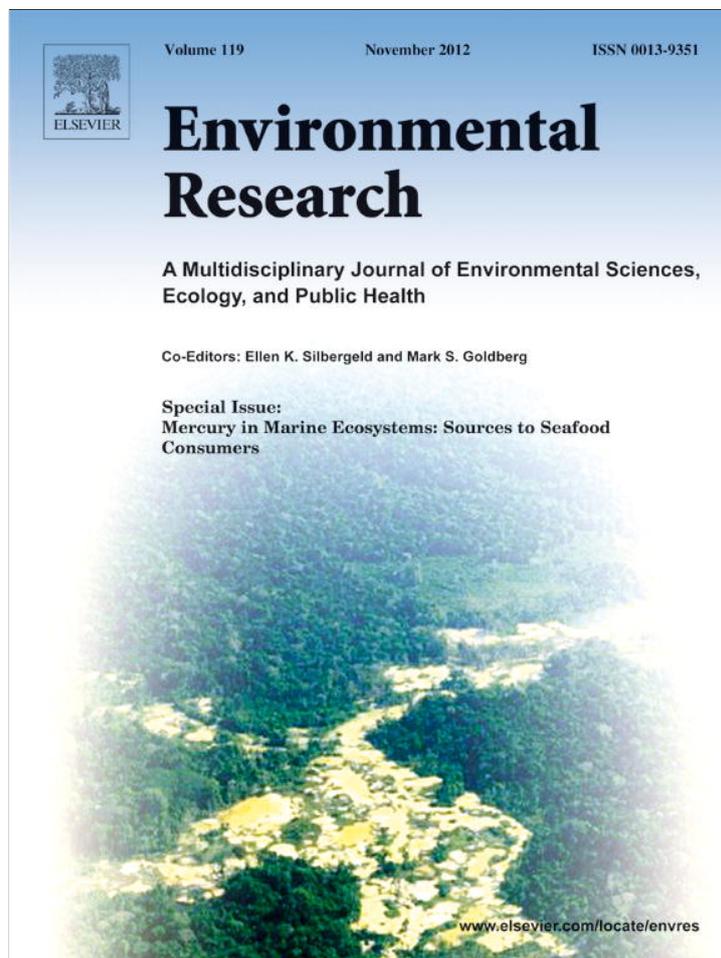


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Nutrient supply and mercury dynamics in marine ecosystems: A conceptual model [☆]

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ABSTRACT

There is increasing interest and concern over the impacts of mercury (Hg) inputs to marine ecosystems. One of the challenges in assessing these effects is that the cycling and trophic transfer of Hg are strongly linked to other contaminants and disturbances. In addition to Hg, a major problem facing coastal waters is the impacts of elevated nutrient, particularly nitrogen (N), inputs. Increases in nutrient loading alter coastal ecosystems in ways that should change the transport, transformations and fate of Hg, including increases in fixation of organic carbon and deposition to sediments, decreases in the redox status of sediments and changes in fish habitat. In this paper we present a conceptual model which suggests that increases in loading of reactive N to marine ecosystems might alter Hg dynamics, decreasing bioavailability and trophic transfer. This conceptual model is most applicable to coastal waters, but may also be relevant to the pelagic ocean. We present information from case studies that both support and challenge this conceptual model, including marine observations across a nutrient gradient; results of a nutrient-trophic transfer Hg model for pelagic and coastal ecosystems; observations of Hg species, and nutrients from coastal sediments in the northeastern U.S.; and an analysis of fish Hg concentrations in estuaries under different nutrient loadings. These case studies suggest that changes in nutrient loading can impact Hg dynamics in coastal and open ocean ecosystems. Unfortunately none of the case studies is comprehensive; each only addresses a portion of the conceptual model and has limitations. Nevertheless, our conceptual model has important management implications. Many estuaries near developed areas are impaired due to elevated nutrient inputs. Widespread efforts are underway to control N loading and restore coastal ecosystem function. An unintended consequence of nutrient control measures could be to exacerbate problems associated with Hg contamination. Additional focused research and monitoring are needed to critically examine the link between nutrient supply and Hg contamination of marine waters.

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1. Introduction

1.1. Background on nutrients (nitrogen), organic carbon and mercury in estuaries

Increases in mercury (Hg) contamination of marine ecosystems, primarily from anthropogenic inputs, have been largely manifested through elevated concentrations of the more bioaccumulative form methylmercury (MeHg) in food webs. Thousands of estuaries and freshwaters in all states and two territories of the United States are listed by the Environmental Protection Agency as impaired due to high concentrations of Hg in fish (Table 1). However, most studies do not show a linear relationship between

Table 1

Summary of waterbody impairments and Total Maximum Daily Loads (TMDLs) for mercury and nutrients in U.S. waters (total and coastal) based on state 303(d) lists submitted to and approved by EPA as required by the Clean Water Act.
Source: U.S. EPA (Environmental Protection Agency), 2011a, 2011b.

Resource	Contaminant	303(d) Waterbody impairments ^c	Approved TMDLs ^d
Total US waters	Mercury	5,004	6946
Total US waters	Nutrients ^b	16,075	8102
US coastal waters ^a	Mercury	196	51
US coastal waters ^a	Nutrients ^b	2,818	199
US coastal waters ^a	Mercury and nutrients ^b	86	10

^a Note information reflects “assessed waters.” Only a small percentage of coastal waters have been assessed. “U.S. coastal waters” includes water classified by as coastal waters, bays or estuaries.

^b For this analysis, nutrient-related impairments and TMDLs include the following impairment categories: algal growth, ammonia, noxious aquatic plants, nutrients, and organic enrichment/oxygen depletion.

^c This column reflects the number of waterbody impairments and not the number of unique waters affected.

^d The number of TMDLs for coastal waters reflect only those for which the state provided information on waterbody type in the 303(d) listing.

Hg inputs and MeHg concentrations in higher trophic level organisms due to many ecosystem factors that can modify causality. We hypothesize that one such factor, the nutrient status, alters Hg dynamics in marine ecosystems, and this is the focus of this paper.

Elevated inputs of nutrients have resulted in water quality problems for estuaries that are adjacent to or receive discharge from developed lands. Coastal ecosystems are naturally productive in plant and animal life. However, because the productivity of temperate coastal ecosystems is generally limited by availability of reactive nitrogen (N), excess nutrient loadings can lead to eutrophication (D’Elia et al., 1992; Fisher and Oppenheimer, 1991; Nixon, 1986; Ryther and Dunstan, 1971), which can affect the biogeochemical cycling of many elements, including Hg. We therefore focus our analysis on the impact of N inputs on Hg and MeHg dynamics in marine ecosystems but our conceptual model should also be relevant to phosphorus and other nutrient-limited ecosystems.

The majority of estuaries that have been evaluated in the U.S. show signs of eutrophication—65% of the assessed ecosystems, representing 78% of assessed estuarine area, have been classified as moderately to severely degraded by nutrient over-enrichment (Bricker et al., 2007). In addition to the direct effects of nutrients on ecosystem eutrophication, excess N can potentially have an impact on the cycling and fate of many other contaminants, such as Hg, due to shifts in organic matter production and subsequent impacts on redox status and habitat. Like N, Hg is a global pollutant and can have substantial impacts on coastal ecosystems (Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009; Kim et al., 2008).

Increased loadings of nutrients to estuaries lead to more frequent harmful algal blooms, hypoxic and anoxic bottom waters, loss of sea grasses, reduced fish stocks, and changes in trophic dynamics and biogeochemical cycles (Boynton et al., 1995; Hallegraeff, 1993; Paerl, 1988, 1995, 1997; Valiela et al., 1990; Valiela and Costa, 1988; Cloern, 2001). The over-enrichment of nutrients in estuaries promotes excessive growth of planktonic algae or cyanobacteria mats, which can shade-out sea grass and other submerged aquatic vegetation that provide critical habitat for fish and other marine organisms. Thus,

eutrophication often leads to greater pelagic versus benthic production in estuaries (Paerl et al., 2001; Cloern, 2001). Furthermore, when the algae die and decompose, oxygen in bottom water is consumed. Low-oxygen conditions, or hypoxia, impair habitat of macrofauna, influence the cycling of elements at the sediment-water interface, and can alter the dynamics of microbial processes, such as Hg methylation and MeHg demethylation. The degree of eutrophication an estuary can tolerate without adverse effects depends on the amount of reactive N it receives as well as its physical characteristics, including size, depth, volume of freshwater runoff, and rate of tidal flushing (water residence time) (Cloern, 2001).

The widespread occurrence of coastal eutrophication in the U.S. has led to regulation of nutrient loads under the U.S. Clean Water Act (CWA). As a first step in managing source loads, total maximum daily loads (TMDLs) for N (or nutrients) have been developed for a number of systems (Table 1). A TMDL is the estimated total amount (or load) of a pollutant that a water body can receive and maintain designated uses such as fishable/swimmable water quality. When concentrations of contaminants and/or nutrients in water bodies exceed thresholds for acceptable levels specified in the CWA, they are listed as impaired, which triggers a requirement for a TMDL to be developed. TMDL also refers to a regulatory process that States, Territories, and authorized Tribes in the U.S. use to determine allowable pollutant concentrations in water bodies and mandate source controls to bring pollutant concentrations below this level (Lambert et al., in press; Shipp and Cordy, 2002; Younos, 2005).

Compared to N, less is known about the dynamics and effects of Hg in coastal and pelagic marine ecosystems. Even less is known about the relationship between changes in N loading and MeHg bioaccumulation in ocean fisheries. In the freshwater literature, however, there are numerous field and experimental studies that show decreases of Hg concentrations in the aquatic food web in response to increasing nutrient inputs. Nutrient enrichment to freshwaters causing algal blooms decreases Hg concentrations in biota through a process referred to as biodilution (Pickhardt et al., 2002). Concentrations of Hg in zooplankton decrease with increasing zooplankton density, resulting in lower fish Hg concentrations (Chen and Folt, 2005). Also, under conditions of high productivity and prey availability, concentrations of Hg in zooplankton and fish may decrease due to growth dilution (Essington and Houser, 2003; Karimi et al., 2007). Field studies have shown that Hg concentrations in freshwater fish decrease under conditions of high nutrient loading and in watersheds with disturbed land cover (i.e., agricultural, urban lands; Chen et al., 2005; Kamman et al., 2004). Note that while freshwater ecosystems are very different from coastal ecosystems, which have more limited and nuanced responses to nutrient loading, exhibit salinity stratification and variable tidal fluxes and ocean inflows, much can be learned from the freshwater literature in the investigation of the effects of nutrient inputs on Hg dynamics in marine ecosystems (Cloern, 2001). For example, in South San Francisco Bay, a phytoplankton bloom caused a three-fold decrease in phytoplankton MeHg concentrations (Luengen and Flegal, 2009) similar to the biodilution phenomenon observed in freshwaters.

In this paper we advance the hypothesis that elevated inputs of limiting nutrients (e.g., N) to coastal waters and the resultant increase in organic carbon (OC) levels in the water column and sediments, decrease Hg availability and ultimately decrease trophic transfer and fish Hg concentrations. We present a conceptual model of how changes in N loading might alter Hg dynamics, net methylation, and fish MeHg concentrations. We follow this with a series of case studies providing information to evaluate this hypothesis and conceptual model. Note that while

our analysis is primarily focused on coastal ecosystems which experience the largest impacts of increases in nutrient (Cloern, 2001) and Hg loadings, we also make use of observations from the open ocean (Section 2.1) and show that comparable factors are important in the pelagic realm (Section 2.2.1).

1.2. Conceptual model of coastal ecosystem Hg response to increases in N loading

Nitrogen enrichment generally increases productivity in coastal waters (Howarth and Marino, 2006), although a “tipping” point can be reached, past which net ecosystem metabolism decreases with increasing N loading. Further, elevated N enrichment is related to the development of hypoxia and anoxia, particularly in coastal ecosystems with a physical structure that supports stratification (Cloern, 2001; Breitburg et al., 2009). Increases in primary and secondary production will increase ecosystem biomass and decrease concentrations of MeHg in invertebrates and fish through biodilution (Chen and Folt, 2005; Kim et al., 2008), assuming Hg inputs, the extent of methylation and bioavailability remain constant (Fig. 1). As discussed further below (see Section 2.2), this hypothesis is valid only if there are not substantial shifts in plankton community composition (e.g.,

cell size, growth rate) in concert with changes in nutrient loadings. Eutrophication also typically results in loss of ecosystem biodiversity (Carpenter et al., 1998). Changes in phytoplankton species composition and growth rate could impact the concentration of MeHg in primary producers and, as a result, in organisms at the higher trophic levels (e.g., Kim et al., 2008).

Increases in net ecosystem production also increases deposition of OC to sediments and facilitates the removal of ionic Hg and MeHg from the water column to the sediments (Fig. 1). Sediment organic matter has a complex role in affecting Hg and MeHg biogeochemistry, net MeHg formation and its bioavailability to the food web (Fig. 1). First, the partitioning of Hg between pore water and the solid phase (K_d) is positively related to sediment organic content in most ecosystems. On average, partition coefficients for Hg increase by almost 3 orders of magnitude in coastal sediments as the organic matter content increases from 2 to 15% (Hollweg et al., 2010). However, as high OC sediments also typically have high inorganic sulfide content (acid volatile sulfide plus chromium reducible sulfur), this relationship may also impact binding to inorganic solid sulfide phases in these environments (Hollweg et al., 2010). Reduced-sulfur functional groups, on particulate and dissolved organic matter, strongly bind ionic Hg and decrease its bioavailability for formation of MeHg by

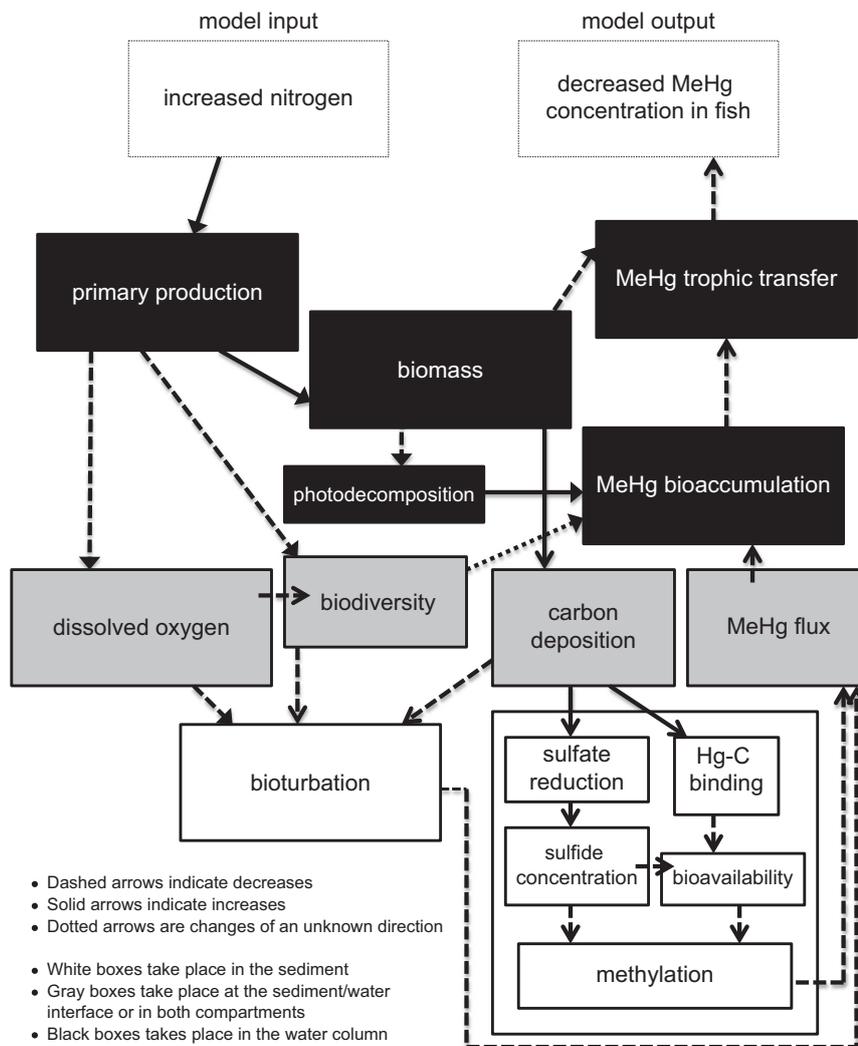


Fig. 1. Schematic diagram illustrating the response of coastal processes relevant to transport, net methylation and trophic transfer of Hg to increases in N loading. The diagram depicts the influence of a change in a process. A dashed arrow indicates a decrease. A solid arrow indicates an increase. A dotted arrow depicts an unknown direction of change. The shading of the boxes depict where in the ecosystem the process occurs: black for water column, gray for the sediment-water interface and white for sediments.

microorganisms in sediments (Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009; Skyllberg, 2008). Dissolved organic matter plays a large but opposing role to that of sediment organic matter, helping to partition Hg in sediment pore waters but not directly increasing methylation rates. This mechanism suggests that eutrophication decreases metal bioavailability by increasing sediment OC concentrations and consequent Hg binding. The relationship between Hg concentration and %OC in sediments is linear in many (e.g., Varekamp et al., 2000; Hammerschmidt et al., 2008) but not all (e.g., Hollweg et al., 2009; Mason and Lawrence, 1999) coastal marine systems. It is probable that the role of inorganic sulfide is more important in some ecosystems as it increases the binding to the solid phase but also alters the porewaters speciation and may increase the relative bioavailability (Hollweg et al., 2010).

Second, organic matter is mineralized in anoxic coastal sediments principally by sulfate-reducing bacteria (Capone and Kiene, 1988), which are thought to be the primary group of Hg methylating microorganisms (Compeau and Bartha, 1985; Gilmour et al., 1992; Fig. 1). The highest net production of MeHg generally occurs at moderate levels of sulfate reduction (Gilmour et al., 1992). However, with increasing loading of nutrients, organic matter and associated sulfate reduction the production of sulfide increases which changes the speciation of dissolved ionic Hg (Benoit et al., 1999a) and may decrease its relative availability to methylating bacteria and the formation of MeHg (Benoit et al., 2003, 2001, 1999b; Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2008; Hollweg et al., 2009, 2010).

Greater respiration of organic matter at the sediment-water interface also reduces levels of dissolved oxygen, which decreases the abundance and activity of benthic macrofauna (Dauer et al., 1992; Diaz and Rosenberg, 1995; Montagna and Ritter, 2006; Fig. 1). Bioturbation has been shown to increase both MeHg production in coastal sediments (Benoit et al., 2009; Hammerschmidt et al., 2004) and facilitate its mobilization to overlying water (Hammerschmidt and Fitzgerald, 2008). Hence, increased loadings of N and resultant sediment organic matter are likely to decrease both MeHg production in sediments and the biologically enhanced flux of MeHg from sediments (Hammerschmidt and Fitzgerald, 2004). Conversely, higher sulfide concentrations change the speciation of aqueous MeHg from control by dissolved organic matter to complexation with inorganic sulfide ligands. Given the larger diffusion coefficient of the smaller inorganic complexes, such a shift in complexation in anoxic environments could enhance the diffusive flux of MeHg from sediments by an order of magnitude (Hollweg et al., 2010).

Past experimental and field studies indicate that bioaccumulation of MeHg in benthic and pelagic fauna decreases with increasing sediment OC (Fig. 1). Lawrence and Mason (2001) found that amphipods exposed to Hg in OC-rich sediment accumulated less Hg than those in sediments with lower organic contents. Across sites that vary in Hg and OC supply in the Northern Coastal Shelf region of the Gulf of Maine, benthic-sediment concentration factors, a measure of bioavailability of MeHg to marine organisms, decrease with total OC in sediments (Chen et al., 2009). These observations suggest that production, bioavailability, and/or assimilation of MeHg decreases with increasing organic content of sediments.

Increased primary production also will decrease penetration of light in the water column and cause a shift in primary production from benthic to pelagic autotrophs (Paerl et al., 2001). Such a shift will change the pathways whereby MeHg enters the food web (Fig. 1). The loss of submerged aquatic vegetation may affect the extent of reducing conditions in estuaries and impact fisheries by loss of habitat. However, and in contrast to the processes by which N loadings are likely to decrease MeHg levels in fish,

reduced light penetration associated with increased algal production should limit photodecomposition of MeHg, increasing the amount bioavailable, and thus enhancing bioaccumulation. Photodecomposition is proposed to be an important loss mechanism of MeHg in the surface waters of some coastal ecosystems (Balcom et al., 2004; Monperrus et al., 2007; Whalin et al., 2007; Fig. 1). The effects of changes in photodecomposition notwithstanding, the overall consequence of increased nutrient loadings to estuaries should be to decrease fish MeHg concentrations.

In this conceptual model we have laid out a number of potential mechanisms by which increased nutrient loading might act to decrease Hg bioavailability, MeHg production and MeHg concentrations in biota (Fig. 1). The extent to which these individual mechanisms are important will depend, in part, on the source of ionic Hg and MeHg inputs to diverse marine ecosystems. Moreover, the response of primary production to a change in loading of the limiting nutrient is complex and variable across coastal waters due to factors such as tidal exchange, hydraulic residence time, photic depth and the importance of suspension feeders (Cloern, 2001). Depending on the watershed area and associated watershed sources, depth, area, bathymetry and exchange with the open ocean, substantial sources of ionic Hg and MeHg to coastal ecosystems could include atmospheric deposition, riverine inputs, coastal sediments and/or the open ocean (Balcom et al., 2010, 2008; Hammerschmidt and Fitzgerald, 2004; Harris et al., this issue; Sunderland et al., in press, 2009). For example if ionic Hg and MeHg inputs are largely derived from riverine sources, then the impacts of nutrients on Hg dynamics might be manifested largely through enhanced deposition (removal) from the water column to sediments, biodilution associated with increased primary, secondary and tertiary production or decreases in photodecomposition (e.g., Bay of Fundy, New York Harbor). In contrast, if MeHg supply to the coastal ecosystem largely originates from internal sediments, then increases in sediment organic matter binding of ionic Hg or elevated sulfide limiting MeHg production could be important mechanisms by which increased nutrient loading decrease fish Hg concentrations (e.g., Long Island Sound).

1.3. Approaches to test hypothesis

There are multiple approaches to test ecosystem-level hypotheses (Carpenter, 1998), including time-series measurements at one or more sites (temporal patterns); ecosystem-level experiments (Harris et al., 2007); gradient studies (i.e., spatial patterns; Chen et al., 2009; Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009); and ecosystem models (Harris et al., this issue; Hudson et al., 1994; Kim et al., 2008). Each has advantages and disadvantages, and research efforts are strengthened by the use of multiple approaches. Examination of nutrient–MeHg interactions in marine ecosystems would benefit from the use of these diverse approaches to test our conceptual model (Fig. 1).

In our examination of the nutrient–MeHg conceptual model we utilized modeling and cross-site analysis. We compiled information from three spatial studies to obtain information that would inform aspects of the hypothesis. First, we evaluated phytoplankton MeHg from a suite of marine ecosystems with contrasting nutrient status, including coastal and open ocean environments. Second, an ocean nutrient–production model and a shallow coastal model were applied to illustrate some of the complexities associated with increases in production, driven by changes in nutrient loadings, in the trophic transfer of MeHg. Third, we examined patterns of nutrients and Hg in the sediments at ten coastal sites in the northeastern United States. These sites exhibit a range of nutrient and Hg concentrations in sediments and were used to probe the conceptual model. Finally, we evaluated Hg

concentrations in sport fish in response to reactive N loading across estuaries in the Atlantic and Gulf coasts, and forage fish Hg concentrations in San Francisco Bay in response to increases in reactive N loading.

2. Case studies

2.1. Comparison across marine nutrient gradient

Phytoplankton bioconcentrate Hg species from water, with MeHg accumulating primarily in the cytoplasm and ionic forms of Hg bound to cell membranes (Mason et al., 1996). If biodilution of MeHg were to occur in marine ecosystems, then one would expect MeHg concentrations in phytoplankton to decrease with greater N loadings and associated primary production. However, such a linear relationship may be confounded by other factors such as changes in the growth rate and size of plankton at the base of a pelagic food chain (see Section 2.2). While a wide range of primary production exists among coastal and open-ocean environs ($\sim 20\text{--}3500\text{ g C m}^{-2}\text{ y}^{-1}$; Behrenfeld and Falkowski, 1997), an empirical investigation of such a gradient is made difficult by differences in MeHg loadings to surface waters inhabited by phytoplankton. For example, shallow estuaries highly contaminated with Hg would likely have greater supply of MeHg to surface waters than an oligotrophic surface gyre in the open ocean. One additional factor contributing to this difference is the tight coupling between the water column and sediments in some coastal waters, and the lack of any benthic influence on an oligotrophic open-ocean environment. Note that the benthic influence is also likely small for offshore areas of coastal ecosystems such as the Gulf of Mexico and the Gulf of Maine (Harris et al., this issue; Sunderland et al., in press). Differences in MeHg inputs/availability can be normalized by calculating a bioaccumulation factor (BAF; L kg^{-1}) for phytoplankton, which is the wet-weight concentration of MeHg in phytoplankton divided by that in filtered water.

There is little information on MeHg in marine phytoplankton, but limited data in the literature suggest that biodilution may occur, although other factors also are important. Both the concentration and BAF of MeHg decrease substantially from oligotrophic to mesotrophic marine ecosystems (Table 2), which is consistent with biodilution of MeHg by a greater pool of biomass in mesotrophic waters. While the dissolved MeHg concentrations increase by an order of magnitude from oligo- to mesotrophic systems, the BAFs decrease by at least two orders of magnitude suggesting that there are important changes in partitioning and bioaccumulation. MeHg concentrations and BAFs in eutrophic ecosystems also are less than the one oligotrophic observation, but are greater than those in the mesotrophic ecosystems. Increased concentrations and BAFs for MeHg in eutrophic vs. mesotrophic ecosystems would not be expected if biodilution were the sole factor affecting the degree of bioaccumulation. The eutrophic ecosystems, Long Island Sound and Jamaica Bay, are highly impacted by watershed inputs of anthropogenic Hg and MeHg (Balcom et al., 2004, 2008). In such contaminated environments, inputs of Hg may negate a relationship between nutrient loadings and MeHg in the food web.

2.1.1. Examination of the impact of biomass changes on methylmercury in pelagic food chains

As noted above, increased inputs of nutrients to coastal environments have led to eutrophication and enhanced oxygen depletion (e.g., Rabalais et al., 2002). Nutrient inputs together with changing climate are likely to increase the extent of oxygen minimum zones in the ocean (Deutsch et al., 2011). Investigators

Table 2
Methylmercury in marine phytoplankton as a function of ecosystem trophic status.

Relative productivity ^a	Location	Filtered MeHg (ng L ⁻¹)	Phytoplankton MeHg		
			(ng g ⁻¹) wet wt ^b	% of total Hg	log BAF (L kg ⁻¹)
Oligotrophic	North Pacific Ocean ^c	0.004	0.8	—	5.3
Mesotrophic	New England Shelf ^d	0.06	0.3	—	3.7
	Belgian coast ^e	0.03	0.12	2	3.6
	North Sea ^e	0.02	0.06	3	3.5
Eutrophic	Bay of Fundy ^f	0.06	0.15	6	3.4
	Long Island Sound, CT/NY ^g	0.03	0.5	9	4.2
	Jamaica Bay, NY ^h	0.02	0.3	10	4.2

^a Assigned classification based on presumed productivity.

^b Literature value or converted to wet-weight concentration assuming 95% water content (Knauer and Martin, 1972).

^c Hammerschmidt and Bowman (2012).

^d Hammerschmidt and Fitzgerald (2006a, 2006b).

^e Baeyens et al. (2003).

^f Sunderland et al., 2010.

^g Balcom et al. (2004).

^h Balcom et al. (2008).

have noted that chlorophyll *a* concentrations in the North Pacific near Hawaii have increased substantially in the recent past (200% between 1968 and 1985; Venrick et al., 1987) although a recent analysis shows the opposite trend across much of the open ocean (Boyce et al., 2010). Given these dynamics, a simple (partition-based) bioaccumulation model was derived to examine the impact of changes in phytoplankton biomass on MeHg concentrations in open-ocean fish.

The base case simulation was developed from literature values (total MeHg 0.02 ng L⁻¹) and it was assumed that the MeHg concentration in the water column was not dependent on biomass (see discussion below). The following ecosystem parameters were used in the base case (DOM=2.075 mg C L⁻¹; algal biomass=0.025 mg L⁻¹ dry weight) (e.g., Shiimoto and Hashimoto, 2000). All trophic dynamics were linearly constrained to the algal biomass (i.e., bacterial mass twice and zooplankton one tenth the algal biomass on a dry weight basis). In the model, the DOM concentration also was varied with algal biomass (ratio of 35 for DOM: algal mass). Partition coefficients (dry weight basis) between water and the various biota and the DOM were based on the literature (Kaiser and Benner, 2009; Kim et al., 2008; Mason et al., 1996). It is assumed that only the fraction of MeHg that is not complexed with DOM is bioavailable to the food chain (e.g., Mason et al., 1996; Lawson and Mason, 1998). Two cases were considered for this open ocean analysis: (1) conditions where the partition coefficients among water and each of DOM, phytoplankton, and bacteria were the same (10^6 L kg^{-1}) with the trophic transfer of MeHg on a mass basis increasing by a factor of three between phytoplankton and zooplankton; and (2) conditions where the DOM partition coefficient was half ($0.5 \times 10^6\text{ L kg}^{-1}$) and the bacterial coefficient twice ($2 \times 10^6\text{ L kg}^{-1}$) that of the phytoplankton, which was kept at 10^6 L kg^{-1} . Under both cases, MeHg in the water column was complexed with DOM (66% in Case 1, 48% in Case 2 for the base case values) to a greater degree than occurred as inorganic (e.g., Cl⁻) complexes (32% in Case 1, 46% in Case 2). The remainder of the MeHg was partitioned among the various biota classes, with similar concentrations for phytoplankton and bacteria in Case 1 (6.3 ng g⁻¹), and 4.6 ng g⁻¹ for phytoplankton in Case 2. The bioavailable MeHg concentration was 0.006 ng L⁻¹ in Case 1 and 0.009 ng L⁻¹ in Case 2.

Increasing algal biomass and an associated linear increase of DOM, bacteria, and zooplankton led to a decrease of MeHg bioaccumulation in both cases (Fig. 2a). Overall, a doubling in algal biomass from the base case (0.025 mg L⁻¹ dry weight) results in a 49% decrease in the MeHg concentration of phytoplankton for Case 1 and a 54% decrease for Case 2. This relative decrease in MeHg concentration is less than the overall increase of biomass, but is still substantial. In the alternative scenario of decreasing algal biomass, the MeHg concentrations increase (35% for Case 1 and 30% for Case 2). These calculations indicate that changes in algal biomass could have a substantial impact on MeHg levels in pelagic food chains.

Empirical evidence and model calculations suggest an increase in the extent of oxygen minimum zones in the ocean (e.g., Deutsch et al., 2011). This change could enhance methylation within these regions given studies which suggest a linear relationship between net Hg methylation and organic matter decomposition rate in the marine water column (Cossa et al., 2011; Heimburger et al., 2010; Sunderland et al., 2009). Thus, we anticipate a proportional increase in the production of MeHg with an increase of algal biomass decomposition upon

sedimentation. Increasing the total MeHg concentration to 0.04 ng L⁻¹ and the algal biomass to 0.05 mg L⁻¹ (a doubling of both) yields an algal MeHg concentration of 13.7 ng g⁻¹, a 34% increase over the base Case 1, suggesting that enhanced net production of MeHg may compensate for biodilution effects on MeHg concentrations in algae; similarly, for the opposite scenario.

However, it is likely that increases in nutrient loadings will also impact algal species composition, resulting in larger phytoplankton if such loadings alleviate the dominant nutrient limitation (i.e., N is the only limiting nutrient). The impact of algal size on MeHg concentration can be examined with the formulation derived by Mason et al. (1996) for MeHg bioaccumulation into phytoplankton (Fig. 2b). The cellular quota (Q : mol cell⁻¹) at steady state depends both on the relative surface area (A) and the volume (V) as the rate of uptake (U) is dependent on the surface area, and the cellular concentration is defined by the cellular volume (Q/V). Growth rate (μ) also is important: $Q=U/\mu$.

$$Q = U/\mu = 4\pi R^2 PC \quad (1)$$

where R is the radius; P the membrane permeability; C the external Hg concentration

Dividing Q by V to determine cellular concentration (Q/V)

$$Q/V = U/\mu V = \frac{4\pi R^2 PC}{4/3\pi R^2} = 3PC/R \quad (2)$$

So, at the same uptake rate, slower growing organisms will have a greater Q . Overall, the cellular concentration is then defined by the inverse of the product of the relative “radius” (i.e., V/A) and μ . So, while increased eutrophication could be expected to lead to greater MeHg bioaccumulation if methylation were stimulated within the ecosystem, such an increase could be offset by the decrease in cellular quota of large phytoplankton (> 10 μm) relative to smaller plankton (< 1 μm). Such effects have been documented in freshwater phytoplankton (Pickhardt and Fisher, 2007). The cellular volume of phytoplankton can vary over three orders of magnitude and the impact of this effect on concentration is substantial, about an order of magnitude difference (Fig. 2b). While these overall simulations suggest that the overall effect of increased nutrient input is a decrease of MeHg in the food web, a more detailed model is needed to examine the complex interactions that exist among food web components, growth rates, bioavailability, and other factors. As the focus of the paper is on coastal ecosystems, the importance of benthic-pelagic coupling and sediment sources also needs to be considered (see Section 2.1.2)

2.1.2. Examination of the impact of eutrophication on methylmercury in a shallow coastal ecosystem

A more detailed examination of the impact of biomass on MeHg bioaccumulation was conducted by Kim et al. (2008) who developed a biogeochemical cycling and bioaccumulation model that included net methylation in sediments that was tied to sediment biogeochemistry, and sediment resuspension/particle settling and diffuse inputs from sediments of both MeHg and nutrients. The authors developed their MeHg bioaccumulation model based on mesocosm experiments that depicted the interactions between the sediment and water column applicable to a shallow estuarine coastal environment (Kim et al., 2004, 2006; Porter et al., 2010).

The Kim et al. (2008) model included one phytoplankton and two zooplankton size classes as well as filter-feeding clams. Phytoplankton growth rate was dependent on nutrient concentrations and light levels. Bioavailability of MeHg to the phytoplankton was dependent on DOM concentration and dissolved MeHg speciation, and trophic transfer to invertebrates was

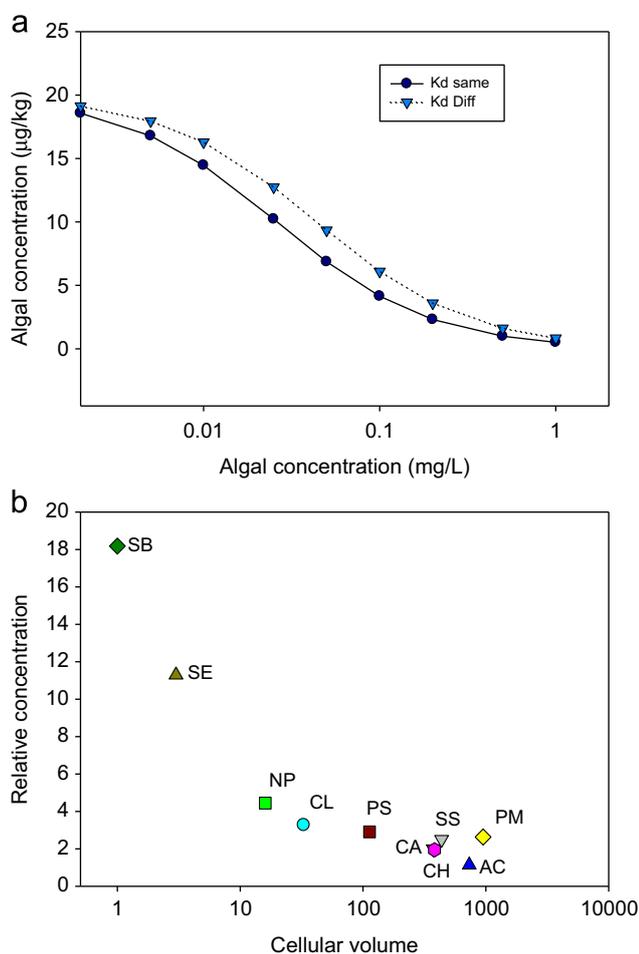


Fig. 2. (a) Model predictions on the impact of changes in algal biomass on the methylmercury concentration in an open ocean system. Note two values for partition coefficients: Case 1 where partition coefficient are the same for dissolved organic matter, phytoplankton and bacteria with water, and Case 2 where they are different. Unpublished data from Kline and Mason; (b) estimation of the concentration of methylmercury in a range of phytoplankton species with different cellular volume using the model for uptake developed by Mason et al. (1996). Note the different symbols refer to different phytoplankton species; AC *Amphidium carterae*; CA *Chaetoceros affinis*; CH *Chlamydomonas* sp.; CL *Chlorella antotrophica*; NP *Navicula pelliculosa*; PM *Prorocentrum minimum*; PS *Proteomonas sulcata*; SB *Syneococcus bacillaris*; SE *Syneococcus elongatus*; SS *Storeatula* sp.

based on feeding rates and assimilation efficiencies from the literature. A sensitivity analysis was conducted to quantify the factors having greatest impact on ecosystem dynamics and MeHg bioaccumulation. Of the parameters tested, phytoplankton growth rate was found to have the greatest impact on the overall system dynamics and biota distributions, as well as MeHg concentrations in the food web. A 20% increase in phytoplankton growth rate led to a 47% increase in phytoplankton biomass and an 18% decrease in MeHg concentration in phytoplankton. These results are consistent with the pelagic model discussed above (Section 2.1.1).

The biomass of higher trophic levels also was stimulated by the increased growth rate as were MeHg concentrations (~20% increase in zooplankton MeHg). Note this pattern of biodilution was evident in phytoplankton but not in the zooplankton, contradicts freshwater observations discussed previously. The increase of MeHg concentration in clams was dampened (~4% increase) by other factors that influence bioaccumulation, such as the competition between zooplankton and clams for the same food source in the model; zooplankton biomass increased in response to increasing phytoplankton growth rate considerably more than clam biomass in the model.

Therefore, the impact of changes in growth rate of phytoplankton had a substantial effect on MeHg in higher trophic levels. In comparison, a 20% increase in the methylation rate in the sediments resulted in a 10–11% increase of MeHg concentration in the various plankton classes. Thus, the impact of changes in methylation rate is less than changes in food chain dynamics, according to the model. To examine this mechanism more closely, the model was applied over a longer simulation period with conditions observed in the mid-Bay region of Chesapeake Bay, including the measured Hg and MeHg concentrations, and for different concentrations of organic matter in the sediments (3, 6 and 12% by mass). The sediment methylation rate was linked to the organic content with decreasing methylation rate as organic matter increased, (respectively, 3.1, 2.3 and $0.67 \times 10^{-3} \text{ h}^{-1}$) based on the results of Hammerschmidt and Fitzgerald (2004).

Not surprisingly, the highest concentrations of MeHg in the food chain were found at the higher methylation rates (i.e., lowest sediment organic content; Fig. 3). Again, the effect was dampened for the filter feeders, but overall these results show that the impact of changes in methylation rate, due to differences in sediment organic matter, propagates through the ecosystem and is reflected in the food web (Fig. 3a). The linkage between MeHg bioaccumulation and changes in sediment Hg methylation rate is exacerbated when sediment resuspension is invoked as a mechanism linking the two pools. In the absence of sediment resuspension, the transfer of MeHg from sediment to the water column was much less efficient and the overall ecosystem response less dynamic (Kim et al., 2008; Fig. 3b). Clearly, the impact of changes in sediment organic matter on bioaccumulation is dependent, in part, on the rate of transfer of MeHg from the sediment to the water column. The results of the model illustrate that all processes (dissolved flux from sediment, resuspension and particle deposition) should be considered when considering the net transfer of MeHg from sediment to the water column (e.g., Sunderland et al., 2010).

2.2. Northeastern Atlantic Estuaries

The nutrient-MeHg conceptual model was also examined by comparing distributions of nutrients and Hg species in sediment at ten intertidal ecosystems in the northeastern United States (Fig. 4). Sediments were sampled in 2008 at locations ranging from Mill Creek in the south, a highly contaminated site in New Jersey to Wells, Maine, in the north. Duplicate samples were collected at all sites, except Waquoit Bay, MA. A total of 19

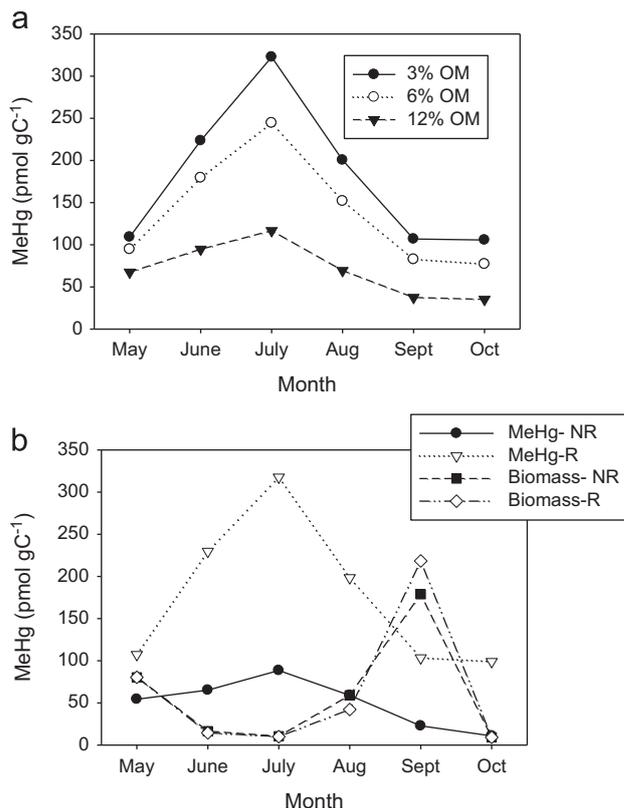


Fig. 3. (a) The modeled concentrations of methylmercury in phytoplankton in different regions of the Chesapeake Bay, as differentiated by the differences in sediment organic content (% OM) based on the biogeochemical model developed by Kim et al. (2008) for a shallow coastal system with tidal resuspension; (b) model results demonstrating the impact of sediment resuspension on methylmercury accumulation but not on phytoplankton biomass. Note R refers to resuspension and NR refers to no resuspension conditions. Biomass refers to phytoplankton biomass. Both figures are from Kim et al. (2008).

samples were collected. Sediments were sampled with a 6 cm diameter coring tube, and the top 2 cm of material from nine cores were composited into a single sample. Aliquots of the homogenized sediment composite were freeze dried and analyzed for total Hg, MeHg, and OC, N, and S concentrations.

We selected the Northeast sites for analysis because of the contrasting spatial patterns of nutrient and Hg concentrations (Fig. 4). In this analysis, we assume that sediment N concentrations are a proxy for N loadings. Relatively high N and OC concentrations in sediment were evident at sites toward the south, including Mill Creek, NJ; Jamaica Bay, NY; Audubon, CT; Smith Neck, CT; Barn Island, CT; and Bold Point, RI. Total Hg concentrations in sediment were exceedingly high at Mill Creek and lower, but still relatively high, at Jamaica Bay, Audubon and Bold Point. Finally, the fraction of total Hg as MeHg (%MeHg) is often suggested as a measure of the bioavailability and net methylation of sediment Hg. Northern sites, having the lowest sediment N concentrations, generally exhibited the greatest %MeHg values, including Wells, Waquoit and Buzzards Bays, MA.

In general, there were strong relationships among OC, N, and S in the Northeast coastal sediments (Fig. 5). The mean mass ratios (± 1 SD) of major elements in sediments were OC/N ratio = 9.4 ± 6.8 , S/N ratio = 1.2 ± 0.5 and S/OC ratio = 0.16 ± 0.1 . The general nutrient stoichiometry of coastal sediments suggests that inputs of N largely drive the fixation of OC through primary production. The mean OC/N ratio was greater than the Redfield ratio of 6.6 and may be attributed to a contribution of allochthonous organic matter from watersheds or preferential loss of N

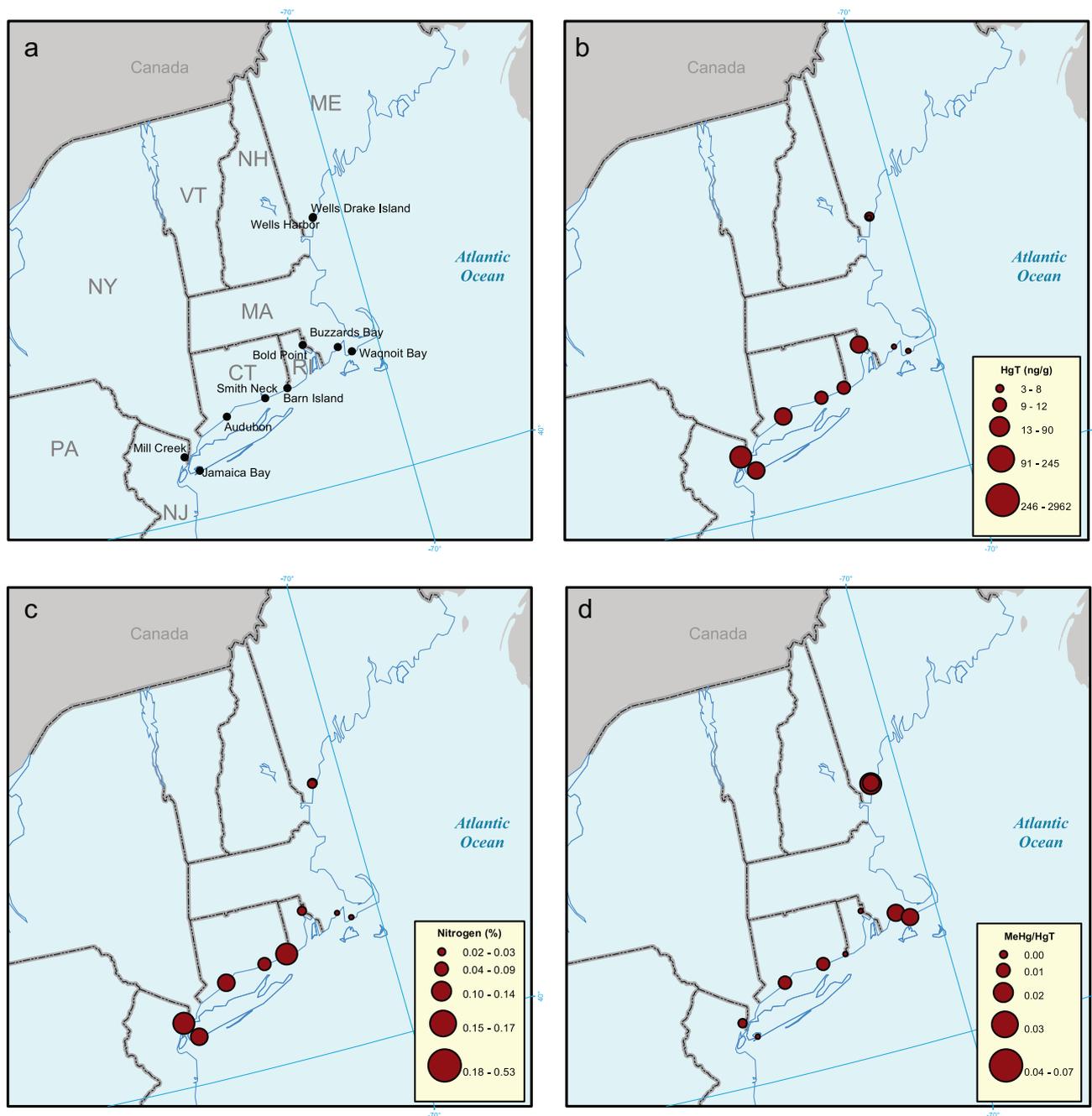


Fig. 4. Maps of the coastal sediment study sites (a) showing the total mercury concentration (b), % nitrogen (%N) (c) and percent of total mercury occurring as methylmercury (%MeHg) (d) in the northeastern U.S.

during sediment diagenesis. In sediments, metabolism of organic matter by sulfate reduction drives the formation of carbon-bonded S and acid volatile sulfide which together largely comprise sediment S concentration. As a result, there is a close correspondence among sediment N, OC and S (Fig. 5).

For many of the sediment sites, these stoichiometric relationships also extended to total Hg (Fig. 6). For most of the sites (8 of 10) the mean Hg/N (ng g^{-1}) ratio is $83,300 \pm 83,100$; and the Hg/OC (ng g C^{-1}) ratio is 8300 ± 6000 , which is comparable to the ratio observed in surface sediments of Long Island Sound (7900 ± 2100 ; Hammerschmidt and Fitzgerald, 2004). Of this group of eight sites, sediments in Buzzards Bay and Waquoit Bay had very low organic contents. At the high end of OC concentrations were sites at Audubon and Bold Point. Beyond the eight sites with comparable Hg/OC ratios, the coastal sediments adjacent to Mill

Creek were highly contaminated with Hg (mean, 2960 ng g^{-1}) and exhibited a large Hg/OC ratio ($49,000 \text{ ng Hg g OC}^{-1}$). The concentrations at Mill Creek are comparable to highly contaminated deposits previously reported for New York Harbor ($40,000 \text{ ng Hg g OC}^{-1}$; Hammerschmidt et al., 2008). The other “outlier” site was Barn Island, where sediments had a relatively high concentration of organic C with relatively low Hg concentration, resulting in a low Hg/C ratio ($2800 \text{ ng Hg g OC}^{-1}$). Barn Island might be considered a “Hg limited” site.

Changes of %MeHg along an N, organic C and S concentration gradient generally support aspects of the conceptual nutrient-MeHg model (Fig. 7). At the lowest N and organic C concentrations, there appears to be an increase of %MeHg up to concentrations of about 0.07% N and 0.5% organic C. The fraction of total Hg as MeHg decreases at sediment N and organic C concentrations greater than

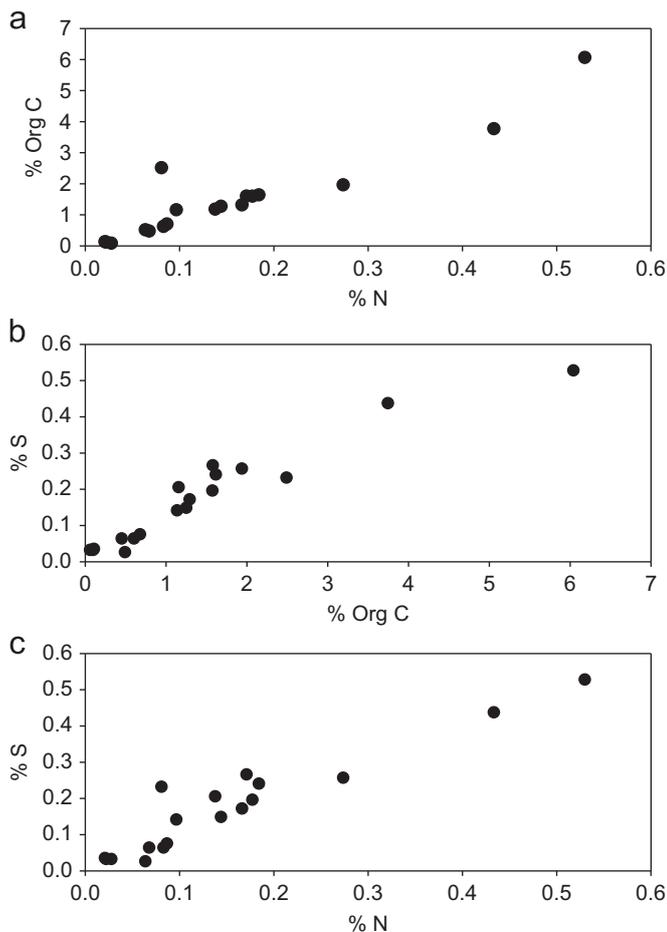


Fig. 5. Concentrations of organic C as a function of N concentration (a), S concentration as a function organic carbon concentration (b) and S concentration as a function of N concentration (c) in Northeast coastal sediment sites.

these values. The highest %MeHg was observed at the lowest sediment S concentrations and decreased with increasing S.

Other studies on the east coast on the U.S. have found patterns similar to those observed in this study of Northeast coastal sediments, including the Chesapeake Bay and adjoining continental margin, Long Island Sound, and New York Harbor. In Long Island Sound and New York Harbor, potential rates of MeHg production were related inversely with organic matter and sulfide contents of the sediment (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2008). In Chesapeake Bay and on the shelf, %MeHg decreased with increasing S in sediments (Hollweg et al., 2009). Except for sites along the continental slope, Hollweg et al. (2009) observed a pattern of decreasing %MeHg with increasing sediment N and OC. However, and in contrast to the Northeast sediment data, they did not observe an apparent increase in MeHg with increasing N at very low sediment N and OC concentrations. The very low sediment N and OC sites in the Northeast sediment study occurred at the sites around Cape Cod (Waquoit Bay and Buzzards Bay), which receive groundwater inputs of Hg (Bone et al., 2007). This behavior may have been a function of unique conditions at these sites or the very low N and organic C concentrations that were not observed in other studies.

2.3. Fish mercury response to N loading

In the previous case studies, measured and modeled MeHg in phytoplankton and sediments are generally consistent with the

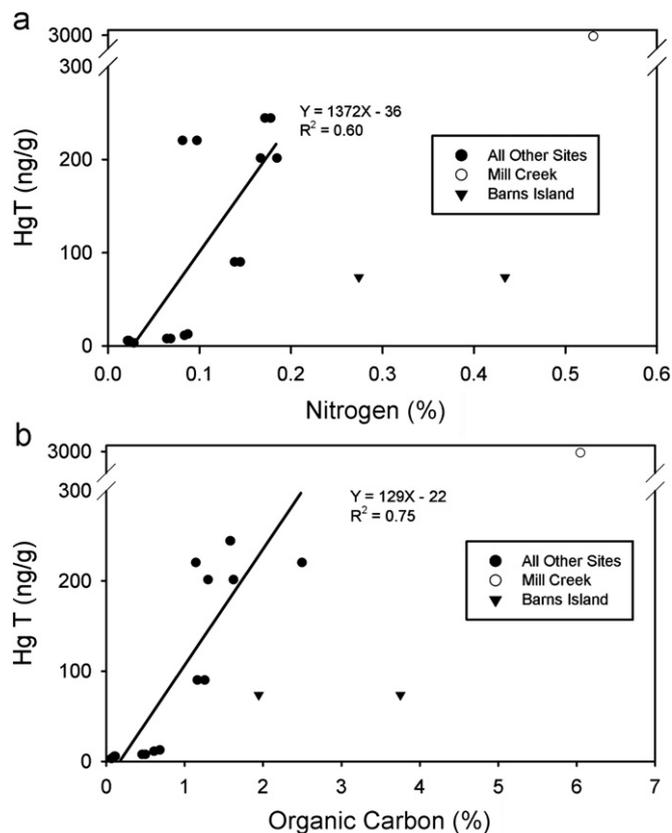


Fig. 6. Total Hg as a function of N concentration (a) and organic C (b) concentration in Northeast coastal sediments. Only closed circles are included in regression analysis.

conceptual model that elevated primary production would result in lower MeHg net production and bioaccumulation at the base of the food web, primarily due to decreased methylation and bioavailability of MeHg, as well as effects of biodilution (Table 2; Figs. 1, 2, and 7). Given the strong spatial and temporal heterogeneity of Hg methylation and phytoplankton uptake, and the need to establish a clear linkage with exposure, Hg concentrations in fish can be used as a measure of ecosystem MeHg exposure to humans and wildlife predators (Harris et al., 2007; Sunderland, 2007). Finfish integrate potential changes in food web structure that may occur with changing nutrient status, and have tracked the impact of increased primary production and biodilution in fresh waters (Essington and Houser, 2003; Chen and Folt, 2005). However, this finding has not previously been described in estuarine or marine ecosystems.

To address this gap, in the fourth case study we examined Hg and MeHg concentrations in multiple species of fish across a range of spatially distinct estuaries as well as within a single estuary subject to differing nutrient loading. Data for Hg tissue concentration in eight species of fish were compiled from the National Coastal assessment database (<http://www.epa.gov/emap/nca/index.html>), and peer reviewed literature (Kannan et al., 1998; Adams and Onorato, 2005; Moore et al., 2005; Hammerschmidt and Fitzgerald, 2006a; Adams et al., 2010; Payne and Taylor, 2010; Senn et al., 2010; Stunz and Robillard, 2011; Szczebak and Taylor, 2011). Estuaries and marine embayments from the North Atlantic Coast (11 water bodies), the South Atlantic coast (4 water bodies), and the Gulf of Mexico (14 water bodies) were considered. Whole body results were converted to fillet concentration using the regression equation for all species of Peterson et al. (2005). Average Hg fish burdens were compared to

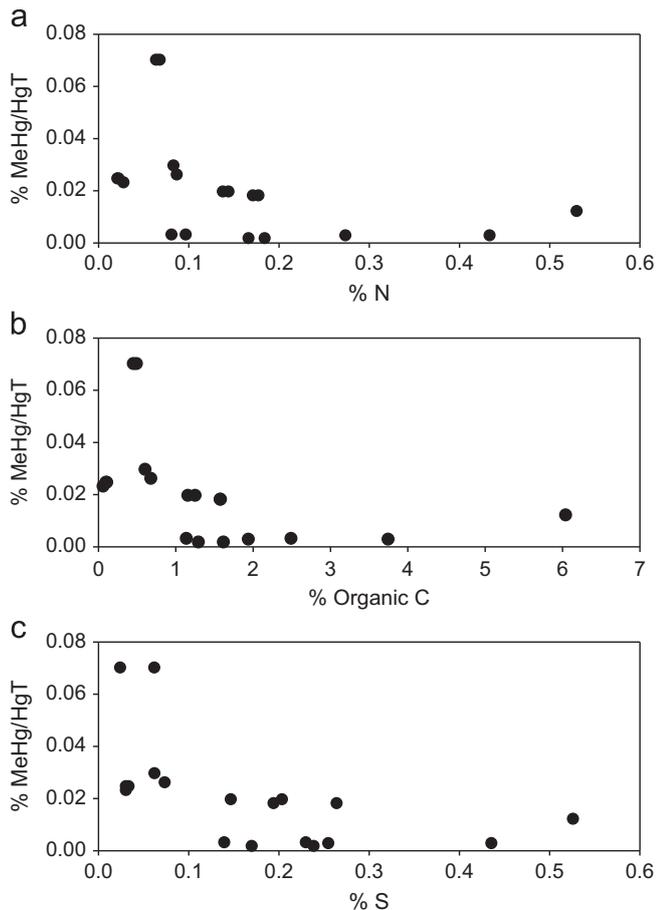


Fig. 7. The percent of total Hg occurring as MeHg (%MeHg) as a function of N (a), organic C (b) and S (c) in Northeast coastal sediments.

estimated estuary N loads using the SPARROW model (Alexander et al., 2000).

Correlation coefficients were low for six fish species (Pearson's correlation coefficient (r) ranging from -0.21 to 0.25). For winter flounder (*Pseudopleuronectes americanus*, $r=0.77$, $n=5$ water bodies) and scup (*Stenotomus chrysops*, $r=0.71$, $n=6$), there was a positive correlation, inconsistent with the expected decrease in fish Hg burdens with increasing N loads. The lack of relationships between fish Hg concentrations and N loadings was likely affected by extracting data from multiple sources; limited sample size for individual fish species; insufficient data to evaluate confounding factors, such as fish body size; not accounting for differing Hg inputs to the estuaries; inconsistent and limited range of N loading; and not considering the variable response of estuaries to nutrient loadings due to their physical characteristics (Cloern, 2001). Future studies having more complete and consistent data sets would aid in determining the overall relationship between nutrient loading and fish mercury biomagnification.

We also compared Hg in silverside collected from the effluent drainage waterways of wastewater treatment plants (WWTP) with elevated nutrient concentrations to nearby reference sites in San Francisco Bay, CA (Table 3). San Francisco Bay is TMDL listed for Hg due to historic mining operations and other sources (Davis et al., this issue) and several drainages have TMDL listed for elevated nutrients. Data were obtained from a three-year survey of spatial and temporal patterns in biosentinel fish Hg concentrations. For this analysis 40 to 80 mm Mississippi silverside (*Menidia audens*) were employed as a local biosentinel due to their wide availability, tendency to stay within nearshore margin

Table 3

Ammonium and NO_x ($\text{NO}_3^- + \text{NO}_2^-$) in four sites exposed to wastewater treatment plant discharge, and ambient (background) concentrations in South San Francisco Bay.

Source	Site	Average ammonium (mg N/L)	Annual ammonium (metric tons)	Annual NO_x (metric tons)
WWTP ^a	East Bay dischargers Authority ^{bc}	20.38	2284	99
WWTP ^a	San Jose/Santa Clara ^d	0.58	86	1377
WWTP ^a	Palo Alto ^d	0.30	16	593
WWTP ^a	Sunnyvale ^d	2.13	37	164
Ambient ^e	Lower South Bay	0.08		
Ambient ^{e,c}	South Bay	0.06		

^a Averaged across flow class data in McKee and Gluchowski, 2011; annual averages are from 2004–2010.

^b Combines discharges from six wastewater treatment facilities.

^c Secondary treatment facility.

^d Advanced treatment facility.

^e Average of 2004–2010 data from the Regional Monitoring Program (SFEI, 2010).

habitats, and limited movement range. Their diets are largely composed of benthic invertebrates, augmented with zooplankton and riparian insects (Greenfield and Jahn, 2010).

In all four comparisons, fish Hg concentrations were lower in the WWTP sites than the reference sites (Fig. 8). Differences were not attributable to fish size, as fish were similar size composites. The lower concentrations in fish near WWTPs are consistent with the general conceptual model discussed in this paper. However, the differences among the four geographically distinct site pairs were generally larger than the differences between paired sites, reflecting the importance of other factors, such as spatial patterns in historic Hg pollution and baywide gradients in methylation potential (Davis et al., this issue).

3. Discussion

The data bases, models, and calculations discussed above suggest that changes in nutrient loadings could have substantial effects on MeHg bioaccumulation through a number of interlinked mechanisms. Unfortunately, these case studies provide only limited information with which we can evaluate our conceptual model. The marine nutrient gradient analysis (Section 2.1) and the Northeast sediment (Section 2.3) results are spatial data limited by the fact that differences in coastal nutrient status are often coincident with variations of Hg contamination, making it difficult to differentiate effects of nutrient and Hg loadings. It seems likely that variations of Hg loadings will alter the extent and the mechanisms to which nutrient inputs affect ecosystem MeHg dynamics.

Our model calculations (Section 2.2) are limited by the difficulty of making an overall prediction, as changes in nutrient levels can have a marked effect not only on the production and partitioning of MeHg within the sediment and water column, but also on trophic dynamics. In particular, changes in phytoplankton size and growth rate can have a large impact on the overall trophic transfer of MeHg. Our spatial fish analysis (Section 2.4) of Atlantic and Gulf coast waters reveals no relationships between fish Hg concentrations and estuary nutrient loading. This lack of relationships is probably not surprising given the relatively coarse analysis conducted and the highly variable responses that estuaries show to nutrient loadings as a result of influences of hydrologic residence time, tidal exchange, light penetration and benthic interactions (Cloern, 2001). In San Francisco Bay,

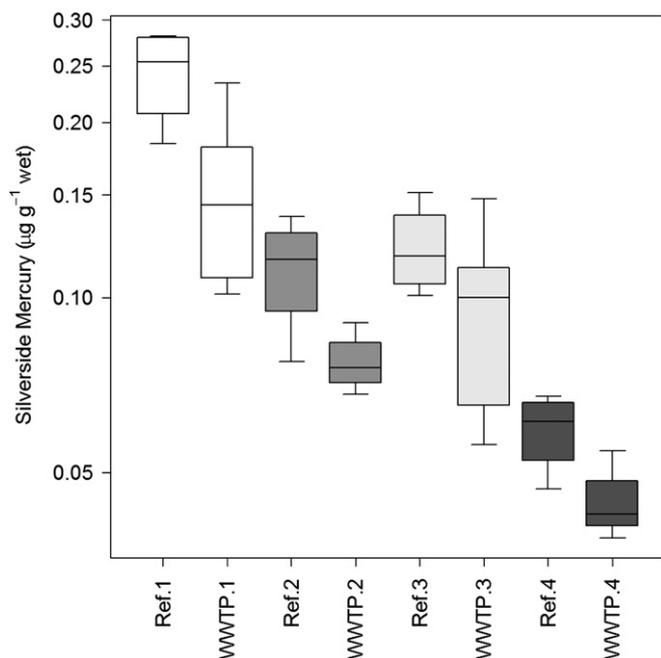


Fig. 8. Mercury concentrations in silverside in wastewater treatment plant (WWTP) and reference station pairs in South San Francisco Bay. Station pairs are indicated by corresponding shading. Results are box and whiskers plots of wet weight mercury concentrations. For each site, the center line represents the median, the bottom and top of the boxes indicate the first and third quartiles, and the whisker ends correspond to approximately 95% confidence intervals for difference in medians. Note log scale Y axis. [The whisker ends represent $\pm 1.58 \times \text{interquartile range} / \sqrt{n}$, corresponding to approximately a 95% confidence interval for difference in medians.]

however, forage fish, concentrations were lower at WWTP discharge locations than nearby reference locations, and WWTP discharge had elevated dissolved nitrogen concentrations compared to ambient concentrations. The finding suggests that estuarine sites with increased anthropogenic nutrient loading will decrease MeHg bioaccumulation in fish, which is consistent with our conceptual model (Fig. 1). This is the first published account of spatial variation in fish mercury being associated with WWTP, but it is limited in scope to a single estuary, and the mechanism underlying the correlation is indeterminate. Potential mechanisms include growth dilution of the forage fish or biodilution among primary producers or lower trophic level consumers (Essington and Houser, 2003; Pickhardt et al., 2002). Clearly, further and more comprehensive examination of these factors with both laboratory and field efforts will improve our understanding of the complex linkage between changes in nutrient inputs and MeHg bioaccumulation into fish.

3.1. Management implications

Although our conceptual model involves considerable speculation, it may have important implications for efforts to manage nutrient loading to coastal waters (Hammerschmidt and Fitzgerald, 2004) and also organic enrichment from aquaculture activities in coastal environments (Sunderland et al., 2006). As mentioned, a large number of TMDLs for N have been established for coastal waters in the U.S., and management efforts are underway in North America, Europe and Asia to control N loadings to estuaries to achieve water quality standards. For example, in 2000, wastewater discharges to Boston Harbor were diverted 15 km offshore, decreasing the external load of total N by about 80% (Benoit et al., 2009; Taylor, 2010). In five years following the decrease in N loading, harbor-wide concentrations

of total N decreased 35%, summer chlorophyll decreased 40%, and dissolved oxygen in bottom water increased by 5%. Increases in benthic invertebrate community densities have also been noted (Bricker et al., 2007; Taylor, 2010). In Long Island Sound, both Connecticut and New York have aggressively pursued N control strategies in wastewater treatment plants to achieve a 30% decrease in N load. These states also are conducting storm water permitting and non-point source control programs to achieve an additional 10% decrease in N inputs. Similarly, the Tampa, FL, region has been actively controlling N inputs to Tampa Bay resulting in a 60% decrease since the 1970s (Bricker et al., 2007).

While these programs appear to be effectively mitigating the adverse effects of decades of elevated nutrient loadings, they may have unintended consequences of altering Hg transport and partitioning, and increasing net methylation and trophic transfer. The San Francisco Bay forage fish case study provides observations that support this concern. Although not as prominent as N effects, there is also increasing concern about the impacts of Hg loadings on coastal waters, as evidence by the number of coastal waters that have TMDLs for Hg and are considered impaired by Hg (Table 1). There is a need to conduct detailed monitoring of Hg before and following the implementation of nutrient control programs for estuaries to examine responses and the effect on MeHg concentrations in biota.

Management of wastewater discharge has often led to a concomitant decrease in Hg loading, as demonstrated by Hg mass balances for the Hudson River and Gulf of Maine and changes in ecosystem Hg (Balcom et al., 2010; Sunderland et al., in press). For many coastal waters, riverine inputs, atmospheric deposition and the open ocean are important sources of Hg and MeHg. Moreover, it is likely that deposition and riverine sources of Hg have changed over the past decades (e.g., Sunderland et al., in press, 2010). Therefore, the premise that decreases in nutrient loadings will result in increased MeHg concentrations in the food web must be evaluated in the context of potentially coincident changes of Hg and MeHg inputs. In some ecosystems, continued external input of Hg would be required to sustain sediment MeHg production because relatively fast rates of sedimentation remove Hg from the rapidly cycling pools over a relatively short timescale (years to decades). While in other ecosystems, bioturbation and redistribution of "legacy Hg" buried within the sediment to zones of active methylation may sustain MeHg production for centuries. Moreover, extreme events such as hurricanes can also remobilize Hg and enhance methylation (Liu et al., 2009).

As an example, Hg concentrations in surface sediments of New York/New Jersey Harbor decreased 50–80% between the 1960s and the 1990s (Balcom et al., 2010; Contaminant Assessment and Reduction Project (CARP), 2007), with an associated decrease in Hg concentrations in the water column (Sanudo-Wilhelmy and Gill, 1999). Much of the input of Hg (~90%) and MeHg (~55%) to New York/New Jersey Harbor is derived from the Hudson and East Rivers (Balcom et al., 2010, 2008). Inputs of MeHg from the sediment are relatively small (~25%). This pattern suggests that MeHg in the Harbor is likely to respond rapidly to changes of external Hg loadings. The Bay of Fundy is likely to respond similarly (Sunderland et al., 2010). For such ecosystems, large and rapid changes in Hg and MeHg loading could easily overwhelm the effects of changing N loading.

However, in contrast, inputs of MeHg from the sediment appear to be the major source to the food web in Long Island Sound (Balcom et al., 2004; Hammerschmidt and Fitzgerald, 2006a) and there is a large legacy of Hg contamination in the sediment (Varekamp et al., 2003). For such ecosystems, changes in N loading could have a marked impact on benthic MeHg production. Sediment cores throughout the Sound have shown that concentrations in surface sediment have decreased to a lesser

degree (~40%; Varekamp et al., 2003) than found in New York Harbor. At this time, it is not possible to conclude what impacts that decreases in N loading will have on levels of MeHg in estuarine and coastal food chains.

Time series investigations would be valuable, overcome some of the limitations associated with spatial studies and provide insight on the mechanisms behind Hg-nutrient interactions. The time scale of the processes is undoubtedly a critical aspect of understanding Hg-nutrient linkages. For example, water column processes could be driven by short-term changes, such as spring algal blooms resulting in seasonal biodilution of MeHg in a temperate estuary, or long-term changes, such as regulatory controls on watershed nutrient loading. In contrast Hg-nutrient interactions that are controlled by sediment processes are likely to be long-term phenomena. Note, it seems likely that, for most estuaries adjacent to developed regions, controls on nutrient loadings would coincide with removal of other contaminants and result in decreased Hg loadings, complicating an evaluation of our conceptual model. Nevertheless, monitoring coupled with process studies and more detailed modeling efforts will be essential to evaluate the mechanisms contributing to changes in Hg cycling in response to modifications in the nutrient status of marine ecosystems. Understanding these mechanisms would inform subsequent Hg management strategies and policies.

3.2. Future studies to evaluate conceptual model

Better understanding of the linkages between nutrient loading and Hg contamination in marine ecosystems is needed for effective management of these two important environmental pollutants. Our analysis of existing datasets and modeling suggest that N inputs to marine ecosystems can interact with MeHg production to decrease its bioavailability. However, our conceptual model would benefit from focused efforts to evaluate pathways and processes of the model as well as entire ecosystem effects. Researchers need to use time-series observations, gradient studies, experimental manipulations and models in coordinated efforts to assess the complexities of nutrient-Hg interactions. There is a particular need to monitor Hg in abiotic and biotic compartments through time as nutrient TMDLs are implemented.

Acknowledgments

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