Tidally Driven Export of Dissolved Organic Carbon, Total Mercury, and Methylmercury from a Mangrove-Dominated Estuary

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ⓢ Supporting Information

ABSTRACT: The flux of dissolved organic carbon (DOC) from mangrove swamps accounts for 10% of the global terrestrial flux of DOC to coastal oceans. Recent findings of high concentrations of mercury (Hg) and methylmercury (MeHg) in mangroves, in conjunction with the common co-occurrence of DOC and Hg species, have raised concerns that mercury fluxes may also be large. We used a novel approach to estimate export of DOC, Hg, and MeHg to coastal waters from a mangrove-dominated estuary in Everglades National Park (Florida, USA). Using in situ measurements of fluorescent dissolved organic matter as a proxy for DOC, filtered total Hg, and filtered MeHg, we estimated the DOC yield to be 180 ($\pm$12.6) g C m^{-2} yr^{-1}, which is in the range of previously reported values. Although Hg and MeHg yields from tidal mangrove swamps have not been previously measured, our estimated yields of Hg species (28 $\pm$ 4.5 μg total Hg m^{-2} yr^{-1} and 3.1 $\pm$ 0.4 μg methyl Hg m^{-2} yr^{-1}) were five times greater than is typically reported for terrestrial wetlands. These results indicate that in addition to the well documented contributions of DOC, tidally driven export from mangroves represents a significant potential source of Hg and MeHg to nearby coastal waters.
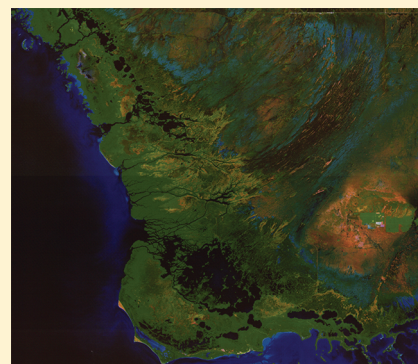
INTRODUCTION

Dissolved organic carbon (DOC) export from mangrove swamps accounts for 10% of the global terrestrial flux of DOC to coastal oceans.[1,2] Given recent reports of high concentrations of mercury (Hg) in mangrove tissues and mangrove marsh waters,[3−5] and the known high affinity of Hg species for DOC in surface waters,[6,7] there is concern that a large Hg flux may accompany the DOC flux from mangroves. In other aquatic environments, transport of Hg species is intimately linked to the transport of DOC because of strong complexation,[8] particularly in tidal wetlands.[9,10] The magnitude of Hg export from mangroves has not previously been assessed.

Elevated mercury levels have long been reported in coastal aquatic food webs from areas near the extensive mangrove swamps of southwest Florida.[3,11,12] In recent years, Hg concentrations in some fish and wading birds in the Everglades have declined, but concomitant declines have not been observed in Florida Bay species.[13−15] These decoupled trends suggest that mitigation efforts may have diminished the terrestrial accumulation of Hg but have not similarly benefited coastal food webs, perhaps because the Hg source to coastal food webs is different than that of the uplands. Methylmercury

(MeHg), the form of Hg that bioaccumulates, has several potential sources in coastal waters: it may be produced in low-oxygen environments in terrestrial systems[16,17] and then exported to coastal waters; it may be produced in coastal wetlands such as mangroves and then tidally pumped into surrounding waters;[9,18,19] or it may be produced within estuarine and coastal sediments.[20] Although elevated tissue concentrations of Hg and MeHg are known to occur in mangroves[5] and high concentrations of aqueous Hg and MeHg have been reported in mangrove-dominated environments,[3,21] remarkably little is known about the magnitudes of Hg and MeHg export from mangrove swamps into coastal and estuarine waters.

This study sought to characterize the export of DOC and Hg from the mesohaline estuarine mangrove swamps and fresher interior sawgrass marshes of the Shark River estuary (Everglades National Park, Florida, USA) to nearshore open coastal

waters to test the hypothesis that mangroves can be significant sources of DOC, Hg, and MeHg to coastal waters. Estimating mass fluxes of carbon and mercury species in estuarine environments is challenging because of bidirectional flows, rapidly changing concentrations, and the multiple factors that affect tidal interactions with wetlands. We capitalized on the known strong association between DOC and Hg and applied a recently developed strategy that uses in situ continuous measurements of fluorescent dissolved organic material (*fDOM*) as a proxy.[9] We first established the relationship of *fDOM* to DOC, total Hg and MeHg concentrations by measuring *fDOM* in situ while collecting discrete water samples throughout the estuary over a range of salinities and constituent concentrations during both wet and dry seasons. We also measured *fDOM* continuously at a fixed site in the middle of the estuary for approximately two weeks of each season. Regression models developed from the estuary-wide data were then applied to convert the seasonal midestuary *fDOM* time series to time series of DOC, total Hg, and MeHg concentrations, which were in turn used to calculate fluxes and yields. The premise of this study was that fluxes past the midestuary site would integrate processes operating over the range of nontidal to tidal domains, thereby providing insight into the production and transport of DOC and mercury species. The concentration and flux time series data improve our understanding of processes controlling production and transport of DOC, total Hg (THg), and MeHg from mangrove-dominated areas, assessments previously unattainable in dynamic estuarine systems.

■ EXPERIMENTAL SECTION

Site Description. The southwest Florida coast is a region of mangrove-dominated tidal inlets and rivers. The Shark River (SI Figure S1) is one such river, located entirely within Everglades National Park. Shark River Slough drains an area of predominantly freshwater sawgrass marsh in its headwaters, and expansive mangrove swamp characterizes the estuary's lower reaches. Tides are semidiurnal with a mean amplitude of approximately 1 m. The Everglades experiences two distinct precipitation seasons: a May−October rainy season and a November−April dry season. Regional average annual rainfall is approximately 1.4 m.[22] Our midestuary sampling site was near Gunboat Island (SI Figure S1), approximately 10 km inland from the coast and adjacent to a U.S. Geological Survey (USGS) tidal-stream gage. Water depth at the site is ∼9 m. Hg deposition and cycling in the region are strongly coupled to the pattern of precipitation.[23] Soil Hg concentrations in the lower Shark River are relatively high (0.15 to 0.30 mg kg^{-1}).[24]

Discrete Water Sampling. During a 2005 reconnaissance study, water samples were collected from a number of southwest Florida coastal rivers (SI Table S1) to identify areas of high Hg. For the follow-on flux study, additional samples were collected from the Shark River estuary during September 21−22, 2010 (wet season) and April 5−6, 2011 (dry season) (SI Figure S1, SI Table S2). Surface water samples were collected by boat directly into 1 L polycarbonate containers. During the September sampling period, water was also collected at Gunboat Island from 0.5 m below the air−sea interface, at 2 m depth, and at 1 m above the bottom. These samples were collected using a peristaltic pump, a 20 cm length of C-flex tubing, and three Teflon tubes (1/4 in. i.d.) fixed to 2 kg solid Teflon weights.

Samples collected for DOC analysis were filtered within 2 h of collection through prerinsed Gelman Gelcap filters (nominal cutoff of 0.45 μm) into precleaned, precombusted 1 L or 125 mL amber glass bottles. These samples were refrigerated and express-shipped on ice to the USGS laboratory in Boulder, CO. Samples were analyzed for DOC content by wet chemical oxidation and for UV absorbance by diode array spectrophotometry (see the Supporting Information for details). Specific UV absorbance (SUVA$_{254}$) was calculated as the UV absorbance at 254 nm divided by the DOC concentration.

Samples collected specifically for total mercury (THg) and methylmercury (MeHg) analyses were drawn directly into acid-washed 1 L PET bottles and then immediately filtered using an all-Teflon filtration tower, fired quartz fiber filters (0.7 μm pore size), and Teflon sample bottles. All field sampling followed mercury-clean procedures and included the collection of numerous field blanks to monitor for possible contamination.[25] Filtered waters were immediately acidified to 1% (v/v) with concentrated HCl and were stored at ambient temperature out of direct sunlight. Filters were immediately frozen in the field. Upon arrival to shore, all samples were express-shipped to the USGS Mercury Research Laboratory in Madison WI. Total Hg and MeHg analyses were performed using U.S. EPA Method 1631 and 1630, respectively, as implemented by the USGS Mercury Research Laboratory (see the Supporting Information for details).

Field Measurements in Situ. Concurrent with collection of each discrete water sample, fluorescent dissolved organic matter (*fDOM*) fluorescence and other parameters were measured in situ with an open-faced optical sensor (WET Labs *ECO*) attached to a water quality sonde (YSI 6920). For continuous measurements, in situ instruments were deployed at the Gunboat Island site during September 20−30, 2010, and April 4−19, 2011. A flow-through *fDOM* fluorometer (WET Labs WETStar; excitation wavelength 370 nm, emission wavelength 450 nm) fitted with a pump (Sea-Bird Electronics 5T) and a water quality sonde (YSI 6920) was mounted approximately 1.5 m above the seabed to collect data at 15 min intervals. The fluorometer was purged for one minute, followed by 60 s of data collection. Temperature, salinity, dissolved oxygen, pH, and turbidity were also measured during the same 60 s interval. The data were binned by averaging over the last 30 s of each data-collection period. Midway through each field deployment, the instruments were briefly removed and cleaned; the resulting data gaps were filled by interpolation.[26]

All *fDOM* instruments were calibrated to solutions of quinine sulfate prior to use. Fluorescence is reported here as quinine sulfate equivalents (QSE; the concentration of quinine sulfate dehydrate in ppb that results in an equivalent instrument response). Clean-water offsets, determined prior and subsequent to field deployment, were less than 1% of the measured in situ sample fluorescence values. The water quality sondes were calibrated to standards immediately before deployment.[27]

Water discharge data were obtained from the USGS Gunboat Island stream gage, which was equipped with a side-looking acoustic Doppler velocimeter that measured cross-sectional velocities every 15 min.[28] Discharge measurements were calibrated using a moving boat equipped with a downward-looking acoustic Doppler current profiler, and discharge was calculated according to published methods.[29]

Estimation of Constituent Time Series and Fluxes. Concentrations of DOC, filtered total mercury (FTHg), and filtered methylmercury (FMeHg) at Gunboat Island were

derived from the continuous in situ $fDOM$ measurements. Discrete-sample data were used to develop season-specific Type I linear regression models to relate DOC, FTHg, and FMeHg concentrations to $fDOM$ as described in Supporting Information section S2; no simple relationships were found to relate particle-associated Hg concentrations to $fDOM$ or other parameters measured continuously in situ. The regression models (one set applicable where freshwater and midestuary waters mixed and another set applicable where midestuary and saline waters mixed) were applied to the continuous $fDOM$ data to obtain continuous time series estimates of DOC, FTHg, and FMeHg concentrations. The freshwater–estuary submodels were applied where $fDOM > 125$ QSE; the estuary–seawater submodels, where $fDOM \leq 125$ QSE, corresponding to inflection points in salinity, SUVA$_{254}$, $fDOM$, and constituent values (Figure 1). Estuary waters at Gunboat
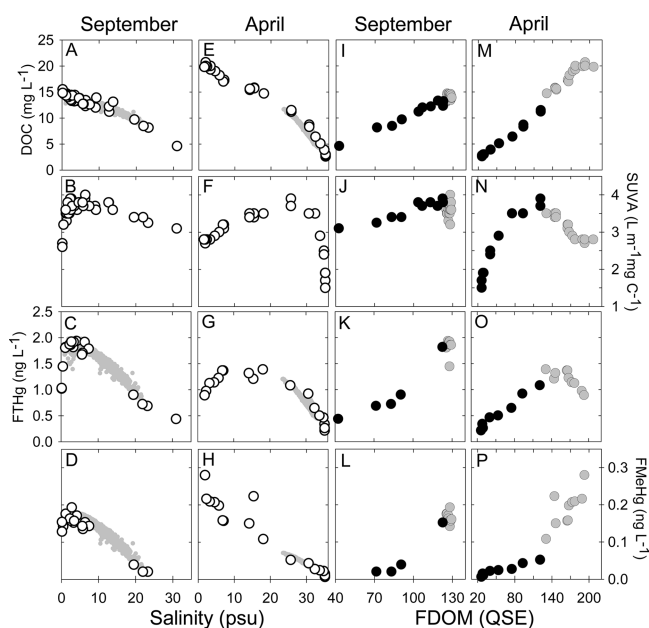
Figure 1. Measured dissolved organic carbon (DOC) and mercury species as a function of salinity (in practical salinity units, psu) and dissolved organic matter fluorescence ($fDOM$; in quinine sulfate units, QSE) in discrete samples of the Shark River estuary, Sept. 21–22, 2010, and April 5–6, 2011: DOC (top row), specific UV absorbance at 254 nm (SUVA; second row), filter-passing total mercury (FTHg; third row), and filter-passing methylmercury (FMeHg; bottom row). Large circles represent values measured in discrete samples. The small gray circles in parts A–H show the modeled constituent values at Gunboat Island for comparison. The large black circles in parts I–P indicate $fDOM < 125$ QSE, while the large gray circles in these figures indicate $fDOM \geq 125$ QSE, corresponding to the two mixing models described in the text.

Island most often fell within the estuary–seawater (low $fDOM$) domain; using only the estuary–seawater regressions resulted in <5% change in the final flux estimates.

Constituent fluxes were calculated for each 15-min interval as the product of the discharge and the estimated constituent concentration. Flux is here defined as positive seaward and negative landward; thus a positive flux represents net export out of the estuary toward the Gulf of Mexico.

Yields (fluxes per unit area) were estimated by dividing constituent fluxes by the area likely contributing DOC and mercury to the midestuary water column. The contributing area

in relatively flat tidal systems cannot be defined in terms of watershed area, as is typically done for estimates of terrestrial yields. Instead, it was estimated for the Shark River site as the planar area covered by the water volume of each deployment's tide of maximum exchange. For the tide of greatest ebb–flood water-height difference at Gunboat Island, the volume of the flooding waters was divided by the accompanying change in water height. This initial estimate of area was then refined by adjusting for the effects of soil porosity and water retention.[9]

Error Estimation. Laboratory measurement error is among the largest sources of uncertainty in this study. The DOC measurement error was ±0.2 mg L^{-1}, for a median error of 1% of the reported values. The laboratory error in FTHg measurements was constrained by laboratory protocols to be less than 10% of the measured value. FMeHg measurement error was ±0.01 ng L^{-1}, for a median error of 9% of the reported value.

Model prediction error is also important. Based on the regression models (SI Figure S2), the root-mean-square errors of prediction (RMSEPs) for the wet-season models were 2% for the DOC model, 11% for FTHg, and 5% for FMeHg. The dry-season RMSEPs were 1% for the DOC model, 6% for FTHg, and 4% for FMeHg. Error in discharge was estimated at 6%.[30]

Cumulative error was estimated as the square root of the sum of the squared error from the component measurements in the flux calculations.[9,30] This method assumes that individual errors are uncorrelated. For the September study period, the average errors were estimated to be 12% of the calculated DOC flux value, 16% of the calculated FTHg value, and 13% of the calculated FMeHg value. For the April study period, the average errors were estimated to be 12% of the calculated DOC flux value, 14% of the calculated FTHg value, and 13% of the calculated FMeHg value.

■ RESULTS AND DISCUSSION

DOC and Hg Concentrations and Sources. The 2005 reconnaissance water sampling of nearshore areas, tidal rivers, and mangrove swamps (SI Table S1) revealed some of the highest reported levels of MeHg for south Florida (>26 ng L^{-1}), including the Everglades. Concentrations of FTHg and FMeHg in samples collected near mangroves were higher than in samples collected from nearby channel waters, suggesting that mangrove areas were contributing large amounts of DOC and mercury to estuary and coastal waters. The 2010–2011 Shark River flux study was designed to assess the magnitude of this contribution.

Water samples and in situ measurements were collected during portions of both the wet and dry seasons to help gauge the range of fluxes that may occur and to provide insights into underlying and perhaps contrasting processes. During the September wet-season sampling period (Figure 2A), the Gunboat Island site experienced much greater precipitation than during the April dry-season period (Figure 2D). The midestuary median salinity was 9 psu in September, with a range of over 21 psu; the median salinity in April was much higher (31 psu), with a much smaller range (9 psu). Median water height during the September period (−0.1 ft) was higher than during April (−0.7 ft). As is discussed below, the salinity gradient, precipitation, and regional water height all have important implications for the estuarine export of DOC, THg, and MeHg.

Sampling during both seasons encompassed freshwater sawgrass slough, mangrove-dominated coastal swampland, and
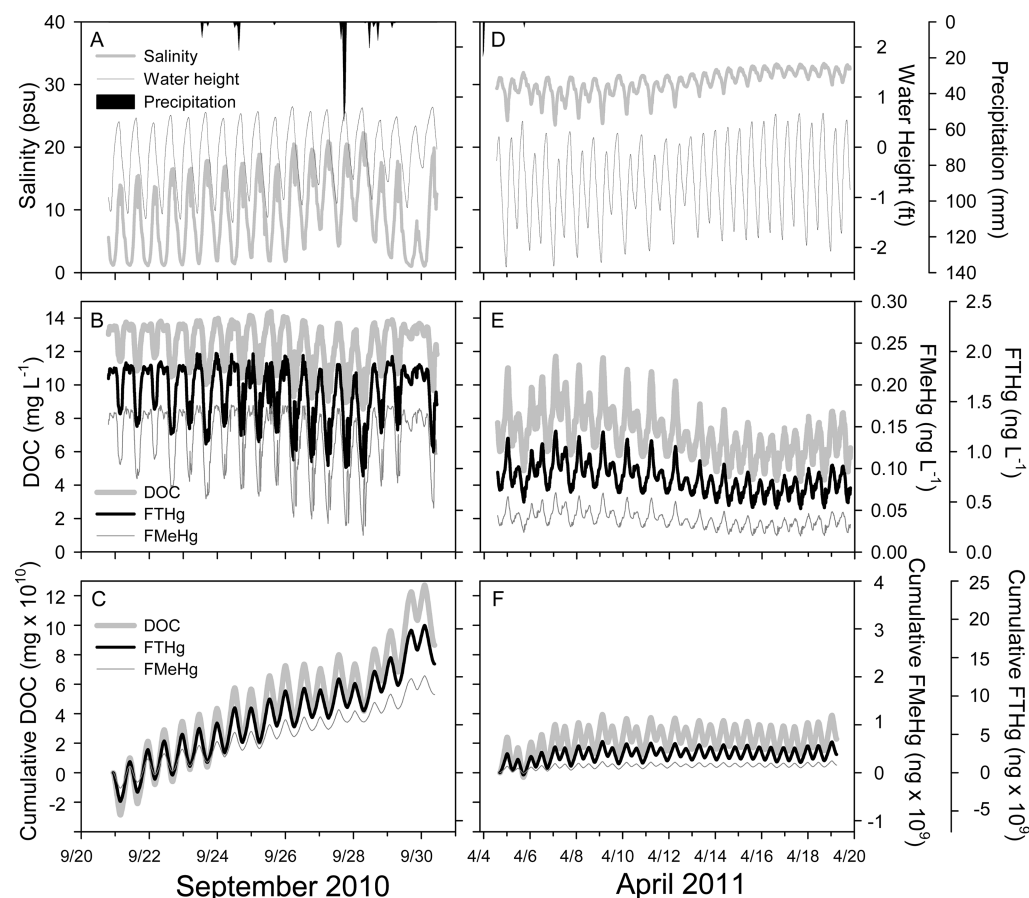
Figure 2. Times series of tidal-stream gage data and modeled constituent concentrations and fluxes in Shark River estuary at Gunboat Island during Sept. 21–22, 2010, and April 5–6, 2011: salinity, water height, and precipitation (top row); modeled dissolved organic carbon (DOC), filtered total mercury (FTHg), and filtered methylmercury (FMeHg) concentrations (middle row), and modeled cumulative DOC, FTHg, and FMeHg fluxes (bottom row).

the higher salinity open coastal waters of Ponce de Leon Bay (SI Figure S1). DOC concentrations were highest near the most inland, low-salinity sampling sites; concentrations were lowest offshore in Ponce de Leon Bay (Figure 1A, SI Table S2). The DOC:salinity concentration gradient was steeper during the April dry-season sampling period than during September (Figure 1A, E).

Similar to DOC, the highest *fDOM* values during both seasons were from inland fresh waters, while the lowest values were found in outer Ponce de Leon Bay (SI Table S2). The down-estuary *fDOM* gradient was steeper in the dry season. During both seasons, *fDOM* and DOC concentrations were strongly positively correlated (Figure 1I, M; r = 0.98 in September; r = 0.99 in April).

In contrast, $SUVA_{254}$, a compositional property of DOC related to DOC aromaticity and source,[31] exhibited maximum values at midrange salinities during both sampling periods (Figure 1B, F). Fall $SUVA_{254}$ values peaked at 5 psu salinity, when the Gunboat Island median salinity was 9 psu (Figure 2A). Spring $SUVA_{254}$ values peaked at 26 psu, when the median salinity at Gunboat Island was 31 psu (Figure 2D).

The spatial distribution of FTHg was similar to that of $SUVA_{254}$ in both seasons (Figure 1), with both quantities peaking near the region of 5 psu salinity in September (close to salinities at Gunboat Island) and near 20 psu salinity in April (also close to salinities at Gunboat Island). Likewise, September FMeHg values peaked near 5 psu salinity, in the mangrove

zone, with the lowest concentrations found at offshore salinities (Figure 1D). In April, however, the spatial distribution of FMeHg more closely resembled that of DOC, with the highest concentrations at inland sites and progressively lower values offshore (Figure 1H). Even so, the April relationship between *fDOM* and FMeHg showed an inflection point (Figure 1P) near 25 psu salinity (Figure 1H), indicating a change in DOC composition from that previously associated with inland FMeHg.

Interestingly, the spatial distributions of particulate THg (PTHg) and particulate MeHg (PMeHg) also resembled those of $SUVA_{254}$ (SI Table S2), suggesting a possible coupling between the particulate and dissolved Hg phases. PTHg was 24($\pm$11)% of THg for September and 39($\pm$17)% for April. PMeHg was 36($\pm$14)% of TMeHg for September and 31($\pm$14)% for April. These values for the distribution of mercury between particulate and filtered phases—with the majority occurring in the filter-passing fractions—are similar to those previously reported for the Everglades.[3,32]

The concurrent change in FTHg, FMeHg, *fDOM*, and $SUVA_{254}$ values at the salinities found near Gunboat Island in both seasons (Figure 1) strongly suggests that the primary zone of production of DOC, THg, and MeHg is geographically fixed within the mangrove portion of the estuary, in the general vicinity of Gunboat Island. If DOC and Hg production and Hg methylation occurred within a specific salinity zone of the estuary, the peak would shift seasonally away from Gunboat

Island salinities. If the large majority of DOC and Hg were produced in the fresh waters of the sawgrass slough or in the outer estuary and this was where the majority of Hg methylation occurred, there would not have been a midestuary maximum. Further evidence that the mangroves supply the majority of DOC, Hg, and MeHg is that midestuary high $SUVA_{254}$ values cannot be explained by invoking an appreciable contribution of freshwater-derived or outer estuary DOC (Figure 1). That the mangrove zone is the primary source of DOC and Hg supply to the coast is consistent with the findings of Romigh et al.,[33] who reported high DOC fluxes from Shark River mangroves. They also agree with Rumbold et al.,[3] who found little Hg contribution from uplands and the highest THg and MeHg concentrations in the transition zone from sawgrass to mangrove, and with the high THg and MeHg concentrations found in our 2005 southwest Florida reconnaissance study (SI Table S1). One implication of this finding is that, since little of the Hg and MeHg is derived from the sawgrass portion of the estuary, reducing Hg loads to sawgrass marsh areas may have little effect on coastal Hg fluxes from mangroves.

DOC and Mercury Time Series and Fluxes. Modeled constituent concentrations in the Shark River estuary at Gunboat Island in September and April generally tracked the water-height variations that marked the flood and ebb of the semidiurnal tides and the longer-period spring–neap fluctuations (Figure 2A, D). The highest modeled DOC, FTHg, and FMeHg concentrations for each time series (Figure 2B, E) most often occurred just after the lowest water of the ebb tide, near the lowest salinity portion of the tidal cycle. Lower concentrations, the result of mixing with coastal waters, were seen coincident with the higher relative salinities that accompanied the flood tides. This difference in concentration between the ebbing and flooding waters drove the majority of flux in Shark River estuary.

Material export from estuaries is driven by both net flow (the residual water flow after tidal exchange) and tidal pumping (net transport resulting from different constituent concentrations in ebbing and flooding waters). For the periods measured, net water discharge from the estuary[28] accounted for less than 5% of the estimated constituent flux in September and less than 1% in April. Most Shark River DOC, FTHg, and FMeHg export was driven by tidal pumping.

Daily fluxes were always positive (seaward), except for a few periods in the middle of the April deployment (Figure 2C, F). For September, estimated daily fluxes from the Shark River estuary averaged 9.1 ($\pm$0.6) $\times 10^9$ mg d^{-1} for DOC, 1.5 ($\pm$0.2) $\times 10^9$ ng d^{-1} for FTHg, and 1.7 ($\pm$0.2) $\times 10^8$ ng d^{-1} for FMeHg. In April, the average estimated total daily fluxes were much smaller: 1.5 ($\pm$0.02) $\times 10^9$ mg d^{-1} for DOC, 1.7 ($\pm$0.1) $\times 10^8$ ng d^{-1} for FTHg, and 1.1 ($\pm$0.04) $\times 10^7$ ng d^{-1} for FMeHg. Despite finding that all constituents were related to $fDOM$, estimated flux through time was different for each constituent (Figure 2). For example, between September 25 and 27, average daily fluxes were lower than those seen during the first three days of the measurement period to a degree that varied depending on the constituent: approximately 70% lower for DOC, 60% lower for FTHg, and 35% lower for FMeHg (Figure 2C).

Although tidal pumping is the engine that drives Shark River DOC and Hg exports, it appears that flux magnitudes are controlled by hydrologic and geomorphic properties that affect material exchanges between marsh/swamp surfaces and tidal channel waters. Water height, for example, seemed to be

important. Tidal exchange volumes were similar during the September and April deployments, but mercury fluxes were significantly larger in the fall than in the spring (9 times higher for FTHg; 17 times higher for FMeHg). Water levels were also elevated in September: median water height was 0.6 ft higher and median high water was approximately 0.2 ft higher (Figure 2A, C). The greater water heights in fall would have inundated more mangrove-swamp surface area, thus making available more mangrove-derived material for ebb transport to channel waters. The effect of this enhanced supply can be seen in the contrast between the modeled concentration time series in September and April (Figure 2B, E). In April, the highest modeled constituent values coincided with the lowest of tides. After the tide reversed, a smooth decline in concentration accompanied the incoming flood. In September, however, modeled constituent values did not decline smoothly with the incoming tide. Instead, high concentrations often persisted into the subsequent flood stage, likely due to greater inundation during this period of higher water height and slow draining, the result of ebb−flood flow hysteresis.[30] It appears from these observations that even modest increases in regional sea level due to storms, wind, or rising global sea level have the potential to significantly alter constituent fluxes from mangroves.

Rainfall also affected Shark River constituent fluxes but with a lagged effect. Following the heavy rains of September 27 (Figure 2A), for example, estimated total daily fluxes doubled for DOC and FTHg and increased by 75% for FMeHg (Figure 2C). Note that elevated modeled constituent concentrations (Figure 2B) did not occur until a full day after the precipitation fell. The heavy rains may have connected a supra-tidal mangrove plain (normally isolated from the Shark River) to interior intertidal zones, supplying them with DOC and Hg. Slow tidal pumping from these areas would account for the observed lag. The modeled concentrations and fluxes of all constituents remained high (Figure 2C). A similar lag effect in flux response to precipitation is seen following the rainfall event of April 4 (Figure 2D, F).

DOC, Total Mercury, and Methylmercury Export. We sought to compare our flux estimates to previously published values and to assess whether exports from mangroves might represent a significant flux of THg and MeHg to coastal waters. To do this, it was necessary to convert our flux values to yields (fluxes per unit area) and make a series of assumptions to generate annual values. We first converted the DOC, FTHg, and FMeHg daily fluxes to annual ones by assuming that our deployment periods were representative of their respective seasons (wet and dry). We then converted these to yields by normalizing the fluxes to the area of influence (see methods). This calculation provided an estimated annual DOC yield for the Shark River estuary of 180 ($\pm$12.6) g C m^{-2} yr^{-1}. This value is somewhat higher than the estimated annual DOC yield reported by Romigh et al.[33] (56 g C m^{-2} yr^{-1}) for a small mangrove subdrainage in the Shark River estuary but is well within the 44−381 g C m^{-2} yr^{-1} range reported for mangrove swamps worldwide in a review by Bouillon et al.[2] The similarity between our results and other published values indicates that our $fDOM$-based methods provided DOC yield estimates of a reasonable magnitude.

The estimated annual yield for FTHg was 28 ($\pm$4.5) μg m^{-2} yr^{-1}: eight times the highest previously reported wetlands value and 20 to 100 times more than is generally reported for wetlands.[34−36] The estimated yield for FMeHg was 3.1 ($\pm$0.4) μg m^{-2} yr^{-1}: 10 to 100 times values previously reported from

terrestrial wetlands for FMeHg and 5 to 100 times previously published values from terrestrial wetlands for unfiltered MeHg.[17,36,37] The estimated Shark River FMeHg yields are more than five times those observed in the St. Mary's River, a north Florida blackwater river with a high DOC concentration and flux.[17] However, the MeHg yields found here are similar to those measured in a tule-dominated tidal marsh in San Francisco Bay (2.5 mg m^{-2} yr^{-1}).[9] Our estimates, in combination with other recent studies of tidal wetlands,[9,18,21,38] indicate that tidal flushing of marshes and swamps represents a potentially large and previously unrecognized source of THg and MeHg to estuarine and coastal aquatic ecosystems.

To assess whether FTHg and FMeHg exports from mangroves to the coastal ocean might be significant in comparison to other potential sources, we multiplied the Shark River yields derived above by the 1400 km^2 of fringing mangrove swamps in southwest Florida. This exploratory calculation resulted in estimated annual exports in the range of 250 MT DOC, 39 kg FTHg, and 4.3 kg FMeHg. To include particulate fractions, we increased the mercury fluxes according to the average ratios of particulate to filter-passing Hg species found in this (SI Table S2) and other studies for the Everglades.[3] The resulting total (combined particulate and filtered) Hg exports were thereby found to be approximately 55 kg for THg and 6.5 kg for MeHg. We caution that these calculations are wholly heuristic in nature, made only to scale up the magnitudes determined in this study for the purpose of understanding the potential implications of our Shark River findings within the context of what is currently known about coastal mercury supply in general. Longer time series—preferably multiyear time series—and studies at multiple locations are needed to adequately constrain fluxes at larger scales.

Do fluxes of this magnitude represent a significant source to the coastal environment in comparison to other potential sources? For THg, the primary source to southwest Florida coastal waters is currently thought to be atmospheric deposition, with freshwater runoff accounting for only a small fraction.[3] Flux from mangroves has not previously been considered. Comparing the potential mangrove flux to estimates of the combined wet and dry deposition of THg to the 5000 km^2 of adjacent coastal waters suggests that mangroves could account for a loading equivalent to approximately 40% of atmospheric THg deposition. It is noteworthy in this context that Lacerda et al.[4] found Hg in waters exported from a mangrove marsh to be more reactive with respect to methylation than was Hg in ambient estuary water.

For MeHg, the dominant source to coastal waters in southwest Florida is presently thought to be local production in coastal sediments and diffusion into overlying waters;[3] the amount discharged from uplands and that attributed to wet and dry atmospheric deposition is small.[3] Again, tidal flux from mangrove areas has not been previously considered. Benthic flux magnitudes of MeHg from Florida coastal sediments have not been reported, but if magnitudes are similar to fluxes observed elsewhere (1 pmol m^{-2} d^{-1} in Chesapeake Bay;[39] 30 pmol m^{-2} d^{-1} in San Francisco Bay[40]), then potential MeHg loading from mangroves to the 5000 km^2 coastal-ocean area would be the equivalent of 2.5 to 20 times the flux from sediments, more than 80% of the total flux.

This assessment, though preliminary in nature, clearly establishes that tidal mangrove systems have the potential to be a significant source of THg and MeHg to tropical coastal waters, in addition to their previously demonstrated contributions of DOC.[2] Our findings, in conjunction with previously published reports from tidal herbaceous wetlands, bolster the suggestion that tidal pumping of DOC and Hg from tidal wetlands may represent an important source to coastal environments. Additional studies are needed to quantify fluxes from mangroves and other tidal systems and to resolve the fate of the material once it enters the nearshore environment.

If the large Shark River fluxes found in this study are generally representative of tidal mangrove systems, there may be global implications. Ding et al.[5] recently reported particularly high concentrations of Hg in tissues and litter fall of mangroves, suggesting that mangroves are particularly efficient at canopy capture of atmospheric Hg. High rates of canopy capture in an environment conducive to methylation combined with the high fluxes found here would result in a system particularly efficient at extracting Hg from the atmosphere and transporting it to the coastal oceans as MeHg, potentially generating large coastal fluxes of MeHg wherever mangroves are found. Evidence for the existence of this phenomenon elsewhere should be investigated.

Continuous in situ measurements of $fDOM$ can serve as a powerful tool for investigating these DOC, THg, and MeHg mass fluxes in many tidal systems. Such measurements are critically needed to improve our understanding of Hg cycling, advance predictive models and budgets of carbon and Hg in coastal areas, and inform Hg total maximum daily load regulation development. Further, high-resolution time series of concentrations and fluxes provide valuable insights into the myriad biological, physical, hydrologic, and geomorphic processes affecting tidal exchange—insights that should in turn improve estimates of carbon and mercury fluxes into coastal oceans.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Tabulated data, additional details about laboratory methods and regression-model development as well as figures showing sampling sites and regression-model results. This material is available free of charge via the Internet at http://pubs.acs.org.

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