Speciation and reactivity of mercury were examined in Berry’s Creek estuary downstream of a highly mercury-contaminated U.S. EPA Superfund site during the summers of 2002 and 2003. Surface water samples from Berry’s Creek estuary, its confluence with the Hackensack River, and upstream of that confluence were analyzed for total (THg), particulate (PHgT), and dissolved (DHg) mercury, total and particulate monomethylmercury (MeHg), dissolved gaseous mercury (DGM), and bacterial merA gene and transcript abundances. Surface water concentrations of THg in Berry’s Creek estuary (210–6800 pM) are among the highest in North America. A downstream gradient of Hg contamination is a permanent feature of Berry’s Creek estuary, and the upper estuary appears to be a perennial source of Hg to the lower estuary and the Hackensack River. MeHg concentrations in Berry’s Creek surface waters ranged from 2 to 14 pM, with the highest concentrations occurring in a midestuary site 2 km downstream of the tide gate. The suspended particle phase dominated Hg and MeHg speciation throughout this system, accounting for >90% of THg in Berry’s Creek estuary and 35–94% of THg in the Hackensack River. Concentrations of DGM in Berry’s Creek estuary (0.1–1.0 pm) are similar to levels of DGM in other much less contaminated estuaries (0.04–0.75 pm). In addition, expression levels of the bacterial mercuric reductase gene, merA, a gene of the inorganic Hg(ll)-regulated, mercury resistance (mer) operon, were low throughout Berry’s Creek estuary. Thus, despite very high concentrations of mercury in Berry’s Creek estuary, relatively low concentrations of DGM and merA gene expression levels indicate limited bioavailability of inorganic Hg in the estuary’s surface waters. A system-wide limitation on the bioavailability of inorganic Hg, together with bacterial demethylation activity, may account for observed MeHg concentrations that, although elevated, are lower than expected given the concentrations of THg in this estuary.

Introduction

Fifty years since the incident of acute mercury poisoning in Minamata, Japan, many industrial sources of mercury to surface waters have been eliminated or controlled, but new industrial sources have emerged (1), and legacy contamination continues to impact aquatic ecosystems. One such historic point source is the Ventron/Velsicol Superfund site located upstream from the tidal estuary of Berry’s Creek in the New Jersey Meadowlands (Figure 1). From 1929 to 1974, 30–400 tons of elemental mercury, mercuric oxides, phenylmercuric acetate, and other mercury compounds were released to the environment from this site through direct discharge and the burial of process waste (2). Although some remediation has occurred, including the removal of mercury-contaminated buildings, excavation of topsoils, and capping of subsurface soils (3), mercury continues to contaminate Berry’s Creek, resulting in total mercury concentrations of up to 21 nM in the freshwater portion (4) and 50 nM in Berry’s Creek estuary (5). The Berry’s Creek estuary ecosystem and the animals that rely on it for food are therefore at risk of exposure to inorganic mercury and monomethylmercury (MeHg), a potent neurotoxicant (6) that is the form of mercury retained by aquatic consumers (7, 8) and transferred through the food web to birds (9), mammals (10), and humans (11).

The estuarine geochemistry of mercury is governed by biological and abiological processes that transform mercury among oxidized, elemental, and methylated forms (12–14) and the modulation of those processes by the complexion of mercury with suspended particles, dissolved organic matter, and sulfide (15–20). This is illustrated by the photochemical production and oxidation of elemental mercury (Hg(0)) in estuarine surface waters (21), where organic complexion controls the amount of Hg(II) available for photochemical reduction (22, 23). Organic complexion may also limit the extent of mercury reduction catalyzed by bacterial mercuric reductase, which is coded by the merA gene of the Hg(II)-regulated, mercury resistance (mer) operon. Thus, the expression of merA provides a specific means to evaluate the reactivity and bioavailability of inorganic mercury in natural waters (4). Mercury speciation and reactivity have not been examined in very highly mercury contaminated estuaries such as Berry’s Creek, where the estuarine mercury cycle may differ from that in less contaminated systems.

The objectives of this study were to assess the speciation, reactivity, and bioavailability of mercury in the highly contaminated surface waters of Berry’s Creek estuary. Toward this end, we measured total (THg), particulate (PHgT), and dissolved (DHg) mercury and total and particulate monomethylmercury (MeHg) in the estuarine water column. In addition, we measured dissolved gaseous mercury (DGM) and merA gene and transcript abundances in Berry’s Creek microflora and estimated mercury volatilization fluxes to the atmosphere through air–water exchange. For comparison of Hg speciation and bioavailability in an urban wetland with nonpoint source mercury inputs similar to those of Berry’s Creek, identical measurements were also made in the Hackensack River estuary, 1.4 km upstream of its confluence with Berry’s Creek estuary.
Experimental Procedures

Study Site. Berry’s Creek estuary is a 5 km tidal extension of a small stream in the New Jersey Meadowlands (Figure 1). The upstream limit of the estuarine portion of Berry’s Creek is separated from the freshwater creek by a tide gate and lies 0.1 km downstream of the heavily mercury-contaminated Ventron/Velsicol Superfund site (Figure 1). Berry’s Creek estuary joins the tidal Hackensack River upstream of Newark Bay and the New York/New Jersey Harbor estuary. Both estuaries are bounded by vegetated (Phragmites) mud flats of the Meadowlands saltmarsh, which are bordered and intersected by urban and industrial development.

Five sites along Berry’s Creek estuary (TG, S04, MW, S02, CON) and one in the tidal Hackensack River (HK), upstream of its confluence with Berry’s Creek, were selected for a preliminary assessment of total Hg concentrations in this system (Figure 1). Subsequent sampling occurred at the tide gate (TG), a point 1.9 km downstream of the tide gate, and midway between it and the confluence with the Hackensack River (MW), at the confluence with the Hackensack River 5 km downstream of the tide gate (CON), and in the Hackensack River, 1.4 km upstream of the confluence (HK).

Sample Collection. Surface water samples from Berry’s Creek were collected by hand from the side of a fiberglass pontoon boat in June 2002 (preliminary assessment for total Hg only), July 2002, September 2002, and July 2003. July 2003 TG samples were collected by hand from the bank of the estuary. Samples were collected in acid-cleaned, Teflon or glass bottles using clean handling techniques. Water samples for THg and DHg were preserved with 0.2% bromine monochloride to oxidize all Hg species. Water samples for MeHg were preserved with 0.2% HCl and stored frozen until analysis. Water samples for dissolved gaseous mercury (DGM) measurements were collected in 1 L Teflon bottles without headspace and stored on ice in the dark until analysis in the laboratory within 5–7 h of collection. Suspended particles were collected by filtering 200–400 mL of water through a precombusted (24 h at 550 °C) 45 mm diameter quartz fiber filter (QMA, nominal particle retention size = 1 µm). Filters were kept frozen until analysis. Filtrates were used to obtain total dissolved mercury concentrations. Total gaseous mercury was measured using a Tekran 2537A continuous Hg vapor analyzer (Tekran, Inc., Toronto, Canada).

Mercury Analyses. The analyses of total Hg (THg) and total dissolved Hg (DHg) were performed following the methods of Bloom and Crecelius (24). In this method, samples are reduced with 0.2% of hydroxylamine hydrochloride to eliminate residual BrCl and are then reduced with stannous chloride to form Hg0, which is preconcentrated onto a gold trap and detected by cold vapor atomic fluorescence spectrometry (CVAFS, Tekran 2500). All samples collected for THg and DHg were analyzed multiple times ($n = 3–16$), and the detection limit for THg and DHg (3 times the standard deviation of laboratory blanks) was 1.8 pM.

Total particulate Hg (PHgT) was also analyzed by Sn reduction and CVAFS following digestion of quartz fiber filters in BrCl (15). The detection limit for Hg in suspended particles was 4.5 pM (3 times the standard deviation of laboratory blanks). Significant differences between measured THg concentrations and the sum of DHg plus PHgT were observed on several occasions (see Table S1, Supporting Information). Measured THg was higher than the sum of DHg plus PHgT on four other occasions the particulate value exceeded that of the total. These differences may be attributed to the incomplete oxidation of particulate matter in either total unfiltered or particle samples (25) or to different particle concentrations in the separate THg and PHgT samples. In these cases, because contamination was unlikely to be due to the very high environmental levels, we used the higher value with measured DHg values to calculate THg or PHgT. It is important to note that actual THg concentrations may have been higher than calculated values if incomplete oxidation occurred in both THg and PHgT samples. Suspended particle partition coefficients ($K_d$) of THg were estimated using corrected PHgT values.
Water samples were analyzed for MeHg by distillation and ethylation—gas chromatography (26, 27). Subsamples (40–60 mL) were distilled with sulfuric acid and potassium chloride followed by ethylation with sodium tetraethyl borate. The monomethylmercury derivative, ethylmethylmercury, was separated by isothermal gas chromatography, converted to dimethylmercury by thermal decomposition, and detected by CVAFS. Recovery rates for MeHg analysis of Berry’s Creek samples ranged from 71 to 116%. The detection limit for MeHg in surface water samples was 0.5 pM. MeHg in suspended particles (PMehg) was analyzed by distilling each filter with H2SO4 and KCl in 30 mL of ultrapure water as described above. The distillate was then ethylated and analyzed. DGM measurements were obtained by stripping water samples with ultrapure argon for 20 min, trapping gaseous mercury on gold-coated sand columns, and analyzing elemental Hg by CVAFS. Total gaseous mercury (TGM) was measured in the air 3 m above Berry’s Creek estuary using a continuous mercury vapor analyzer (Tekran 2537A) and 6 mm diameter Teflon tubing at a flow rate of 1.5 L min⁻¹ and an analysis interval of 5 min.

Physical and chemical parameters, including pH, salinity, conductivity, temperature, and dissolved oxygen, were measured in the field using a multiparameter sonde (Table S2, Supporting Information). Total suspended matter (TSM) and the fraction of organic matter (fOM) in particulate samples were measured gravimetrically on subsamples of the filters analyzed for PHg; after drying at 60 °C (TSM) and combusting at 450 °C for 12 h (fOM). Dissolved organic carbon (DOC) was measured by high-temperature combustion at the Nutrient Analytical Services Laboratory, Somelons, MD. Tide and wind speed data were obtained from the Meadowlands Environmental Research Institute (MERI) database. Streamflow data were acquired from the USGS Hackensack River station at New Milford, NJ (http://nj.water.usgs.gov/flowstatistics).

**Elemental Hg Flux Calculation.** Gaseous elemental mercury fluxes from Berry’s Creek surface waters were estimated using measured TGM and DGM concentrations in the two-layer model of air–water exchange assuming that diffusion through the water-side microlayer dominates the resistance to gas exchange (28). In this model, water to air flux (F) is given by

\[
F = k_w(DGM - TGM/K')
\]

where kw is the water-side mass transfer coefficient (cm h⁻¹), DGM is the dissolved gaseous mercury concentration in the water, TGM is the total gaseous mercury concentration in the air, and K' is the dimensionless Henry’s law constant (temperature corrected) for elemental Hg. The Henry’s law constant was temperature corrected using \( H' = 0.0074T + 0.1551 \) (29) with T in °C. The water-side mass transfer coefficient was calculated from the wind speed according to (30)

\[
k_w = (0.45u^{1.64}[Scw(\text{Hg})/Scw(\text{CO}_2)]^{-0.5}
\]

where u is the daily average wind speed (m s⁻¹) and Scw(x) are the Schmidt numbers for CO2 and Hg in water (28).

**Extraction of Nucleic Acids and Detection of merA Genes and Transcripts.** Planktonic bacteria were collected by filtration for DNA and RNA extraction (4). RNA and DNA were separated using the Total RNA/DNA kit (Qiagen), and each was resuspended into 20 µL of 1 mM EDTA. RNA was quantitated by fluorescence measurement using SYBR II intercalating dye and pure 18S/23S rRNA (Sigma) as a reference standard. The RNA (500 ng) was reverse-transcribed into cDNA using random hexamers and Superscript III (Invitrogen) in 20 µL of 1 mM reaction volumes, according to the manufacturer’s instructions. Sufficient removal of DNA from RNA extracts was verified by the absence of merA-specific PCR products in reactions containing RNA that was incubated without reverse transcriptase.

**Real-Time qPCR for the Quantitation of merA Transcripts.** Real-time qPCR using the iQ SYBR Green Supermix kit (Bio-Rad, Hercules, CA) was used to quantitate merA transcripts and genes in nucleic acid extracts of microbial biomass from Berry’s Creek waters according to the manufacturer’s instructions and as described in ref 4 (for qPCR details, see Supporting Information).

**Statistics.** For each sampling event, THg and MeHg concentrations were compared between sites using one-way analysis of variance (ANOVA). An overall two-way ANOVA was performed for THg and MeHg with site and date as independent variables to examine differences in concentrations among the sites during each sampling event and overall differences between the mean concentrations of all sites among the three sampling events.

**Results and Discussion**

**Total and Methylmercury in Berry’s Creek Surface Waters.** Total Hg (THg) concentrations in tidal Berry’s Creek estuary ranged from 210 to 6800 pM (Figure 2; median = 1400 pM) and are among the highest in North American rivers or estuaries. THg in surface waters typically varies from 2 to 25 pM (15, 17, 18), but can be as high as 100–400 pM in more contaminated systems such as the Anacostia River (25) and San Francisco Bay (19, 20). THg concentrations in the Hackensack River (11–150 pM) were similar to those in other urban/industrial estuaries.

A gradient in THg concentrations was observed in Berry’s Creek estuary from the tide gate near the mercury-contaminated Superfund site downstream to the confluence (CON) with the Hackensack River (Figure 2). The decreasing downstream trend in THg concentrations is likely due to the sedimentation of particulate mercury at the estuarine turbidity maximum zone near the MW site and dilution with less contaminated Hackensack River water.

In September 2002, total and particulate mercury concentrations at the tide gate were 5–100 times lower than those measured in June 2002, July 2002, and July 2003. This does not appear to be related to streamflow, which for the Hackensack River (at New Milford) was 0.01–0.02 m³ s⁻¹ in
June, July, and September 2002 and increased to 0.3 m³ s⁻¹ in July 2003, but rather may have resulted from a higher tide on this date (Supporting Information). Nonetheless, even in September 2002, THg shows a large decrease from the MW site to the confluence with the Hackensack River. Indeed, THg concentrations at the MW, CON, and Hackensack River sites within each sampling event were significantly different from each other (P < 0.001), indicating that the downstream gradient of mercury contamination is a permanent feature of Berry’s Creek estuary and that the upper estuary is a perennial source of mercury to the lower estuary and the Hackensack River. In the only other comprehensive study of mercury in Berry’s Creek estuary conducted in 1977–1978 (31), THg levels decreased from 3500 and 3900 pM at the tide gate and near the MW site, respectively, to 2000 pM near our June 2002 S02 site, halfway between the MW and CON sites. Sampling and analytical differences notwithstanding, there appears to have been little change in mercury levels in Berry’s Creek estuary over the past 30 years. This is consistent with the lack of vertical concentration gradients of mercury in sediments deposited on nonvegetated mudflats in Berry’s Creek over the past 40 years (5).

The particulate phase dominated mercury speciation throughout this system, accounting for >90% of THg in Berry’s Creek estuary and 35–94% of THg in the Hackensack River. Dissolved Hg (DHg) in Berry’s Creek estuary followed the same patterns as THg and PHg, increasing with proximity to the tide gate (Table S1), and was correlated with PHg: \( r^2 = 0.78, p < 0.01 \), indicating a tight coupling of the dissolved and particulate pools.

Suspended particle partition coefficients (\( K_d \)) for mercury in Berry’s Creek and the Hackensack River varied from 10⁻⁹ to 10⁻¹ (3) (Table S1), similar to those found in other aquatic systems (16, 25). Within the July 2002 and September 2002 sampling events, \( K_d \) values increased with increasing total suspended matter (Figure 3), which is in contrast to the commonly observed particle concentration effect (19, 32) where increasing TSM results in lower mercury \( K_d \) values, presumably due to increased levels of colloidal material. The lack of an observed particle concentration effect in July and September 2002 is due to the overriding effects of a strong correlation \( r^2 = 0.75, p < 0.01 \) between TSM and PHg. TSM values decreased at all stations from July 2002 to September 2002; however, \( K_d \) values increased (Figure 3). The increase in \( K_d \) values over this time period, which was a transition from drought to wet conditions, may have resulted from a change in particle composition or a drop in salinity (Table S2). The effects of lower pH in September 2002, which would be expected to lower mercury adsorption to suspended particles, were apparently less important than other factors. The \( K_d \) values for July 2003 were similar to those in September 2002 at about half the TSM load, perhaps reflecting the increase in suspended particle organic matter content (fom) from September 2002 to July 2003 (Supporting Information).

The concentrations of MeHg in Berry’s Creek estuary (2.4–14 pM, median = 7 pM) were somewhat elevated with respect to those in the Hackensack River (1–3 pM; Figure 4) and other urban/industrially impacted estuaries such as the St. Lawrence (2–7.5 pM) (33), the Petaquamiccot (≤3 pM) (15), and San Francisco Bay (0.05–2.3 pM) (20, 34), but were 20–40-fold higher than the maximum concentrations observed in the Chesapeake Bay and its tributaries (0.3 pM) (17, 18). Thus, although Berry’s Creek is highly enriched (factors of 100–1000) in THg, it is less enriched in MeHg (factors of 2–40) compared with other estuaries.

Concentrations of MeHg were highest at the MW site 2 km downstream from the tide gate (Figure 4) and therefore did not coincide with the highest observed THg levels (tide gate in July 2002 and 2003). Peak MeHg concentrations at the MW site in Berry’s Creek estuary (median = 11 pM) were generally higher than those in the freshwater portion of Berry’s Creek just upstream of the tidegate (median = 3 pM (4), indicating that MeHg is mainly formed in the estuary. With the exception of the September 2002 tide gate samples, the proportion of THg present as MeHg in the surface waters of Berry’s Creek estuary varied from 0.1 to 1%. This range is lower than that in the Hackensack River (0.6, 3, and 4%), but similar to that of the turbidity maximum zones of the Loire (16) and Hudson River estuaries (14). The percent of THg as MeHg tends to be highest in less contaminated aquatic systems (4), but overall MeHg in Berry’s Creek estuary was poorly correlated with THg \( r^2 = 0.14, p = 0.33 \).

PMehg concentrations exceeded TMeHg concentrations in two-thirds of the samples from Berry’s Creek estuary and the Hackensack River (Table S1), indicating that suspended particulate matter accounts for a major fraction of MeHg in these estuaries. Indeed, TMeHg was correlated with TSM in July 2002 \( r^2 = 0.9, p = 0.06 \) and 2003 \( r^2 = 0.8, p = 0.13 \).
TABLE 1. Wind Speed and Dissolved Gaseous Mercury (DGM) Concentrations in Surface Waters, Total Gaseous Mercury (TGM) Concentrations in Air, and Daytime Volatilization Fluxes in the Berry’s Creek and Hackensack River Estuaries

<table>
<thead>
<tr>
<th>Date</th>
<th>Site</th>
<th>Wind Speed (m s⁻¹)</th>
<th>DGM (µM)</th>
<th>TGM (pmol m⁻³)</th>
<th>Flux (pmol m⁻² h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 2002</td>
<td>TG</td>
<td>2.46</td>
<td>0.4</td>
<td>10</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>MW</td>
<td>2.46</td>
<td>1.05</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>CON</td>
<td>2.46</td>
<td>0.25</td>
<td>11</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>HK</td>
<td>2.46</td>
<td>NS*</td>
<td>11</td>
<td>NS</td>
</tr>
<tr>
<td>Sept 2002</td>
<td>TG</td>
<td>2.08</td>
<td>0.15</td>
<td>13</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>MW</td>
<td>2.08</td>
<td>0.15</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>CON</td>
<td>2.08</td>
<td>0.10</td>
<td>9.3</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>HK</td>
<td>2.08</td>
<td>0.05</td>
<td>7.7</td>
<td>0.50</td>
</tr>
<tr>
<td>July 2003</td>
<td>TG</td>
<td>2.94</td>
<td>1.05</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>MW</td>
<td>2.94</td>
<td>0.55</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>CON</td>
<td>2.94</td>
<td>0.10</td>
<td>11</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>HK</td>
<td>2.94</td>
<td>0.40</td>
<td>9.6</td>
<td>13</td>
</tr>
</tbody>
</table>

*Not sampled.

Mercury Reactivity and Bioavailability. The reactivity and bioavailability of inorganic Hg in the surface waters of Berry’s Creek estuary were evaluated through measurements of dissolved gaseous mercury (DGM) and merA gene expression. Because the primary source of DGM to surface waters is the abiotic and microbial reduction of dissolved Hg(II), its concentration is linked to the reactivity and bioavailability of Hg(II) (22). Elemental mercury is also produced by the reductive demethylation of MeHg (4). Concentrations of DGM in Berry’s Creek estuary (0.1–1.0 µM) include values toward the upper end of those found in estuarine waters (e.g., 0.9 µM in San Francisco Bay) (20) as well as those near the low end of the observed range (e.g., 0.1 µM in Chesapeake Bay) (18), and the median concentration (0.25 µM) is similar to levels (0.04–0.75 µM) observed in other much less contaminated estuaries (16–18, 22, 28, 35). DGM concentrations in Berry’s Creek estuary and the Hackensack River were positively correlated with THg (r² = 0.78, p < 0.001) and DHg (r² = 0.57, p < 0.01), and the highest concentrations of DGM (0.4–1 µM) were observed at the two most contaminated upstream sites. These concentrations were lower than expected given DHg concentrations >100 µM (Table S1). The relatively low DGM concentrations in Berry’s Creek indicate that only a small fraction of the dissolved or particulate mercury is available for biological or photochemical reduction in this highly contaminated system.

DGM production is sensitive to DOC, which provides photoreductant but also reduces the amount of light available for mercury photoreduction and decreases the concentration of photoreducible mercury (23, 36). In lakes, DOC concentrations >5 mg L⁻¹ were found to lower mercury photoreduction (23). With DOC concentrations of 8–12 mg L⁻¹, Berry’s Creek surface waters may support only limited Hg photoreduction. Thus, microbially catalyzed mercury reduction may be more important than abiotic (photochemical) reduction in this dark water system. In addition to limits on production, however, photooxidization of Hg⁰ (15) may keep DGM low despite elevated concentrations of THg and DHg in this high DOC, brackish estuary.

As a more specific test of mercury reactivity and bioavailability, the presence and expression of the inorganic Hg-regulated merA gene was quantified in Berry’s Creek microbial biomass in July 2003. Inorganic mercury is known to induce the mer-operon in bacteria that possess it, leading to high mercury reduction rates in systems with high concentrations of inorganic Hg (37). The presence of the merA gene was confirmed by the detection of merA PCR amplification product in stained agarose gels following PCR with merA specific primers, but were below quantitation limits in all but the tide gate sample. ND, not determined.

TABLE 2. merA Gene and Transcript Abundances in Surface Water Microbial Biomass from the Berry’s Creek and Hackensack River Estuaries, July 2003, As Determined by (RT)-qPCR

<table>
<thead>
<tr>
<th>Site</th>
<th>merA Genes (copies ng DNA⁻¹)</th>
<th>merA Transcripts (copies ng RNA⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG</td>
<td>0.91 ± 0.17</td>
<td>128 ± 99</td>
</tr>
<tr>
<td>MW</td>
<td>&lt;0.4</td>
<td>&lt;3</td>
</tr>
<tr>
<td>CON</td>
<td>ND</td>
<td>&lt;14</td>
</tr>
<tr>
<td>HK</td>
<td>&lt;0.02</td>
<td>&lt;3</td>
</tr>
</tbody>
</table>

* merA genes and transcripts were present in all samples tested as confirmed by the detection of merA PCR amplification product in stained agarose gels following PCR with merA specific primers, but the levels of merA gene were below that which could be quantitated by real-time qPCR at the MW and Hackensack River sites. In situ merA expression was detected at all sites in Berry’s Creek and the Hackensack River, but downstream from the tide gate, merA transcripts were present at the limits of detection for RT-qPCR (Table 2). Thus, in July 2003, merA genes and gene transcripts were most abundant near the tide gate where THg and DHg concentrations were highest. The inverse relationship between merA transcript number and salinity reflects lower levels of mer induction and/or gene selection as mercury concentrations decrease with distance from the tide gate as well as decreased mercury bioavailability as chloride and sulfide increase downstream.

Levels of merA expression in Berry’s Creek estuary can be compared with those measured directly upstream of the tide gate in the freshwater portion of Berry’s Creek, 100 m downstream of the source of Hg contamination. The number of merA transcripts in upstream freshwater site samples ranged from 6000 to 2200 copies ng of RNA⁻¹ (4), at least 17-fold higher than in Berry’s Creek estuary. Although the concentrations of THg were very high, and similar above and below the tide gate, merA expression levels indicate lower Hg(II) availability to microorganisms downstream of the tide gate compared with those observed upstream. Salinity and DOC concentrations were identical just above and below the tide gate, but significantly higher in the estuary, may lower Hg(II) bioavailability by sorption to cellular material (39) and formation of organic ligand–Hg complexes, respectively, and, consequently, lower the extent of mer induction in the estuary.
by 24 h). Although this 24 h average flux may overestimate the true mercury volatilization flux if photochemical reduction is the main source of DGM, it indicates that mercury volatilization from the Berry’s Creek waterway is approximately balanced by atmospheric deposition. The loss of mercury to the atmosphere from vegetated and tidally exposed mudflats flanking Berry’s Creek estuary, however, has yet to be evaluated.

More than 30 years after the termination of mercury processing activities at the Ventron-Velsicol facility, Berry’s Creek estuary remains highly contaminated with mercury. Indeed, total Hg concentrations in the water and sediments of Berry’s Creek estuary are among the highest currently observed. In comparison, MeHg concentrations, although elevated, are lower than expected given the levels of inorganic Hg, perhaps as a consequence of a system-wide limitation on Hg bioavailability to Hg methylating organisms or microbial demethylation of MeHg in sediments or the water column (4, 41). As the cleanup of Berry’s Creek and other legacy contamination sites progresses (3), research addressing the speciation, bioavailability, and abiotic and biological transformations of MeHg in such sites is needed to manage current contamination and guide future remediation efforts.

Acknowledgments
We thank Ed Konsevik and Joseph Sarnoski (Meadowlands Environmental Research Institute) for assistance in sample collection. The work was supported by the National Science Foundation (EAR-9110268 to T.B.), the New Jersey Water Resources Research Institute, and the Department of Education through a Graduate Assistance in Areas of National Need Grant.

Supporting Information Available
Information regarding sampling locations and surface water properties in Berry’s Creek estuary and the Hackensack River. This material is available free of charge via the Internet at http://pubs.acs.org.

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