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Shallow Groundwater Mercury Supply in a Coastal Plain Stream

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Supporting Information

ABSTRACT: Fluvial methylmercury (MeHg) is attributed to methylation in up-gradient wetland areas. This hypothesis depends on efficient wetland-to-stream hydraulic transport under nonflood and flood conditions. Fluxes of water and dissolved (filtered) mercury (Hg) species (FMeHg and total Hg (FTHg)) were quantified in April and July of 2009 in a reach at McTier Creek, South Carolina to determine the relative importance of tributary surface water and shallow groundwater Hg transport from wetland/floodplain areas to the stream under nonflood conditions. The reach represented less than 6% of upstream main-channel distance and 2% of upstream basin area. Surface-water discharge increased within the reach by approximately 10%. Mean FMeHg and FTHg fluxes increased within the reach by 23–27% and 9–15%, respectively. Mass balances indicated that, under nonflood conditions, the primary supply of water, FMeHg, and FTHg within the reach (excluding upstream surface water influx) was groundwater discharge, rather than tributary transport from wetlands, in-stream MeHg production, or atmospheric Hg deposition. These results illustrate the importance of riparian wetland/floodplain areas as sources of fluvial MeHg and of groundwater Hg transport as a fundamental control on Hg supply to Coastal Plain streams.

INTRODUCTION

Methylmercury (MeHg) contamination in fish is a global concern[1,2] and the leading cause of fish consumption advisories in the United States (U.S.).[3] In streams, dissolved MeHg concentrations strongly predict fish Hg burdens.[4,5] While notable exceptions exist,[6] up-gradient wetland/floodplain areas are hypothesized to be the primary source of dissolved MeHg in many stream systems,[4,7−10] based on (1) strong correlations between wetland area and fluvial MeHg concentrations,[11−14] (2) higher dissolved MeHg concentrations in wetlands than in adjacent stream habitats,[12,13] (3) hydraulic gradients favoring solute transport from wetlands to stream,[12,13] and (4) low stream-bed MeHg concentrations and methylation activities.[7,13,15] The validity of the wetland-MeHg-source hypothesis, however, depends on efficient hydraulic transport from wetland/floodplain areas to the stream.[9,10,12,13]

Episodic flood events optimize wetland–stream hydraulic connectivity by maximizing surface water exchange[16] and the surface area for exchange of wetland-porewater with overlying surface water.[12,17] The importance of floods as drivers of in-stream dissolved MeHg concentrations, however, depends on their frequency and timing relative to critical aquatic life-cycle periods[4] and on the direction of the hydraulic gradient under flood conditions.[12] Elevated dissolved MeHg concentrations under high-flow conditions have been reported for a number of streams,[11,17−22] attributed to improved surface water exchange and increased wetted area for Hg methylation,[12,17−19] and are consistent with episodic flood events as fundamental drivers of fluvial MeHg concentrations and, by extension, Hg bioaccumulation.[4]

However, floods are relatively infrequent, even in systems where dissolved MeHg concentrations increase with discharge. Moreover, decreased dissolved MeHg concentrations during high flow events have been reported in several basins,[11,21,23−26] indicating net dilution of dissolved MeHg under flood conditions. For example, a number of studies have demonstrated that Coastal Plain streams in the southeastern U.S. are particularly vulnerable to MeHg bioaccumulation[5,8,10,13,14,27−32] and have attributed this vulnerability in part to wetland abundance and strong wetland–stream hydraulic connectivity.[9,10,12,13] In the McTier Creek study area of the South Carolina Coastal Plain during 2007–2009, filtered MeHg (FMeHg) concentrations decreased significantly with increasing stream discharge (Supporting Information (SI) Figure 1) and flood conditions existed less than 10% of the year (less than 5% of the April–September growing season).

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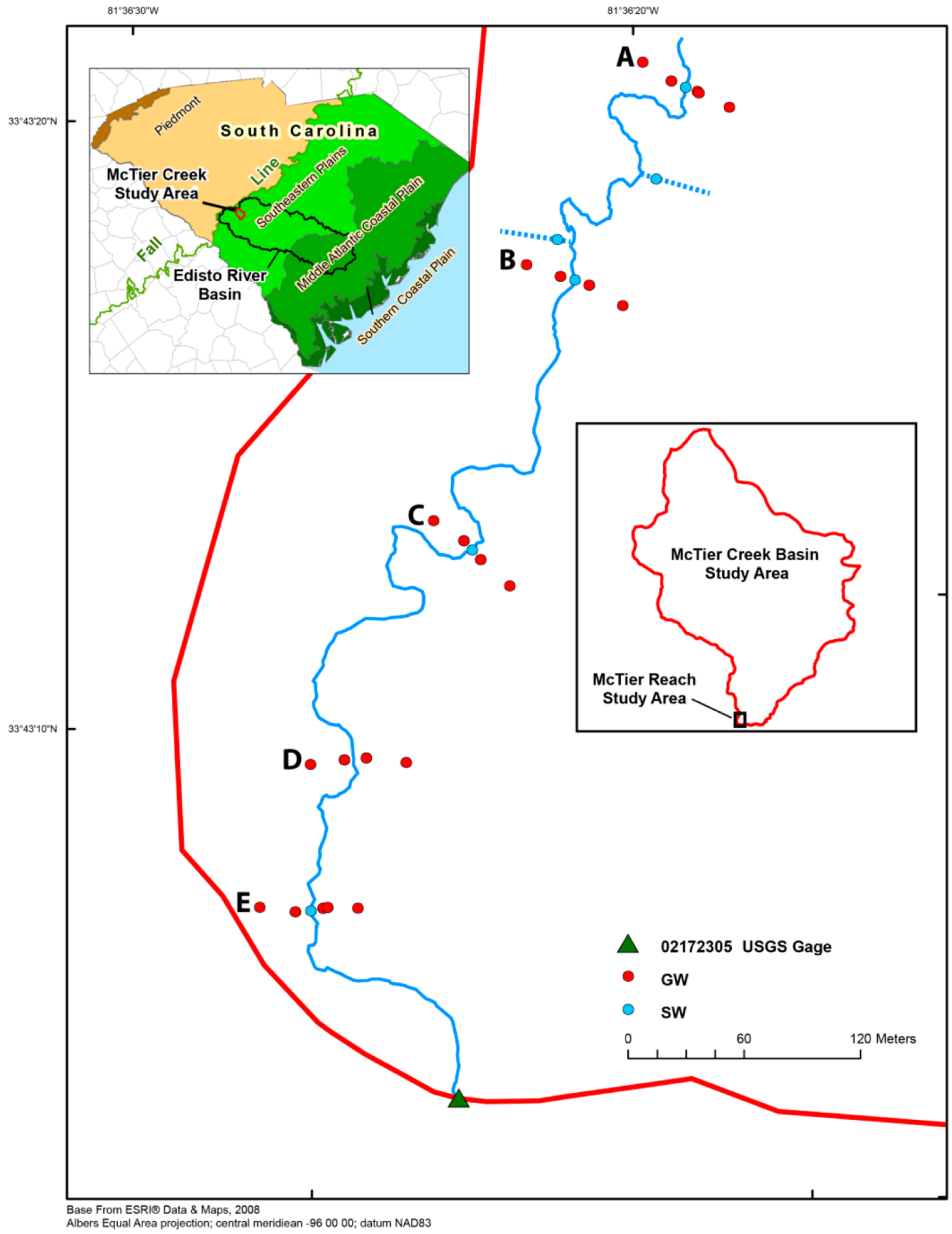

Figure 1. Map of McTier Creek study reach upstream of gage 02172305 (green ▲). Upper inset indicates location of McTier Creek study area within Edisto River basin and ecoregions[34] in South Carolina. Lower inset indicates position of study reach within McTier Creek study area. Blue line indicates main channel. Dashed blue lines indicate tributaries. Letters indicate well transects. Circles indicate groundwater (red ●) and surface water (blue ●) sampling locations. Red line indicates drainage boundary for McTier Creek study area.

These observations indicate that wetland–stream hydraulic connectivity under nonflood conditions is a primary determinant of the importance of wetland/floodplain environments as sources of fluvial dissolved MeHg. This study evaluated the hypothetical role of wetland/floodplain areas as primary sources of dissolved MeHg in Coastal Plain streams by assessing the flux of water and filtered Hg species (MeHg and total Hg (THg)) from surface water and groundwater sources in a short reach at McTier Creek.

■ MATERIALS AND METHODS

Study Basin. The Edisto River basin is entirely within the Coastal Plain of South Carolina[33] (corresponds to the Middle Atlantic Coastal Plain and Southeastern Plains Ecoregions[34]), free-flowing (no dams on main channels), and characterized by low stream-gradients and extensive riparian wetlands.[12,13,15,35] Edisto River largemouth bass (*Micropterus salmoides*) Hg concentrations are among the highest for top predator fish in the U.S.[27,29] The McTier Creek study area (Figure 1) has been described in detail previously.[12,13]

Study Reach Delineation. Fluxes of water and water-borne Hg species from wetland/floodplain areas to the adjacent stream were assessed in a 765-m study reach (Figure 1) established near the downstream margin of the McTier study area (MC3 in ref 13). The downstream boundary (Transect E) was approximately 100 m upstream of USGS gage 02172305.[36]

The coefficient of variation of quadruplicate stream discharge (Q) measurements (acoustic Doppler) at Transect E under low flow conditions was less than 2%. Transect A was established at the minimum upstream distance where a statistically significant ($p < 0.05$) change in Q ($\Delta Q_{Reach} > 4\%$) was observed under low-flow conditions. Three intermediate transects (B−D; Figure 1) were established downstream of A. The study reach included one perennial (west bank) and one transient (east bank) tributary.

Well Locations and Shallow Riparian Stratigraphy. The east bank of the study reach was transiently inundated riparian floodplain. The west bank was dominated by perennially flooded wetland at the western edge of transects B−D and covering part of E transect. Except at the western half of transect E, three distinct shallow subsurface strata were apparent throughout the reach area (see SI Figure 2). Uppermost were two silty-sand strata, with gray coloration indicating reduced redox conditions and potential for microbial Hg(II) methylation. The top stratum (0−60 cm below land surface (bls)) included the root zone, with oxidized iron (orange−red) microzones around viable roots, and a thin O horizon (approximately 0−10 cm bls). Microconduit infrastructure attributed to former roots suggested increased hydrologic connectivity compared with the otherwise indistinguishable, underlying (root-free) stratum (60 cm bls to approximately 180 cm bls). The third stratum (of undetermined thickness) comprised coarse sands and gravels. Coloration, physical composition, and upper contact elevation consistent with the surface of adjacent streambed sediments indicated this lower stratum was comparatively high permeability, channel lag deposit. Very low permeability, kaolinitic alluvium of undetermined thickness was present at the western half of the E transect at a depth of approximately 30 cm bls. Hand auger surveys indicated the perennial wetland was a perched feature formed by up-gradient groundwater trapped above the kaolin deposit.

Groundwater monitoring wells (2.5 cm diameter; 30 cm screened interval) were installed on both banks at each transect (Figure 1; SI Figure 3). Reach stream width was approximately 6 m. Shallow wells were emplaced 3 m from the stream bank (approximately 6 m from center of channel) within the root zone (screened interval 30−60 cm bls). Deeper wells (screened intervals 150−200 cm bls) were emplaced at 3 and 21 m from the stream bank, with the screened interval centered across the contact between second and third strata to assess MeHg transport from overlying, reduced floodplain sediments to the stream within the channel lag deposit. Hyporheic piezometers (4−5 total; 1 cm diameters; 30 cm screened intervals) were emplaced at the edge of water on each bank and equidistant across the channel with the top of screen set at 20 cm below the bed sediment/surface water interface.

Sampling Event Hydrologic Setting. Flux assessments were initiated 4 and 5 days after separate flood events during April 2009 and July 2009, respectively (SI Figure 4). April and July events bracketed the range of normal flow conditions for McTier Creek, representing approximate 30% and 70% exceedance conditions, respectively, for the 30 year flow record at an upstream USGS gage (02172300). An approximate synoptic assessment of water elevations and corresponding Hg concentrations was achieved by sampling surface water then groundwater. Water elevations were measured by surveyed staff gage (stream) or electric water level tape (hyporheic porewater and groundwater) within 8 h of the first surface water sample. Hyporheic Hg samples were collected within 8 h of the first surface water sample. Groundwater Hg sampling was completed as soon after the collection of the first surface water samples as possible (within 54 and 34 h for April and July events, respectively) with near-stream locations sampled first.

Streamflow Data Collection. USGS operated a gaging station (02172305) at McTier Creek basin from 2007 to 2009.[36] Continuous streamflow data were computed using standard USGS stage/discharge techniques and stored in the USGS National Water Information System database.[36] Instantaneous stream discharge (Q) was measured during surface water sampling immediately downstream of transect E using acoustic Doppler. Surface-water samples were collected at the midtime of respective discharge measurements. After surface water collections were completed at transects A and E, paired Lagrangian discharge measurements were made in triplicate (1-h intervals), with measurements offset by the average surface water transport time (approximately 40 min) from transect A to E. Surface-water transport time was calculated using the average streamflow velocity measured by acoustic Doppler immediately downstream of transect E before sample collection. Discharge from reach tributaries was measured immediately following completion of paired reach discharge measurements.

Water-Quality Data. For each event, triplicate surface water samples were collected at transects A and E using a Lagrangian sampling approach. Transect A surface water was collected at 1-h intervals without entering the stream, by attaching sample bottles to a pole sampler and positioning them at mid-depth in the center of flow until full. Corresponding transect E samples were collected following a delay equivalent to the average surface water transport time from transect A to E. Tributary water samples were collected in the same manner immediately after reach surface water sampling was completed. Ultratrace-level clean-sampling, processing, and Hg analysis procedures were as described in refs 11 and 12 (see SI for details). Filtered (0.7-μm quartz-fiber filter) MeHg (FMeHg) and total Hg (FTHg) included both dissolved and filter-passing colloidal fractions. The reporting limit for FMeHg and FTHg was 0.04 ng/L.

Hyporheic porewater samples were collected from in-stream piezometers using a peristaltic pump (flow <50 mL min^{-1}) and low-volume (200 mL purge; 1 L total pumped volume) sampling techniques. A preliminary assessment of water quality parameters (pH, conductivity, and temperature) over time was conducted to verify streamwater entrainment did not occur in McTier Creek bed sediments under these flow conditions. Samples were filtered in the field in a temporary glovebox (see SI Figures 3 and 5), stored on ice, and shipped overnight to the lab. Fresh gloves, glovebox bags, and precleaned filter assemblies were used for each sample. Peristaltic tubing was acid cleaned (5% HCl) and rinsed (distilled water) between samples. Groundwater wells were purged (3 well volumes) on day 1, immediately after water-elevation measurements. Groundwater was sampled and processed as described for hyporheic samples.

Water samples for oxygen and hydrogen stable isotope analyses were collected and analyzed as in refs 37 and 38. Surface sediment (0−2 cm) was collected within the reach during the 2008 growing season from 4 in-channel locations. MeHg production potential (MPP) rates were determined as in ref 13. Method details for MPP, isotope, and end-member mixing analyses are presented in the Supporting Information.

Quality assurance quality control (QAQC) samples (15% of samples) for FTHg during April and July included field/method blanks (generally less than 5% of environmental sample concentrations, less than 10% in all cases), duplicate analyses (percent relative standard deviation (%RSD) = 4.4%), matrix spikes (recovery = 99.0% ± 7.3%), and check samples. Corresponding FMeHg QAQC samples included field/method blanks (less than detection in all cases), duplicate analyses (% RSD) = 4.6%), matrix spikes (recovery = 97.1% ± 21.6%), and check samples. Additional details are provided in Supporting Information.

Statistical Analyses. The one-tailed paired t-test (Q only) and Wilcoxon one-sided signed rank test were employed to assess differences between two groups (e.g., shallow and deep groundwater samples) and for comparisons of Q, FMeHg concentrations, and FTHg concentrations between paired surface water measurements at the top and bottom of the study reach. A significance level (α) of 0.1 was employed for surface water FMeHg and FTHg comparisons between the top and bottom of the study reach, for which $n = 3$. For all other statistical comparisons, $\alpha = 0.05$. Kruskal–Wallis ANOVA on ranks was combined with Dunn's multiple comparison method for comparisons of more than two groups (overall $\alpha = 0.05$).

RESULTS AND DISCUSSION

Previous observations at McTier Creek suggested that good hydraulic connectivity and efficient MeHg transport in Coastal Plain systems were not limited to flood conditions. Close correspondence between stream stage and shallow-groundwater levels adjacent to McTier Creek demonstrated that good hydrologic connectivity exists prior to flood conditions (12 and SI Figure 6), even in areas with no apparent surface water connectivity (no tributary drainage). This observation suggested that shallow groundwater may be the primary mechanism for MeHg transport between wetland/floodplain sediments and the stream habitat and, thus, a fundamental control on in-stream MeHg concentrations under nonflood conditions.

Reach Flux Assessment. Fluxes of water, FTHg, and FMeHg increased significantly within the study reach in April 2009. Q increased by 10.3 ± 0.1% (mean ± standard deviation) within the reach (Figure 2; Table 1). Coefficients of variation for triplicate measurements of Q were less than 2% for A and E transects, indicating ΔQ_{Reach} was significant (one-tailed paired t-test; $p < 0.0001$). No significant ($\alpha = 0.1$, for sample size n less than five) differences in FMeHg or FTHg concentrations were observed between transects A and E (Wilcoxon one-sided signed rank; $n = 3$; $p = 0.625$; SI Table 1). Instantaneous flux was calculated for each surface water sample as Q times the mean Hg concentration observed at that transect. Mean flux increases (for paired sample/discharge measurements) between A and E were 27.5 ± 0.2% and 9.3 ± 0.1% for FMeHg and FTHg, respectively (Table 1).

Fluxes of water, FTHg, and FMeHg also increased significantly within the study reach in July 2009. Q increased by 10.8 ± 0.3% within the reach (Figure 2; Table 1). Coefficients of variation for triplicate measurements of Q were less than 2.5% for A and E transects, indicating ΔQ_{Reach} was significant (one-tailed paired t-test; $p < 0.0001$). No significant difference ($\alpha = 0.1$, for sample size n less than five) in FTHg concentrations was observed between transects A and E (Wilcoxon one-sided signed rank; $n = 3$; $p = 0.125$; SI Table 1). FMeHg concentrations increased (Wilcoxon one-sided signed rank; $n = 3$; $p = 0.087$) from 0.15 ± 0.00 to 0.17 ± 0.01 ng L^{-1} at transects A and E, respectively, corresponding to an increase in FMeHg flux of 23.1 ± 0.3% within the reach. FTHg flux increased within the reach by 14.7 ± 0.3%.

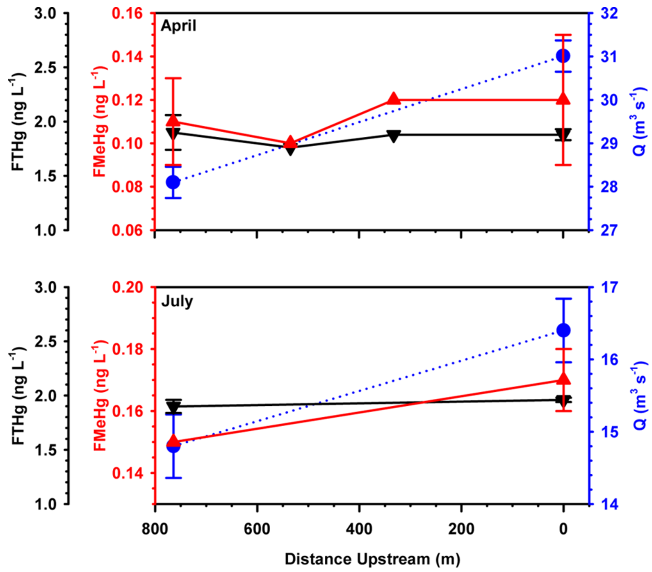

Figure 2. Relation of surface water discharge (Q, blue circles, ●), filtered methylmercury (FMeHg, red triangles, ▲) concentrations, and filtered total mercury (FTHg, black triangles, ▲) concentrations with distance upstream of transect E for April (upper graph) and July (lower graph) sampling events. Data are means ± standard deviations for triplicate samples collected at the A (750 m upstream) and E (0 m upstream) transects. Data for intermediate locations in April are for single samples.

Reach Water Supply. In the absence of precipitation, the increase in discharge within the reach (ΔQ_{Reach}) was attributable to surface water and groundwater inputs. Percentage increases in water flux attributable to surface water discharge from the two small tributaries within the study reach were approximately 12% and 20% during April and July, respectively (Table 1). Potentiometric profiles revealed strong hydraulic gradients toward the stream during both sampling events (Figure 3; SI Figure 7). The δ^2H-based, end-member mixing analysis results corroborated the conclusions that deeper groundwater was the primary source of water and that the groundwater contribution to surface water increased within the reach (Figure 4; SI Figure 8). Several visible groundwater seeps within the reach (SI Figure 9) provided independent confirmation of substantial groundwater discharge and good hydrologic connectivity between the shallow groundwater system and the stream. Thus, groundwater discharge ($Q_{groundwater} = \Delta Q_{reach} - Q_{tributaries}$) was the primary source of water gained within the reach under nonflood conditions. The results agree with the reported predominance of groundwater discharge in Coastal Plain streams[12,35,39−41] and with the hypothesized importance of groundwater Hg transport from floodplain areas to the stream habitat.

Reach FTHg Supply. Possible sources for the increase in FTHg flux within the stream reach include (1) atmospheric THg deposition directly to the stream surface, (2) surface water discharge from the two reach tributaries, and (3) groundwater discharge. No wastewater or mining sources exist in McTier basin and no Hg-bearing deposits were found in a soil/sediment survey within the reach.[42] Because the stream bed and

Table 1. Mass Balances for Changes in Water, FTHg, and FMeHg Observed within Study Reach during April and July 2009

April 2009							
		Q		FTHg		FMeHg	
reach location		(m^3 s^{-1})	(L s^{-1})	(ng L^{-1})	(ng s^{-1})	(ng L^{-1})	(ng s^{-1})
top of reach		0.80 ± 0.01	796 ± 10	1.9 ± 0.2	1509 ± 20	0.11 ± 0.02	85 ± 1
east tributary		0.0001	0.1	0.8	0.1	0.04	0.00
west tributary		0.01	9.9	2.6	25.7	0.12	1.19
bottom of reach		0.88 ± 0.01	878 ± 10	1.9 ± 0.1	1650 ± 19	0.12 ± 0.03	108 ± 1
		water		FTHg		FMeHg	
reach summary		(L s^{-1})	(%)	(ng s^{-1})	(%)	(ng s^{-1})	(%)
flux change[a]		82 ± 0	10.3 ± 0.1	141 ± 0	9.3 ± 0.1	23.4 ± 0.2	27.5 ± 0.2
contribution[b]	tributary[c]	10	12.1 ± 0.0	25.8	17.9 ± 0.0	1.19	5.1 ± 0.0
	dry precipitation[d]			3.5	<3	0.08	<1
	bed sediment[e]					0.23	<1
	groundwater[f]	72	87.9 ± 0.0	112	79.1 ± 0.1	21.9	92.9 ± 0.7
July 2009							
		Q		FTHg		FMeHg	
reach location		(m^3 s^{-1})	(L s^{-1})	(ng L^{-1})	(ng s^{-1})	(ng L^{-1})	(ng s^{-1})
top of reach		0.42 ± 0.01	419 ± 12	1.9 ± 0.1	795 ± 23	0.15 ± 0.00	63 ± 2
east tributary		0.0	0.0	0.9	0.0	0.27	0.00
west tributary		0.01	9.1	2.8	25.3	0.27	2.45
bottom of reach		0.46 ± 0.01	464 ± 12	2.0 ± 0.1	912 ± 24	0.17 ± 0.01	77 ± 2
		water		FTHg		FMeHg	
reach summary		(L s^{-1})	(%)	(ng s^{-1})	(%)	(ng s^{-1})	(%)
flux change[a]		45 ± 0	10.8 ± 0.3	117 ± 1	14.7 ± 0.3	14.5 ± 0.2	23.1 ± 0.3
contribution[b]	tributary[c]	9.1	20.0 ± 0.0	25.3	21.6 ± 0.2	2.45	16.8 ± 0.2
	dry precipitation[d]	g		4.5	<4	0.08	<1
	bed sediment[e]					0.23	<2
	groundwater[f]	35.9	80.0 ± 0.0	87	74.4 ± 0.5	11.9	80.2 ± 1.2

[a]Equal to flux at bottom of reach minus flux at top of reach. Percent change is relative to top of reach. [b]Contributions expressed as mass flux and as percentage of the change in flux observed in the reach. [c]Mass flux and percentage contribution from two tributaries in April and one tributary in July. [d]High FTHg estimate equal to wet deposition rate measured at nearby MDN sites in April and July 2009. High FMeHg estimate equal to two times the maximum annual wet deposition rate given in 11. [e]FTHg flux from bed sediment is indistinguishable from shallow aquifer contribution and is accounted for under "Groundwater." Bed sediment FMeHg was estimated from methylation experiments as described in the Supporting Information and assuming 10% organic fines and 90% coarse sand. [f]Groundwater fluxes and percentage contributions were estimated as the reach flux change minus contributions from tributaries, dry precipitation, and bed sediment. Percentage contributions are estimated assuming the maximum limit for dry precipitation and bed sediment contributions. [g]Not applicable.

channel lag deposits, which underlie the wetland/floodplain areas, are connected and geochemically indistinct, stream-bed sediment is not a disproportionate source of THg to the dissolved phase (i.e., the stream-bed sediment contribution to the dissolved phase is comparable to that of the adjacent shallow aquifer). In the absence of precipitation, direct atmospheric THg inputs are limited to dry deposition on the approximately 4600 m^2 reach stream surface. Maximum weekly THg wet deposition rates reported at nearby Mercury Deposition Network (MDN) sites in April (462.9 ng m^{-2} at SC03) and July (588.9 ng m^{-2} at SC019) 2009 were used as high estimates of THg dry deposition to McTier Creek (THg wet deposition is reportedly 4−7 times greater than corresponding dry deposition in southeastern Coastal Plain settings[11] with annual dry deposition dominated by seasonal litterfall[43]). High estimates of FTHg dry deposition explained less than 4% of the increase in FTHg flux observed within the reach in April and July. Tributary discharge contributed approximately 18% and 22% to the observed increase in reach FTHg flux during April and July events, respectively (Table 1).

The results indicate that groundwater discharge was the primary source of FTHg within the study reach, accounting for approximately 75% of the observed increase in FTHg flux. This conclusion is supported by (1) clear hydraulic gradients toward the stream during both sampling events (Figure 3; SI Figure 7), (2) δ^2H-based, end-member mixing results demonstrating increasing groundwater contribution in the reach (Figure 4; SI Figure 8), and (3) visible groundwater seeps within the reach (SI Figure 9). Groundwater FTHg concentrations comparable to or higher than those observed in the stream confirmed a chemical gradient toward the stream. Constant FTHg concentrations and comparable water and FTHg flux increases within the reach also are consistent with shallow groundwater FTHg transport to the stream. Higher FTHg concentrations in 24 m deep well samples than in deep well samples at 6 m (SI Table 1) and the lack of geologic Hg deposits in shallow soil/sediment in the reach[42] are consistent with atmospheric Hg deposition on the terrestrial landscape as the distal source of FTHg to groundwater.

Reach FMeHg Supply. Possible sources for the increase in FMeHg flux within the stream reach include (1) atmospheric MeHg deposition directly to the stream surface, (2) MeHg production in the streambed sediment, (3) surface water discharge from the two reach tributaries, and (4) shallow groundwater discharge. In the absence of precipitation, direct

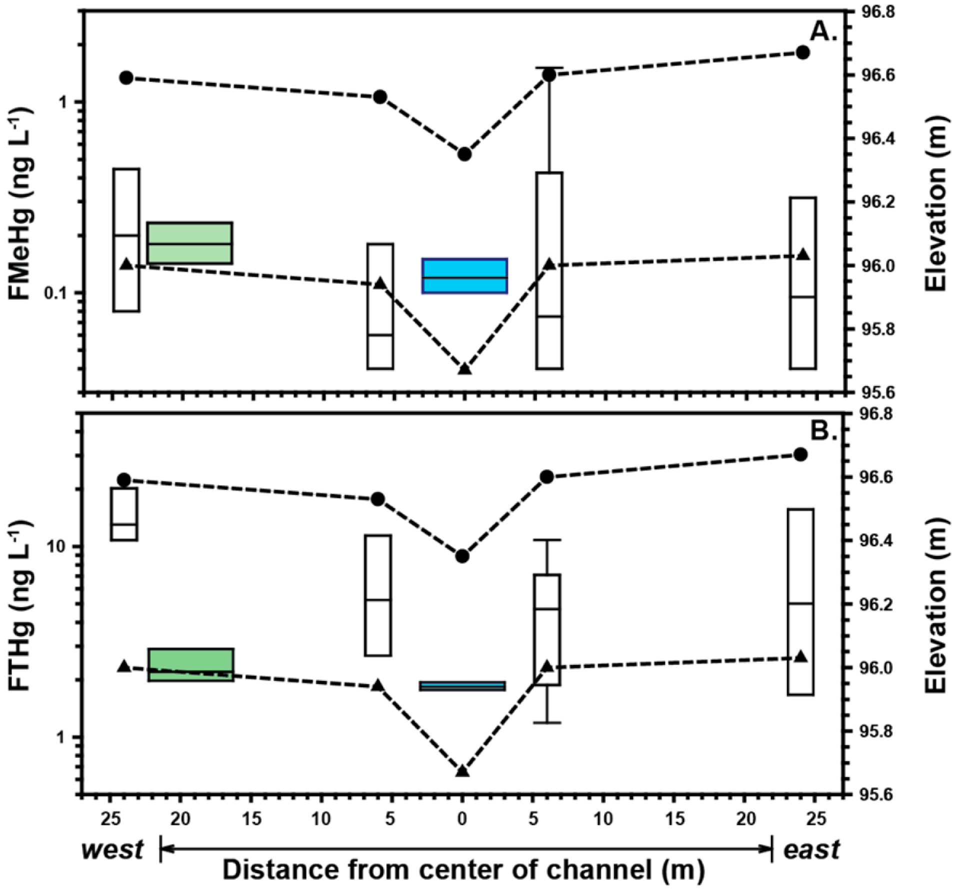

Figure 3. Lateral gradients in water elevation (● and ▲ indicate transects A and D, respectively) and FMeHg (upper graph) or FTHg (lower graph) concentrations (box plots; white, blue, and green indicate groundwater, streamwater, and wetland water, respectively) during April 2009. Boxes, centerlines, and whiskers indicate interquartile ranges, medians, and 10th and 90th percentiles, respectively. See SI Figure 7 for July data.

atmospheric inputs are limited to MeHg dry deposition, previously estimated as less than 10% of THg dry deposition in southeastern Coastal Plain settings.[11] Comparable annual rates of dry and wet MeHg deposition were reported recently for a Mercury Deposition Network site in coastal South Carolina (SC05), but annual dry deposition was dominated by seasonal litterfall[43] and litterfall was not significant during the current reach study. Using twice the maximum annual wet MeHg deposition rate (280 ng m^{-2}) reported previously for Coastal Plain streams[11] as a high estimate, dry MeHg deposition on McTier Creek accounted for less than 1% of the increase in reach FMeHg flux observed in April and July. Using 10% of the maximum weekly wet deposition rates reported at nearby MDN sites in April (462.9 ng m^{-2} at SC03) and July (588.9 ng m^{-2} at SC019) 2009 as high estimates of dry MeHg deposition, dry MeHg deposition accounted for less than 3% of the increase in FMeHg flux observed within the reach. Tributary discharge contributed approximately 5% and 17% to the observed increase in reach FMeHg flux during April and July events, respectively (Table 1).

Several lines of evidence indicate that streambed sediment Hg(II) methylation did not contribute significantly to the observed increase in FMeHg flux within the reach. MeHg production potential (MPP) rates[16,40,44] were determined under anaerobic conditions for organic rich fines and coarse sandy bed sediment collected from McTier in 2008, as described.[13,16,40,44] MPP rates were much higher in organic rich fines (40 ± 4 ng m^{-2} d^{-1}) than coarse sand (less than 0.4 ng m^{-2} d^{-1}).[13,16] A survey of the reach channel in July 2009 indicated organic rich fines and coarse sand represented less than 10% and greater than 90%, respectively, of the streambed area. The theoretical contribution of bed sediment Hg(II) methylation (assuming 90% sand/10% fines and uniformly anaerobic bed sediment conditions) was less than 1% of the observed increase in FMeHg flux within the study reach. Furthermore, anaerobic conditions (dissolved oxygen <0.05 mg L^{-1}) were observed only in stream bank piezometers (not in piezometers within the stream channel) during the April and July events, verifying that redox conditions conducive to Hg(II) methylation were not common in the coarse sand McTier Creek bed sediment. Elevated surface water filtered MeHg concentrations and much higher sediment methylation activities in the riparian floodplain also indicated that out-of-channel areas, rather than streambed sediment, were the primary source of MeHg to the stream.[13,15,16] Finally, the median FMeHg concentration in water collected from piezometers located at the edge of the stream was significantly (Kruskal–Wallis ANOVA on Ranks; $p = 0.023$) greater than in water from the center-of-channel piezometers (Figure 5). The intermediate median FMeHg concentration in the streamwater was consistent with mixing of relatively dilute, deeper groundwater discharge at the center of the channel with shallow groundwater discharge containing significantly higher FMeHg concentrations at the edge of the stream.

Thus, the results indicate that shallow groundwater discharge also was the primary source of FMeHg within the reach under

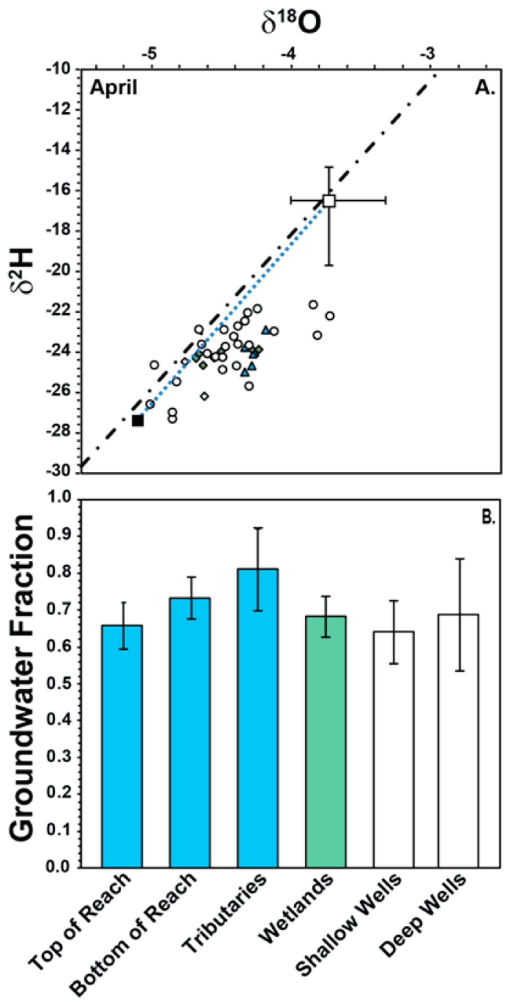

Figure 4. Relation between δ^2H and δ^{18}O isotope ratios for streamwater (▲), wetland-water (♦), and groundwater (○) samples collected from the study reach in April 2009 (upper graph). Dashed line indicates local meteoric water line. Environmental end-members used for mixing analysis were groundwater collected within McTier basin from 20 m below the water table (■) and precipitation collected from nearby National Atmospheric Deposition site SC06 (□; error bars indicate interquartile range of precipitation data) during April 2009. Blue dotted line indicates theoretical mixing line for selected end members. Contribution of "deeper" groundwater to water samples estimated from end-member mixing analysis using δ^2H isotope ratio data (lower graph). See SI Figure 8 for July data.

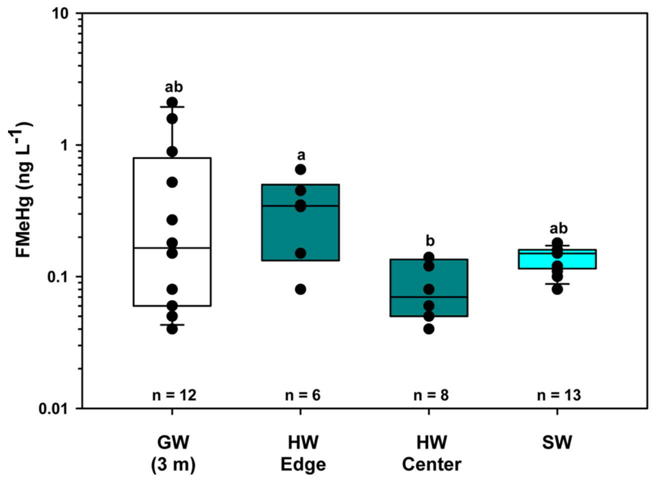

Figure 5. FMeHg concentrations in groundwater (GW) collected from wells (includes shallow and deep) 6 m from stream center, hyporheic water (HW) collected from edge of water and center of the channel, and streamwater (SW) at transects A and E during April and July 2009. Boxes, centerlines, and whiskers indicate interquartile ranges, medians, and 10th and 90th percentiles, respectively. Circles (●) indicate individual data points and "n" indicates number of total samples. Different letters indicate statistically different groups (Kruskal–Wallis ANOVA on ranks, $p = 0.023$; and Dunn's multiple comparison method, $p < 0.05$).

these study conditions, accounting for 80% or more of the observed increase in FMeHg flux. Several lines of evidence support this conclusion, including (1) clear hydraulic gradients toward the stream during both sampling events (Figure 3, SI Figure 7), (2) δ^2H-based, end-member mixing results demonstrating increasing groundwater contribution in the reach (Figure 4; SI Figure 8), (3) visible groundwater seeps within the reach (SI Figure 9), (4) groundwater FMeHg concentrations comparable to or higher than those observed in the stream (Figure 3, SI Figure 7), and (5) similar estimates of groundwater and groundwater FMeHg fluxes to the reach (Table 1).

Because local meteoric water MeHg concentrations are quite low (<0.04 ng/L), groundwater FMeHg indicates net methylation of THg along the shallow groundwater flow path. Net Hg methylation appears to occur throughout the shallow subsurface wetland/floodplain areas at the McTier study reach, because no significant difference (Wilcoxon one-sided signed rank; $p > 0.1$) in FMeHg concentrations was detected between (1) shallow and deep well samples, (2) distal (24 m) and proximal (6 m) deep well samples, or (3) transiently flooded, east-bank (dry during both events) and perennial-wetland, west-bank groundwater samples (SI Table 1). The lack of significant difference in FMeHg with depth of groundwater samples is consistent with vertically distributed Hg methylation and/or with efficient vertical transport of FMeHg over the 30–200 cm range of well depths in this study.

Implications for MeHg Availability in Coastal Plain Stream Habitats. The changes in FMeHg and FTHg fluxes along a defined stream reach are a net reflection of out-of-channel surface water and groundwater sources and of the relative efficiency of water movement from out-of-channel areas to the stream. For MeHg, microbial production within the stream channel also is a potential source of FMeHg, although in-channel MeHg production is reportedly small relative to watershed inputs.[11,45] The results of this study indicate that, under nonflood conditions, the primary supply of water, FMeHg, and FTHg within (excluding upstream surface water influx) the reach is groundwater discharge, rather than tributary transport from wetlands or in-stream MeHg production. The predominance of groundwater discharge under flood conditions was demonstrated previously for Coastal Plain streams.[12] The current results indicate that, in Coastal Plain streams, flood conditions are not required for efficient transport of MeHg from out-of-channel (wetland and riparian floodplain) source areas to the stream aquatic habitat, providing further insight into hydrogeologic characteristics that contribute to elevated MeHg bioaccumulation in Coastal Plain streams in the southeastern U.S.

■ ASSOCIATED CONTENT

Supporting Information

Method details, water-level gradient profiles, Hg/discharge regressions, sampling diagrams and photos, and July results. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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