison of concentrations is not appropriate. In any case, the core data are not an obvious verification that the wetland sediments were the source of the net ΣHg increases calculated for the riparian wetland reaches.

Net generation of MeHg in the riparian wetland reaches (to $8 \mu\text{g}/\text{m}^2/\text{yr}$) measured by Waldron and others (in press) was 15-fold greater than that reported in an unaffected wetland. Thus, high concentrations of ΣHg in the wetland may have had an effect on MeHg concentrations in the wetland-reach water column. On a depth-integrated basis, MeHg concentrations differed by a factor of six, between the most contaminated wetland core and the Hop Brook reference core. Also MeHg concentration in the Sudbury River wetland sediment generally was greater than that reported for wetlands in uncontaminated systems by a factor of about seven. Together, these factors indicate a substantial MeHg reservoir in the Sudbury River wetlands compared to that of an uncontaminated wetland, and are compatible with the hypothesis that the source of the Sudbury wetland MeHg generation is the wetland sediments. As was the case for ΣHg ,

apparent MeHg transport from sediment to water was more efficient in the wetlands, where advection can operate, than in the reservoirs.

Environmental Significance of the Methylmercury Transport and the Total Mercury-Methylmercury Correlation in Sediments

The apparent transport of MeHg from sediments to the water column is environmentally significant for the Sudbury River. The general correlation between ΣHg and MeHg in bulk sediment (fig. 5) may be connected with the transport of MeHg from wetland sediments but does not in itself establish that high ΣHg concentrations caused high MeHg transport. The correlation was between concentrations and relates to transport only if MeHg is being constantly removed from the sediment by transport processes and replenished by methylation of inorganic mercury. Also, the ΣHg -MeHg correlation was not strong at the sediment surface, so the response of sediments enriched in Hg only near the surface, such as occurs from atmospheric deposition sources, is uncertain. Concurrent investigation of the concentration and transport of Hg, including experiments with sediment columns, and more investigation of sediment data that extends throughout the year, would be needed to establish a cause and effect relation.

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District Chief
Massachusetts–Rhode Island District
U.S. Geological Survey, Water Resources Division
10 Bearfoot Road
Northborough, Massachusetts 01532
