Mercury Bioavailability and Bioaccumulation in Estuarine Food Webs in the Gulf of Maine

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MARCH 2009

Impact Factor: 5.33 · DOI: 10.1021/es8017122 · Source: PubMed

6 AUTHORS, INCLUDING:

Darren Ward
Humboldt State University
17 PUBLICATIONS **330** CITATIONS
SEE PROFILE

Stefan Stürup
University of Copenhagen
78 PUBLICATIONS **1,556** CITATIONS
SEE PROFILE

Article

Mercury Bioavailability and Bioaccumulation in Estuarine Food Webs in the Gulf of Maine

Celia Y. Chen, Michele Dionne, Brandon M. Mayes, Darren M. Ward, Stefan Sturup, and Brian P. Jackson

Environ. Sci. Technol., **2009**, 43 (6), 1804-1810• DOI: 10.1021/es8017122 • Publication Date (Web): 13 February 2009

Environ. Sci. Technol. **2009,** *43,* 1804–1810

Mercury Bioavailability and Bioaccumulation in Estuarine Food Webs in the Gulf of Maine

CELIA Y. CHEN,* MICHELE DIONNE,† BRANDON M. MAYES,‡ DARREN M. WARD, STEFAN STURUP,§ AND BRIAN P. JACKSON||

Department of Biological Sciences, HB 6044 Gilman Hall, and Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, Wells National Estuarine Research Reserve, Laudholm Farm Road, Wells, Maine 04090, Long Trail Brewery, Bridgewater Corners, Vermont 05035, and Department of Pharmaceutics and Analytical Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Received June 23, 2008. Revised manuscript received January 16, 2009. Accepted January 19, 2009.

Marine food webs are important links between Hg in the environment and human exposure via consumption of fish. Estuaries contain sediment repositories of Hg and are also critical habitat for marine fish and shellfish species consumed by humans. MeHg biotransfers from sites of production in estuarine sediments to higher trophic levels via both benthic and pelagic pathways. In this study, we investigated the potential for Hg biotransfer to estuarine food webs across a Hg contamination gradient in the Gulf of Maine. Despite the variation in sediment Hg concentrations across sites (>100 fold), Hg concentrations in biota ranged by only 2−4 fold for each species across sites. Sediment contamination alone explained some variation in Hg and MeHg concentrations in biota across sites. However, biogeochemical and ecological factors also explained significant variation in Hg bioaccumulation across species. Contaminated sites had higher total organic carbon concentrations in sediments, which related to a decrease in Hg bioaccumulation (measured as biota−sediment concentration factors). Moreover, concentrations of MeHg were higher in pelagic-feeding than benthic-feeding fauna (determined from $\delta^{13}C$), indicating the importance of pelagic pathways in transferring MeHg. Lastly, the proportion of total Hg as MeHg increased with trophic level (measured as $\delta^{15}N$). These results reveal the importance of both biogeochemical and ecological factors in determining the bioavailability and trophic transfer of MeHg in estuarine food webs.

Introduction

Hg is a ubiquitous environmental contaminant and a potent neurotoxin that accumulates in aquatic ecosystems, posing a risk to humans and wildlife. Mercury enters the environment from both natural and anthropogenic sources, but predominantly from coal-fired power plant emissions (*1*), and eventually enters aquatic systems via direct deposition and watershed transport. In freshwater and marine ecosystems, inorganic Hg is methylated in sediments and in the water column and MeHg is biomagnified in the food web. Human exposure is almost entirely due to fish consumption that is comprised mostly of marine fish and shellfish. In fact, marine fisheries make up more than 90% of the global fish harvest (*2*) and provide an important source of protein for the global population (*3*). Hg levels in many top predatory marine fish are often above the USEPA recommended criterion of <0.29 μg/g (wet weight) for safe unrestricted consumption (*4*).

On the basis of Hg budgets calculated for the oceans, MeHg produced in coastal sediments may provide an important source of MeHg to offshore pelagic food webs (*5, 6*). Coastal sediments, particularly in estuaries with many industrialized watersheds, are known repositories of contaminants (*7*). Estuaries are also critical areas of Hg methylation, due to geochemical conditions in sediments that are conducive to MeHg production, such as anoxia and periodic wetting and drying from tidal flux (*8*−*10*). MeHg from estuarine sediments may be transferred to offshore fisheries via physical or ecological transport processes.

Estuaries are critical habitat for many commercially and recreationally harvested fish and shellfish species (*11, 12*) that are consequently exposed to MeHg produced in situ. Estuaries support many species over their entire life cycle and provide nursery grounds for other species that move to deeper portions of the estuary as they develop and grow (*13*). MeHg produced in estuaries may be transported offshore via the "trophic nekton relay" (*13, 14*) or "bioadvection" (*6, 15*) through feeding by transient subtidal species on resident intertidal species and migration of juveniles to offshore adult habitat (*16*). This horizontal trophic transfer also results in biomagnification of MeHg to top predator species consumed by humans and wildlife (*17*).

While MeHg produced in the water column is likely bioaccumulated in marine food webs via direct uptake by phytoplankton and pelagic feeding, MeHg that is produced in sediments can be taken up through either benthic or pelagic pathways (*9, 18*). Chemical flux from sediments or methylation in the water column makes MeHg available to phytoplankton at the base of the pelagic food web, whereas feeding in or on sediments links MeHg to the benthic food web. Feeding and burrowing activities by benthic epifauna and infauna influence methylation as well as expose them to MeHg (*19*). However, despite their direct contact with sediments, benthic food webs in lakes have lower levels of Hg than pelagic food webs, even in relatively contaminated systems (*20*). This counterintuitive relationship may be due to Hg speciation in these different food webs and the influence of organic carbon on the bioavailability of Hg and MeHg. The question remains as to whether benthic fauna are important links between MeHg production in sediments and higher trophic levels in marine food webs.

In this study, we investigate Hg biotransfer from sediments to benthic and pelagic food webs across a gradient of sites, from pristine to highly industrialized. We seek to test the following hypotheses: (1) Hg bioaccumulation in intertidal fauna varies with concentrations in sediments; (2) Hg and MeHg bioaccumulation does not differ between benthic and pelagic fauna; and (3) MeHg biomagnifies in intertidal food webs. These are fundamental transfer processes that need to be addressed in order to determine the pathways of MeHg transfer from sites of production in estuarine sediments to coastal fisheries.

* Corresponding author phone: (603)646-2376; fax: (603)646-1347; e-mail: celia.chen@dartmouth.edu.
† Wells National Estuarine Research Reserve.
‡ Long Trail Brewery.
§ University of Copenhagen.
|| Department of Chemistry, Dartmouth College.

10.1021/es8017122 CCC: $40.75

Published on Web 02/13/2009

Methods

We studied four sites in the Gulf of Maine (GOM) and measured Hg, MeHg, and percent of total Hg as MeHg (%MeHg) in benthic and pelagic fish and invertebrates and compared them to in situ sediment concentrations and to their stable isotope signatures (^{13}C and ^{15}N). To represent a wide range of functional feeding groups and trophic levels, we sampled major benthic primary consumers, secondary consumers, and tertiary consumers. In 2003, we collected a full range of taxa and in 2004, we focused on four focal taxa: a filter feeder (*Mytilus edulis*), a vertebrate omnivore (*Fundulus heteroclitus*), a benthic grazer (*Littorina littorea*), and a benthic omnivore (*Carcinus maenas*).

We sampled at four sites in intertidal areas with similar patterns of tidal inundation but differing in degrees of Hg contamination. Sites were located in (1) Adams Point (ADAMS) in southeast Great Bay, NH, where Hg inputs are low (*21*) and land use is relatively forested; (2) the Portsmouth Harbor Region of Great Bay (PHGB), which is highly industrialized and adjacent to numerous contaminated sites; (3) the Webhannet Estuary in Wells, ME (WELLS), which is undeveloped except for some residential areas (mostly seasonal); and (4) Northeast Cove on Mount Desert Island, ME (MDI), adjacent to Acadia National Park, which is pristine but receives relatively high atmospheric inputs of Hg (*22*).

Sediment Sampling and Analysis. Sediment samples were collected in summer 2004 and 2006 at different sites using a 6 cm diameter coring tube. The top 2 cm of nine sediment cores were composited into a single sample. Subsamples of the composite were freeze-dried, homogenized, and analyzed for total Hg (THg as μg/g DW) and percent total organic carbon (%TOC using thermal partitioning at 550 °C; EPA 440.0; see Supporting Information).

SEM-AVS (simultaneously extracted metals−acid volatile sulfides) is a measure of biovailability in which the AVS (largely iron sulfides available for binding divalent cationic metals to form insoluble metal−sulfide complexes) reduces the metal biovailability and toxicity of metals in sediments. Values <1.0 indicate no bioavailability of metals. Separate sediment samples (three replicates per site) were collected for SEM-AVS analysis by taking a plug of sediment under water to prevent contact with air. Samples were frozen immediately and later analyzed (see Supporting Information).

Chlorophyll and Zooplankton Sampling. We collected chlorophyll, dissolved organic carbon (DOC), and zooplankton samples in summer 2003 at each GOM site at high tide. These samples were not indicative of conditions throughout the tidal cycle but a measure to compare aqueous conditions across sites at a single time point. Zooplankton samples were collected at high tide using a 202 μm nonmetallic plankton net for multiple vertical tows. Samples were collected and stored in 30 mL acid-cleaned Teflon vials (*23*). In the laboratory, samples were freeze-dried, milled in acid-cleaned Teflon vessels with Teflon-coated steel balls, and split for Hg and stable isotope analyses. Trace metal clean protocols were used in all field and analytical work (*24*). Reagents were trace-metal grade wherever possible, and procedural blanks were included in all cases.

Benthic Invertebrate Sampling. Invertebrates were sampled using plastic trowels, minnow traps, D nets, pitfall traps, or collected by hand. Sediment samples were sieved through a 0.5 mm, nylon-coated mesh, returned to the laboratory where invertebrates were sorted, and identified to the lowest practical taxon. All samples were handled with trace metal clean technique and stored in either acid-cleaned plastic bags or acid-cleaned Teflon vials (for smaller organisms) and frozen. Later, frozen samples were thawed, rinsed with ultraclean water, weighed, and freeze-dried. Mollusks were removed from their shells prior to freeze-drying.

Fish Sampling. Fish sampling was conducted at mid to high tide levels using fish seines, fyke nets, and minnow traps. Fish total lengths and wet weights were measured. Sizes of individuals for each fish and invertebrate species were standardized for Hg tissue samples to reduce the influence of size on feeding habits and trophic position (*25*). Fish were frozen in acid-rinsed plastic bags for storage and prepared as in Chen and Folt (*26*).

Stable Isotope Analysis. Whole fish tissue, whole invertebrates, and gastropods without shells all sampled in 2004 were analyzed for stable isotopes at the Colorado Plateau Stable Isotope Laboratory. Animal samples were freeze-dried, ground, and homogenized. Isotopic signatures ($^{13}C/^{12}C$, $^{15}N/^{14}N$) were measured for each species. ^{13}C was used to identify food sources (*27*) such as benthic vs pelagic production (*28*) or marsh plants versus phytoplankton (*29*). ^{15}N was used to identify the trophic levels of the organisms studied (*27*). Stable isotope samples of *M. edulis* were not collected from Wells in 2004 but samples from 2006 were used after stable isotope values from multiple years were compared to ensure minimal year to year variation.

Hg and MeHg Analysis. All metal samples were analyzed by the Dartmouth Trace Element Core Facility using a magnetic sector inductively coupled plasma-mass spectrometer (ICP-MS ELEMENT2, Thermo-Finnigan, Waltham, MA). Total Hg samples were microwave-digested for analysis with a nitric acid digestion (Seastar). Total Hg in biota and sediments was analyzed using cold vapor-ICP-MS (instrument detection limits of ca. 0.1 ng L^{-1}). External quality control was achieved by digesting and analyzing similar amounts of standard reference materials (SRM's: NIST SRM 2976 mussel tissue, $n = 4$, and DORM-2, NRC-CNRC Canada). Average Hg recovery rates were 103.5 ± 5% for the mussel SRM and 93% for DORM-2. For total Hg the method detection limit is approximately 2 ng g^{-1} based on a sample weight of 30 mg and digestion volume of 10 mL. Field blanks for zooplankton were 16 ng L^{-1}, 100 times lower than the average sample concentrations.

Samples from 2004 were analyzed for Hg speciation using isotope dilution gas chromatography-ICPMS. Samples were freeze-dried, spiked with an appropriate amount of enriched inorganic ^{199}Hg (Hg_i) and enriched methyl[^{201}Hg]mercury (MeHg) and then extracted in 2−3 mL of KOH/methanol (25% w/v). One of two methods for Hg speciation was employed depending on the expected level of Hg in the original sample, a function of the initial available sample mass. For <20 mg, the methodology involved purging with inert gas and trapping on a Tenax trap that was thermally desorbed and Hg species were quantified by isotope dilution GC−ICP-MS using a high sensitivity Element2 ICP-MS in low resolution mode. For >20 mg, samples were analyzed according to Perna et al. (*30*). The latter methodology is less time-consuming than the purge and trap method but has higher detection limits and is only suitable for larger initial sample masses. Quality control was conducted through the analysis of two SRM's: NIST 2976, mussel tissue with MeHg certified at 0.0278 ± 1.1 μg g^{-1}, and CRC (Ottawa, Canada) DORM-2, dogfish muscle, MeHg concentration of 4.47 ± 0.32 μg g^{-1}. Average recovery for MeHg in DORM2 was 108% ($n = 13$, rsd = 3.4%), and for NIST 2976, average recovery was 114% ($n = 12$, rsd = 10%). Method detection limits for MeHg analysis by isooctane extraction and capillary GC−ICP-MS (Agilent 7500c, Palo Alto, CA) are 5 ng g^{-1} assuming an initial sample mass of 200 mg. For the purge and trap GC−ICP-MS (Element 2, Thermo-Fisher, Bremen, Germany) method, detection limits are 0.2 ng g^{-1} based on an initial sample weight of 25 mg.

Data Analysis. We used $\log_{10}$-transformed metal concentrations in all analyses, as this equalized variance and normalized residuals. All analyses were conducted using the

TABLE 1. Sediment and Water Attributes of Four Sites (ADAMS, PHGB, WELLS, MDI) in the Gulf of Maine[a]

system	site	sediment TOC (%)	SEM-AVS	sediment total Hg (μg/g DW)	Chl *a* (μg/L)	DOC (mg/L)
Webhannet, ME	Harbor Road (WELLS)	0.071	−0.77	0.008	1.4 ± 0.3	0.95
Mount Desert, ME	Northeast Creek (MDI)	1.39	−14.08[b]	0.069	5.2 ± 0.8	0.59
Great Bay, NH	Adams Point (ADAMS)	2.17	−11.66	0.424	3.1 ± 0.3	0.65
Great Bay, NH	Portsmouth Harbor (PHGB)	2.76	−27.99	1.135	2.0 ± 0.4	0.71

[a] Sediment samples (%TOC, SEM-AVS, total Hg) from composites of nine sediment subsamples collected in 2006. Chl *a* (value ± SD) and DOC were from water column samples collected in 2003. [b] Sample taken from Somes Sound also on Mount Desert Island.

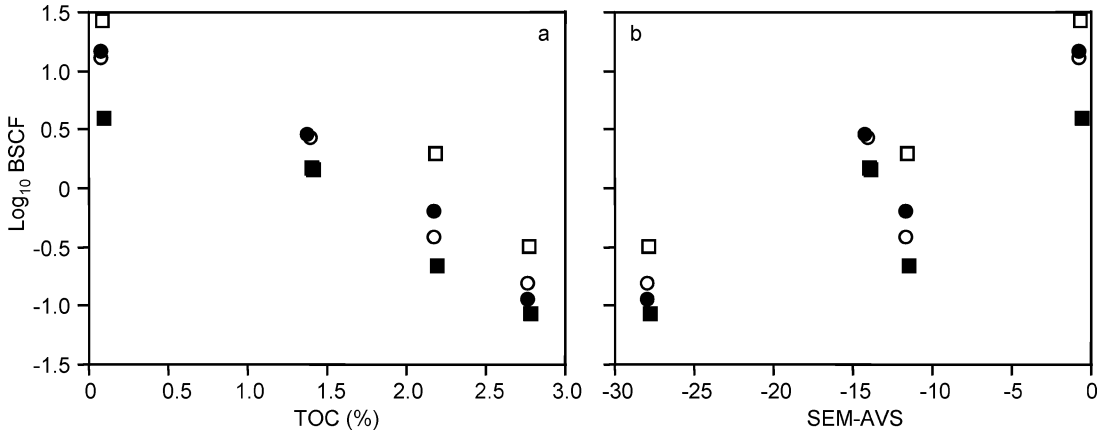

FIGURE 1. Relationship of BSCFs across sites (ADAMS, PHGB, WELLS, MDI) and four focal taxa to (a) TOC (2006) and (b) SEM-AVS (2006). Symbols: (open square) *Mytilus*, (solid square) *Carcinus*, (open circle) *Littorina*, (solid circle) *Fundulus*. Equation for %TOC ANCOVA: $\log_{10}$ BSCF = *X* − 0.69 × %TOC, where *X* = 0.87 for *Carcinus*, 1.23 for *Fundulus*, 1.19 for *Littorina*, and 1.46 for *Fundulus*; see Table 2 for statistics. Equation for SEM-AVS ANCOVA: $\log_{10}$ BSCF = *X* − 0.067 × SEM-AVS, where *X* = 0.68 for *Carcinus*, 1.03 for *Fundulus*, 1.01 for *Littorina*, and 1.27 for *Fundulus*; see Table 2 for statistics.

statistical software program JMP 5.01a. Biota−sediment concentration factors (BSCF) were calculated for the four focal taxa collected in 2004 (BSCF = THg concentration in biota/THg concentration in sediment). The relationship between BSCF values and %TOC or SEM-AVS across sites was determined using analysis of covariance (ANCOVA) with species as an additive classification term. We used ANCOVA to test for a relationship between sediment THg vs Hg and MeHg concentrations in the focal species across sites. The ANCOVA model included species as a classification term and sediment Hg as a covariate, with mean Hg or MeHg for each species at each site as the response. In ANCOVA analyses, we initially tested for interaction terms, but none were significant and were dropped from the models. We only conducted this analysis for the 2004 data, as not all species were collected at all sites in 2003. We used factorial analysis of variance (ANOVA) to test for differences in Hg and MeHg concentrations in focal species across sites. The ANOVA model included classification terms for both species and site, as well as their interaction.

We analyzed stable isotopes of N and C to identify organisms that feed more on pelagic resources (more depleted ^{13}C) and feed at higher trophic levels (more enriched ^{15}N). These patterns in stable isotopes reflect position within a food web, but there was confounding spatial variation in isotopic signatures across sites. Therefore, we included site as an additive blocking factor in an ANOVA to test for differences among the focal species. Thus, stable isotope values were compared between taxa within sites not across sites.

Results

The four sites investigated in this study captured a range of Hg concentrations in sediments from 0.008 to 1.135 μg THg g^{-1} DW (Table 1). As expected, the more industrialized Great Bay, NH sites had higher sediment concentrations of total Hg and %TOC. Although grain size was not measured, there was variation across sites, with the WELLS site (the most pristine site) having the greatest contribution of sand vs silt. The WELLS site also had the lowest sediment Hg concentrations by more than 2 orders of magnitude and the lowest %TOC. All sites had excess AVS relative to total SEM, but the WELLS site had the least negative SEM-AVS levels (−0.77, all others <−10.0) suggesting it had the smallest amount of sulfide available to bind free metal ions. DOC concentrations in the water column were similar across sites, but chlorophyll concentrations differed between sites, being the highest at MDI followed by ADAMS, PHGB, and WELLS (Table 1; $p = < 0.0001$).

There was a significant positive relationship between Hg in sediments and %TOC across our sites (Figure S1, Supporting Information, $P = 0.003$). Consistent with higher Hg in sediments at sites with high %TOC, Hg concentrations in the four focal taxa were also positively related to %TOC (Table 2, $P = 0.05$). However, BSCF's calculated for the four focal taxa across the four sites were negatively related to %TOC (Table 2; $P < 0.001$, Figure 1a). Calculated BSCF's were also positively related to SEM-AVS (Table 2, $P < 0.001$, Figure 1b), indicating that WELLS, the most pristine site with the least negative SEM-AVS, had the highest BSCF. The negative AVS-SEM values across all the sites would suggest that inorganic Hg is not bioavailable at any of the sites, but the bioaccumulation data indicate otherwise.

Both total Hg and MeHg concentrations in organisms collected in 2004 tended to be higher at sites where sediment total Hg concentrations were higher (Table 2, THg, $P = 0.04$; MeHg, $P = 0.06$). However, sediment Hg concentrations alone were a poor predictor of concentrations in organisms (partial $r^2 < 0.3$) and the 2−4-fold range in organism Hg and MeHg concentrations for each taxa across sites did not reflect the

TABLE 2. Summary of Statistical Analyses for Relationships between Hg and MeHg in Biota, BSCF's, %TOC, Sediment Concentrations, and Sites

analysis	response	term	degrees of freedom	sum of squares	ANOVA F statistic	*p*-value	r^2 (%)
ANCOVA	tissue $\log_{10}$THg	species	3	0.72	5.32	0.02	66
		sediment $\log_{10}$ THg	1	0.24	5.23	0.04	
		error	11	0.5			
	tissue $\log_{10}$MeHg	species	3	0.63	4.25	0.03	61
		sediment $\log_{10}$ THg	1	0.21	4.27	0.06	
		error	11	0.54			
ANCOVA	tissue $\log_{10}$THg	species	3	0.72	5.23	0.02	65
		sediment %TOC	1	0.23	4.96	0.05	
		error	11	0.5			
	tissue $\log_{10}$MeHg	species	3	0.63	4.25	0.03	61
		sediment %TOC	1	0.21	4.29	0.06	
		error	11	0.54			
ANCOVA	$\log_{10}$BSCF	species	3	0.72	5.23	0.02	94
		sediment %TOC	1	7.81	172.78	<0.0001	
		error	11	0.5			
	$\log_{10}$BSCF	species	3	0.72	1.69	0.22	83
		AVS-SEM	1	6.75	47.5	<0.0001	
		error	11	1.56			
ANOVA	tissue $\log_{10}$THg	site	3	1.17	18.1	<0.0001	86
		species	3	2.21	34.14	<0.0001	
		site*species	9	1.04	5.34	0.0002	
		error	32	0.69			
	tissue $\log_{10}$MeHg	site	3	0.73	10.94	<0.0001	84
		species	3	1.7	25.44	<0.0001	
		site*species	9	1.38	6.86	<0.0001	
		error	32	0.71			
	tissue %MeHg	site	3	0.06	5.82	0.0027	95
		species	3	1.78	160.48	<0.0001	
		site*species	9	0.6	18.1	<0.0001	
		error	32	0.12			
ANOVA	tissue δ^{13}C	site	3	55	18.38	<0.0001	62
		species	3	12.99	4.34	0.0095	
		error	41	40.89			
	tissue δ^{15}N	site	3	30.51	9.13	<0.0001	70
		species	3	74.3	22.24	<0.0001	
		error	41	45.66			

more than 100-fold range in sediment Hg concentrations (Figure 2a−c). Furthermore, PHGB sediments were by far the most contaminated, but organisms at PHGB did not consistently have the highest total Hg or MeHg concentrations.

Hg concentrations in 2004 biota varied significantly across both sites and species (Table 2, Figure 2; site, $P < 0.0001$; species, $P < 0.0001$). However, there was a significant interaction (Table 2, $P = 0.0002$); species with the highest Hg concentrations were not the same across sites. MeHg concentrations also varied significantly across both sites and species (Table 2; site, $P < 0.0001$; species, $P < 0.0001$), again with a significant interaction (Table 2, $P < 0.0001$). Despite the interaction, *Fundulus* and *Mytilus* clearly tend to have higher MeHg concentrations than *Carcinus* and *Littorina* (Figure 3). The %MeHg varied significantly across species (Table 2, $P < 0.0001$) with a relatively small but statistically significant difference across sites (Table 2, $P = 0.003$) and an interaction (Table 2, $P < 0.0001$). Despite the interaction, predatory species, *Fundulus* and *Carcinus*, clearly tend to have higher %MeHg than *Littorina* and *Mytilus* (Figure 4).

Differences in food source and trophic levels between the four focal taxa across sites were related to MeHg concentrations and %MeHg. δ^{13}C signatures differed significantly across species (Table 2; δ^{13}C, $P < 0.0001$; Figure 3a) and were more depleted for the nominal pelagic feeding species (*Mytilus* and *Fundulus*), confirming that the *Mytilus* and *Fundulus* species utilize more pelagic food sources than the benthic-feeding *Carcinus* and *Littorina*. As indicated above, these pelagic-feeding species also tended to have elevated MeHg concentrations. δ^{15}N values differed significantly across species (Table 2; δ^{15}N, $P < 0.0001$; Figure 4a) and were higher in the predator/omnivore species (*Carcinus* and *Fundulus*), confirming that *Carcinus* and *Fundulus* feed at higher trophic position than *Littorina* and *Mytilus*. Although MeHg concentration was not elevated in the predators/omnivores, as indicated above, the %MeHg was elevated, indicating that MeHg biomagnifies in these intertidal food webs.

Discussion

Hg deposition in eastern North America is elevated (*1*) and Hg levels in fish from New England coastal basins are among the highest in the country (*31*−*33*). In general, estuaries with major anthropogenic inputs receive higher concentrations of organic and inorganic contaminants as well as nutrients and organic matter, which influence the redox status at the sediment−water interface and control metal flux (*34*). Both the supply of organic matter and the supply of Hg to the sediments influence Hg bioavailability to methylating bacteria and bioaccumulation by benthic and pelagic organisms (*10, 35, 36*).

Biogeochemical Factors. Studies of Hg biogeochemistry and bioaccumulation in estuarine systems (*5, 9, 10, 37*−*39*) show methylation increasing in sediments with increasing inorganic Hg but decreasing methylation with high levels of carbon and sulfides. However, the presence of organic rich carbon pockets or bulk sulfides, indicating the presence of organic carbon, can also provide a substrate for enhanced MeHg production (*40, 41*). In this study, total Hg and %TOC in sediments were positively related suggesting, as others have found (*33, 38, 40*−*42*), that a significant portion of the

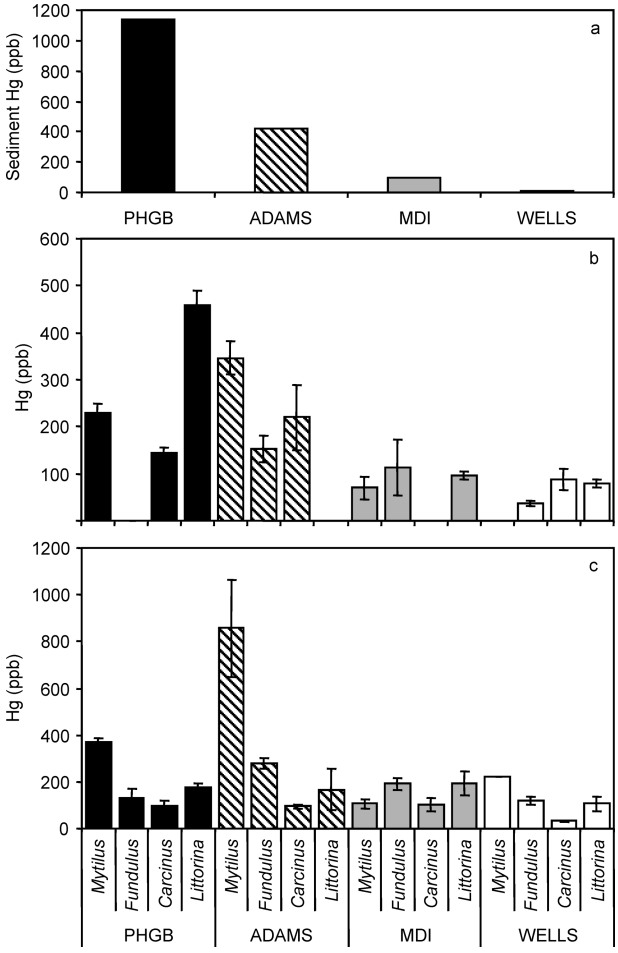

FIGURE 2. Concentrations (μg/g DW) of THg across sites (ADAMS, PHGB, WELLS, MDI) in (a) sediments (collected in 2006) and four focal species collected in (b) 2003 (not all four species collected at all sites) and (c) 2004 (percent moisture for each taxa: *Carcinus*, 76 $\pm$ 9%; *Fundulus*, 71 $\pm$ 3%; *Littorina*, 78 $\pm$ 2%; and *Mytilus*, 84 $\pm$ 5%). Note the difference in vertical scale for panel b. Bars = SE.

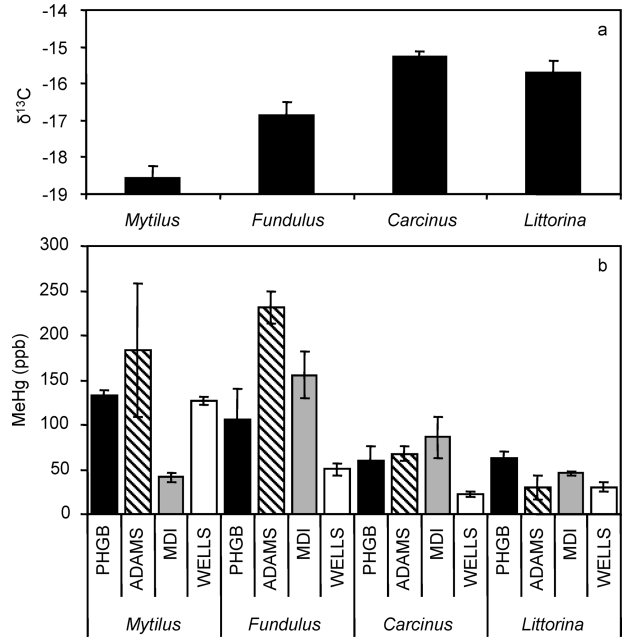

FIGURE 3. (a) δ^{13}C signatures and (b) MeHg concentrations (μg/g DW) in four focal taxa collected in 2004 across four GOM sites (ADAMS, PHGB, WELLS, MDI). Bars = SE.

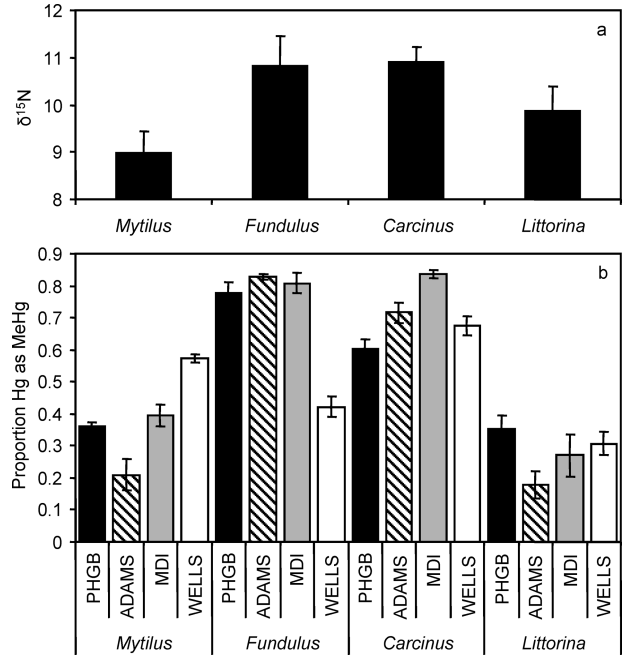

FIGURE 4. (a) δ^{15}N signatures and (b) percent of THg as MeHg in four focal taxa collected in 2004 across four GOM sites (ADAMS, PHGB, WELLS, MDI). Bars = SE.

variance in total Hg in sediments is due to retention by %TOC. In other studies, this relationship is also related to grain size, where finer sediments are associated with higher %TOC concentrations (*41, 43*).

%TOC and AVS are also biogeochemically linked to one another, since TOC in sediments produces the anaerobic conditions under which AVS are created. The extent to which divalent metals bind to AVS is determined by the solubility product of their respective sulfides. Among the heavy metals, HgS is the least soluble and Hg is therefore bound most tightly (i.e., it is the least soluble of metal sulfides). Consequently, the presence of excess AVS at all of our sites implies that all inorganic Hg should be bound (and not bioavailable).

Elevated organic carbon in sediments reduces bioaccumulation of MeHg by benthic fauna (*44*). In a range of sites in Chesapeake Bay, where sediment concentrations of Hg vary by 25 times, concentrations in benthic invertebrates vary by only 2−4 times (*42, 45, 46*). Data in the present study show similar trends, where total concentrations of Hg in sediments vary by more than 2 orders of magnitude across sites but the concentrations in biota vary by only 2−4 times. Thus, despite the higher supply of Hg in sediments and the slightly higher bioaccumulation in more contaminated sites, the bioavailability of Hg and MeHg to benthic fauna appears to be strongly influenced by organic carbon.

The effect of organic carbon on Hg bioaccumulation becomes evident when examining the relationship between BSCF, a measure of bioaccumulation relative to in situ sediment Hg concentrations, and %TOC or SEM-AVS. As in previous metal studies, there is a negative relationship between BSCF and %TOC and a positive relationship with SEM-AVS (*42, 45, 46*). The significant positive relationship between BSCF and SEM-AVS indicates that, when normalized to sediment concentration, the greater binding capacity in the sediments with more excess AVS lowers bioaccumulation in benthic fauna. However, all of the sites in this study had excess AVS, which did not prevent Hg bioaccumulation in benthic fauna. In fact, the higher biotic THg and MeHg concentrations in sites with the most excess AVS suggests that the SEM-AVS is not a good predictor of bioavailability.

Thus, TOC may play a greater role in controlling Hg bioavailability in these sediments.

Ecological Factors. MeHg transfer from sites of methylation in sediments to higher trophic levels involves both benthic and pelagic pathways. Studies of food web structure in estuarine systems using stable isotope reveal that primary and secondary consumers utilize a mixture of detrital and algal based food sources (*13, 47*). Numerous studies have shown that more pelagic consumers feeding on phytoplankton are more depleted in ^{13}C than benthic consumers feeding on benthic microalgae and saltmarsh vegetation (*47*−*49*). In the food webs studied here, our four focal species represent different functional feeding groups and trophic levels. $\delta^{13}C$ signatures confirm that *Mytilus* is the most pelagic in its feeding on phytoplankton and particulate organic matter. *Fundulus*, an omnivorous resident species, is slightly less depleted in ^{13}C, reflecting its pelagic−benthic diet of zooplankton, benthic microalgae, and *Spartina* detritus (*27, 29, 47, 50, 51*). The two benthic epifauna, *Littorina* and *Carcinus*, have more enriched ^{13}C signatures reflective of their diets on benthic algae and benthic invertebrates, respectively.

In the intertidal food webs studied here, MeHg concentrations are higher in more pelagic feeding species (more depleted $\delta^{13}C$ signature), suggesting that the more important pathway from MeHg production in sediments to marine fish may be chemical flux into the water column and absorption by and ingestion of particulates rather than direct ingestion of sediments. The more pelagic taxa, *Mytilus* and *Fundulus*, represent different trophic levels, but both derive a major portion of their diet from particulates or organisms feeding on particulates and both contain higher concentrations of MeHg. Total Hg concentrations for these two taxa are within the ranges found in other studies (*Fundulus*, 250 ± 160 ppb DW (*52*); mussels, 250−1200 ppb DW (*53*)). The two benthic taxa (*Littorina*, *Carcinus*) also representing different trophic levels have lower MeHg concentrations, potentially due to their sediment-based diets. The bioconcentration of MeHg by particulates that can range up to 6 orders of magnitude may drive the higher exposures to MeHg in pelagic fauna than benthic fauna. The importance of the pelagic pathway in transferring MeHg also suggests that methylation in the water column could have an important role in supplying MeHg to pelagic food webs and marine fish species that humans consume.

In this study of the lower trophic levels of benthic and pelagic food webs, the %MeHg increases with trophic level while MeHg concentrations do not. The biomagnification of MeHg in most aquatic food webs results in increasing concentration or %MeHg with trophic level (*1, 54*). However, these generally involve food webs extending from lower trophic levels to apex predators (*1, 5, 17*). For most piscivorous fish species, total Hg is comprised almost entirely of MeHg (>95%), making these species particularly important vectors of human exposure. However, lower trophic level organisms where MeHg enters marine food webs vary greatly in their %MeHg, ranging from 5 to 80% (*1, 35*). Similar to these studies, we find that %MeHg ranges from 18 to 35% in *Littorina*, 20 to 57% in *Mytilus*, 60 to 84% in *Carcinus*, and 42 to 82% in *Fundulus*.

These estuarine food webs are potential sources of MeHg biotransfer from sediments to coastal food webs by virtue of their proximity to MeHg production and flux from the sediments and their ecological connection to offshore fisheries via a "trophic nekton relay" (*13, 14, 47*). This ecological transport mechanism of both energy and contaminants may be an important source of MeHg to offshore fish that reside in environments far from MeHg sources (*3, 5*). Thus, the biogeochemical and ecological processes mediating MeHg bioaccumulation in lower trophic levels in estuarine sediments can have far reaching effects on the ultimate fate of MeHg in marine food webs. Although more contaminated sites have much greater supply of Hg for methylation and uptake, Hg bioavailability to benthic fauna is substantially reduced by sediment organic matter. In addition, across a range of estuarine sites, benthic feeding in or on sediments may provide a less efficient pathway for MeHg biotransfer than pelagic feeding on suspended particulate organic matter.

Acknowledgments

We gratefully acknowledge the assistance of Chip Glaholt, Amy Wallace, Heather Hudenko, Richard Mackenzie, Ata Bilgili, Jim Dochtermann, and Jeremy Miller in conducting fieldwork. We thank Lorenzo Perna and Angela Lacroix-Fralish for their analytical assistance and David Shay at the UNH Jackson Estuarine Laboratory and the Wells National Estuarine Research Reserve for making facilities available for our use. The paper also was greatly improved by the comments of four anonymous reviewers. This research was supported by NIH Grant Number P42 ESO7373 (to C.L.F. and C.Y.C.) from the National Institute of Environmental Health Sciences, SERDP Project ER-1503 funds, UNH Sea Grant development funds, Dartmouth CEHS pilot funds, and a New Investigator Award from the Mount Desert Biological Laboratory.

Supporting Information Available

Methods descriptions, Figure S1, and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Driscoll, C. T.; Han, Y. J.; Chen, C. Y.; Evers, D. C.; Lambert, K. F.; Holsen, T. M.; Kamman, N. C.; Munson, R. K. Mercury contamination in forest and freshwater ecosystems in the Northeastern United States. *BioScience* **2007**, *57* (1), 17–28.

(2) UNEP. *Global Mercury Assessment*; United Nations Environment Programme: New York, 2003.

(3) Sunderland, E. M. Mercury exposure from domestic and imported estuarine and marine fish in the U.S. seafood market. *Environ. Health Persp.* **2007**, *115* (2), 235–242.

(4) USEPA. *Origin of the 1 meal/week noncommercial fish consumption rate in national advisory for mercury*; Office of Water, National Fish and Wildlife Contamination Program: Washington, DC, 2004.

(5) Hammerschmidt, C. R.; Fitzgerald, W. F. Bioaccumulation and trophic transfer of methylmercury in Long Island Sound. *Arch. Environ. Contam. Toxicol.* **2006**, *51*, 416–424.

(6) Fitzgerald, W. F.; Lamborg, C. H.; Hammerschmidt, C. R. Marine biogeochemical cycling of mercury. *Chem. Rev.* **2007**, *107* (2), 641–662.

(7) Long, E. R. Spatial extent of sediment toxicity in U.S. estuaries and marine bays. *Environ. Monit. Assess.* **2000**, *64*, 391–407.

(8) Marvin-DiPasquale, M. C.; Agee, J. L.; Bouse, R. M.; Jaffe, B. E. Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. *Environ. Geol.* **2003**, *43*, 260–267.

(9) Mason, R. P.; Lawrence, A. L. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* **1999**, *18*, 2438–2447.

(10) Sunderland, E. M.; Gobas, F. A. P. C.; Branfireun, B. A.; Heyes, A. Environmental controls on the speciation and distribution of mercury in coastal sediment. *Mar. Chem.* **2006**, *102*, 111–123.

(11) Jury, S. H.; Field, J. D.; Stone, S. L.; Nelson, D. M.; Monaco, M. E. *Distribution and Abundance of Fishes and Invertebrates in North Atlantic Estuaries*; U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service: Silver Spring, MD, 1994; p 221.

(12) Nelson, D. M.; Monaco, M. E. *National Overview and Evolution of NOAA's Estuarine Living Marine Resources (ELMR) Program*; U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service, National Centers for Coastal Ocean Science, Center for Coastal Monitoring and Assessment: Silver Spring, MD, 2000; p 60.

(13) Deegan, L. A.; Hughes, J. E.; Rountree, R. A. Salt marsh ecosystem support of marine transient species. In *Concepts and Controversies in Tidal Marsh Ecology*; Weinstein, M. P., Kreeger, D. A., Kreeger, D. A., Eds.; Kluwer Academic Publishers: Boston, 2000; pp 333−365.

(14) Kneib, R. T. Salt marsh ecoscapes and production transfers by estuarine nekton in the southeastern United States. In *Concepts and Contoversies in Tidal Marsh Ecology*; Weinstein, M. P., Kreeger, D. A., Eds.; Kluwer Academic Publishers: Boston, 2000; pp 267−291.
(15) Mason, R. P.; Lawson, N. M.; Lawrence, A. L.; Leaner, J. J.; Lee, J. G.; Sheu, G. R. Mercury in the Chesapeake Bay. *Mar. Chem.* **1999**, *65*, 77–96.
(16) Chen, C.; Amirbahman, A.; Fisher, N.; Harding, G.; Lamborg, C.; Nacci, D.; Taylor, D. Methylmercury in marine ecosystems: Spatial patterns and processes of production, bioaccumulation, and biomagnification. *Ecohealth*, in press.
(17) Bank, M. S.; Chesney, E.; J.P., S.; Maage, A.; Senn, D. B. Mercury bioaccumulation and trophic transfer in sympatric snapper species from the Gulf of Mexico. *Ecol. Appl.* **2007**, *17*, 2100–2110.
(18) Monperrus, M.; Tessier, E.; Point, D.; Vidimova, K.; Amouroux, D.; Guyoneaud, R.; Leynaert, A.; Grall, J.; Chauvaud, L.; Thouzeau, G.; Donard, O. F. X. The biogeochemistry of mercury at the sediment−water interface in the Thau Lagoon. 2. Evaluation of mercury methylation potential in both surface sediment and the water column. *Estuar. Coast. Shelf Sci.* **2007**, *72*, 485–496.
(19) Benoit, J. M.; Shull, D. H.; Robinson, P.; Ucran, L. R. Infaunal burrow densities and sediment monomethyl mercury distributions in Boston Harbor, Massachusetts. *Mar. Chem.* **2006**, *102*, 124–133.
(20) Power, M.; Klein, G. M.; Guiguer, K.; Kwan, M. K. H. Mercury accumulation in the fish community of a sub-Arctic lake in relation to trophic position and carbon sources. *J. Appl. Ecol.* **2002**, *39*, 819–830.
(21) Jones, S. H. *A Technical Characterization of Estuarine and Coastal New Hampshire*; New Hampshire Estuaries Project: Portsmouth, NH, 2000.
(22) Kahl, J. S.; Nelson, S. J.; Fernandez, I. H., T.; Norton, S.; Wiersma, G. B.; Jacobson, G.; Amirbahman, A.; Johnson, K.; Schauffler, M.; Rustad, L.; Tonnessen, K.; Lent, R.; Bank, M. E., J.; Eckhoff, J.; Caron, H.; Ruck, P.; Parker, J.; Campbell, J.; Manski, D.; Breen, R.; Sheehan, K.; Grygo, A. Watershed nitrogen and mercury geochemical fluxes integrate landscape factors in long-term research watersheds at Acadia National Park, Maine, USA. *Environ. Monit. Assess.* **2007**, *126*, 9–25.
(23) Chen, C. Y.; Stemberger, R. S.; Klaue, B.; Blum, J. D.; Pickhardt, P. C.; Folt, C. L. Accumulation of heavy metals in food web components across a gradient of lakes. *Limnol. Oceanogr.* **2000**, *45*, 1525–1536.
(24) *USEPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. EPA 821-R-95-034*; U.S. Environmental Protection Agency, Office of Water: Washington, DC, 1995.
(25) Bennett, W. A.; Ostarch, D. J.; Hinton, D. E. Larval striped bass condition in a drought-stricken estuary: Evaluating pelagic food-web limitation. *Ecol. Appl.* **1995**, *5*, 680–692.
(26) Chen, C. Y.; Folt, C. L. Bioaccumulation and diminution of arsenic and lead in a freshwater food web. *Environ. Sci. Technol.* **2000**, *34*, 3878–3884.
(27) Peterson, B. J.; Fry, B. Stable isotopes in ecosystem studies. *Annu. Rev. Ecol. Syst.* **1987**, *18*, 293–320.
(28) Stribling, J. M.; Cornwell, J. C. Identification of important primary producers in a Chesapeake Bay tidal creek system using stable isotopes of carbon and sulfur. *Estuaries* **1997**, *20*, 77–85.
(29) Sullivan, M. J.; Moncreiff, C. A. Edaphic algae are an important component of salt-marsh food-webs—Evidence from multiple stable isotope analyses. *Mar. Ecol.- Prog. Ser.* **1990**, *62*, 149–159.
(30) Perna, L.; LaCroix-Fralish, A.; Stürup, S. Determination of inorganic mercury and methylmercury in zooplankton and fish samples by speciated isotopic dilution GC−ICP-MS after alkaline digestion. *J. Anal. At. Spectrom.* **2005**, *20*, 236–238.
(31) Brumbaugh, W. G.; Krabbenhoft, D. P.; Helsel, D. R.; Weiner, J. G.; Echols, K. R. *A National Pilot Study of Mercury Contamination in Aquatic Ecosystems along Multiple gradients: Bioaccumulation in Fish*; U.S. Geological Survey Water Resources Investigations; USGS: Reston, VA, 2001.
(32) Robinson, K. W.; Flanagan, S. M.; Ayotte, J. D.; Campo, K. W.; Chalmers, A.; Coles, J. F.; Cuffney, T. F. *Water quality in Ne England coastal basins, Maine, New Hampshire, Massachusetts, and Rhode Island, 1999−2001*; U.S. Department of the Interior and U. S. Geological Survey: Washington, DC, 2004.
(33) USEPA. *Environmental Monitoring and Assessment Program, National Coastal Assessment*; 2007; http://www.epa.gov/emap/index.html.
(34) Covelli, S.; Faganeli, J.; Horvat, M.; Brambati, A. Porewater distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste (Northern Adriatic Sea). *Est. Coast. Shelf Sci.* **1999**, *48*, 415–428.
(35) Benoit, J. M.; Gilmour, C. C.; Heyes, A.; Mason, R. P.; Miller, C. L. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In *Biogeochemistry of Environmentally Important Trace Elements*; Cai, Y., Braids, O. C., Eds.; American Chemical Society: Washington, DC, 2003; Vol. 835, pp 262−297.
(36) Lambertsson, L.; Nilsson, M. Organic material: The primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. *Environ. Sci. Technol.* **2006**, *40*, 1822–1829.
(37) Baeyens, W.; Meuleman, C.; Muhaya, B.; Leermakers, M. Behaviour and speciation of mercury in the Scheldt estuary (water, sediments and benthic organisms). *Hydrobiologia* **1998**, *366*, 63–79.
(38) Hammerschmidt, C. R.; Fitzgerald, W. F. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* **2004**, *38*, 1487–1495.
(39) Heyes, A.; Miller, C.; Mason, R. P. Mercury and methylmercury in Hudson River sediment: Impact of tidal resuspension on partitioning and methylation. *Mar. Chem.* **2004**, *90*, 75–89.
(40) Lawrence, A. L.; Mason, R. P. Factors controlling the bioaccumulation of mercury and methylmercury by the estuarine amphipod *Leptocheirus plumulosus*. *Environ. Pollut.* **2001**, *111*, 217–231.
(41) Sunderland, E. M.; Gobas, F. A. P. C.; Heyes, A.; Branfireun, B. A.; Bayer, A. K.; Cranston, R. E.; Parsons, M. B. Speciation and bioavailability of mercury in well-mixed estuarine sediments. *Mar. Chem.* **2004**, *90*, 91–105.
(42) Sunderland, E. M.; Gobas, F. A. P. C.; Branfireun, B. A.; Heyes, A. Environmental controls on the speciation and distribution of mercury in coastal sediments. *Mar. Chem.* **2006**, *102*, 111–123.
(43) Loring, D.; Asmund, G. Geochemical factors controlling accumulation of major and trace elements in Greenland coastal and fjord sediments. *Environ. Geol.* **1996**, *28*, 2–11.
(44) Muhaya, B.; Leermakers, M.; Baeyens, W. Total mercury and methylmercury in sediments and in the polychaete *Nereis diversicolor* at Groot Buitenschoor (Scheldt estuary, Belgium). *Water Air Soil Pollut.* **1997**, *94*, 109–123.
(45) Wright, D. A.; Mason, R. P. Biological and chemical influences on trace metal toxicity and bioaccumulation in the marine and estuarine environment. *Int. J. Environ. Pollut.* **2000**, *13*, 226–248.
(46) Mason, R. P. Chapter 6: The bioaccumulation of mercury, methylmercury, and other toxic elements into pelagic and benthic organisms. In *Coastal and Estuarine Risk Assessment*; Newman, M. C., Roberts, M. H. J., Hale, R. C., Eds.; Lewis Publishers: Boca Raton, FL, 2002; pp 127−149.
(47) Deegan, L. A.; Garritt, R. H. Evidence for spatial variability in estuarine food webs. *Mar. Ecol.-Prog. Ser.* **1997**, *147*, 31–47.
(48) Michener, R. H.; Kaufman, L. Chapter 9: Stable isotope ratios as tracers in marine food webs: An update. In *Stable Isotopes in Ecology and Environmental Science*; Lajtha, K., Michener, R. H., Eds.; Blackwell Scientific: Boston, 2006; pp 238−282.
(49) Winemiller, K. O.; Senol, Akin.; Zeug, S. C. Production sources and food web structure of a temperate tidal estuary: Integration of dietary and stable isotope data. *Mar. Ecol.-Prog. Ser.* **2007**, *343*, 63–76.
(50) Hughes, J. E.; Deegan, L. A.; Peterson, B. J.; Holmes, R. M.; Fry, B. Nitrogen flow through the food web in the oligohaline zone of a New England estuary. *Ecology* **2000**, *81*, 433–452.
(51) Kneib, R. T. Bioenergetic and landscape considerations for scaling expectations of nekton production from intertidal marshes. *Mar. Ecol.-Prog. Ser.* **2003**, *264*, 279–296.
(52) Weis, P.; Ashley, J. T. F. Contaminants in fish of the Hackensack Meadowlands, New Jersey: Seasonal relationships as related to health risks. *Arch. Environ. Con. Tox.* **2007**, *52*, 80–89.
(53) Chase, M. E.; Jones, S. H.; Hennigar, P.; Sowles, J.; Harding, G. C. H.; Freeman, K.; Wells, P. G.; Krahforst, C.; Cooms, K.; Crawford, R.; Pederson, J.; Taylor, D. Gulfwatch: Monitoring spatial and temporal patterns of trace metal and organic contaminants in the Gulf of Maine (1991−1997) with the blue mussel, *Mytilus edulis* L. *Mar. Pollut. Bull.* **2001**, *42*, 491–505.
(54) Mason, R. P.; Laporte, J. M.; Andres, S. Factors controlling the bioaccumulation of mercury, methylmercury, arsenic, selenium, and cadmium by freshwater invertebrates and fish. *Arch. Environ. Contam. Toxicol.* **2000**, *38*, 283–297.

ES8017122