2012

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Charles T. Driscoll
Syracuse University

Celia Y. Chen
Dartmouth College

Chad R. Hammerschmidt
Wright State University

Robert P. Mason
University of Connecticut

Cynthia C. Gilmour
Smithsonian Environmental Research Center

Recommended Citation

Driscoll, Charles T., Chen, Celia Y., Hammerschmidt, Chad R., Mason, Robert P., Gilmour, Cynthia C., Sunderland, Elsie M., . . . Lamborg, Carl H. (2012). Nutrient supply and mercury dynamics in marine ecosystems: A conceptual model. Environmental Research, 119(0), 118-131. doi: http://dx.doi.org/10.1016/j.envres.2012.05.002

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

Charles T. Driscoll[a*], Celia Y. Chen[b], Chad R. Hammerschmidt[c], Robert P. Mason[d], Cynthia C. Gilmour[e], Elsie M. Sunderland[f], Ben K. Greenfield[g], Kate L. Buckman[h], Carl H. Lamborg[i]

[a*]Department of Civil and Environmental Engineering, Syracuse University, 151 Link Hall, Syracuse, NY 13244, USA, 315-443-3434 (phone), 315-443-1243 (fax), ctdrisco@syr.edu

[b,h]Department of Biological Sciences, Dartmouth College, HB 6044, Hanover, NH 03755, USA, Celia.Y.Chen@Dartmouth.edu; Kate.L.Buckman@Dartmouth.edu

[c]Department of Earth & Environmental Sciences, Wright State University, 3640 Colonel Glenn Highway, Dayton, OH 45435, USA, chad.hammerschmidt@wright.edu

[d]Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road, Groton, CT 06340, USA, robert.mason@uconn.edu

[e]Smithsonian Environmental Research Center, PO Box 28, Edgewater, MD 21037, USA, gilmourc@si.edu

[f]Harvard School of Public Health, Harvard University, 401 Park Drive, Boston, MA 02215, USA, elsie_sunderland@harvard.edu

[g]San Francisco Estuary Institute, 7770 Pardee Lane, Oakland, CA 94610, USA, bengreenfield@berkeley.edu

[i]Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA, clamborg@whoi.edu

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 bioavailabilty 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.

Keywords: eutrophication; coastal ecosystems; marine ecosystems; mercury; nitrogen; nutrients

This publication was made possible by NIH Grant Number P42 ES007373 from the National Institute of Environmental Health Sciences (to CC and RM). Support also was provided by New York State Energy Research and Development Authority (to CTD), the U.S. National Science Foundation in two separate grants (to CRH and to RM and CG), and the Hudson River Foundation (to RM). This is a contribution of the C-MERC initiative.

This research has not involved human subjects or experimental animals.

1.0 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 primarily 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 Hg inputs and MeHg concentrations in higher trophic level organisms due to many ecosystems factors that can modify the 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).

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

132 Compared to N, less is known about the dynamics and effects of Hg in coastal and
133 pelagic marine ecosystems. Even less is known about the relationship between changes in N
134 loading and MeHg bioaccumulation in ocean fisheries. In the freshwater literature, however,
135 there are numerous field and experimental studies that show decreases of Hg concentrations in
136 the aquatic food web in response to increasing nutrient inputs. Nutrient enrichment to
137 freshwaters causing algal blooms decreases Hg concentrations in biota through a process
138 referred to as biodilution (Pickhardt et al., 2002). Concentrations of Hg in zooplankton
139 decrease with increasing zooplankton density, resulting in lower fish Hg concentrations (Chen
140 and Folt, 2005). Also, under conditions of high productivity and prey availability,
141 concentrations of Hg in zooplankton and fish may decrease due to growth dilution (Essington
142 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).

164 **1.2 Conceptual model of coastal ecosystem Hg response to increases in N loading**

165 Nitrogen enrichment generally increases productivity in coastal waters (Howarth and
166 Marino, 2006), although a "tipping" point can be reached, past which net ecosystem
167 metabolism decreases with increasing N loading. Further, elevated N enrichment is related to
168 the development of hypoxia and anoxia, particularly in coastal ecosystems with a physical
169 structure that supports stratification (Cloern, 2001; Breitburg et al., 2009). Increases in primary
170 and secondary production will increase ecosystem biomass and decrease concentrations of
171 MeHg in invertebrates and fish through biodilution (Chen and Folt, 2005; Kim et al., 2008),
172 assuming Hg inputs, the extent of methylation and bioavailability remain constant (Figure 1). As
173 discussed further below (see section 2.2), this hypothesis is valid only if there are not
174 substantial shifts in plankton community composition (e.g., cell size, growth rate) in concert
175 with changes in nutrient loadings. Eutrophication also typically results in loss of ecosystem
176 biodiversity (Carpenter et al., 1998). Changes in phytoplankton species composition and
177 growth rate could impact the concentration of MeHg in primary producers and, as a result, in
178 organisms at the higher trophic levels (e.g., Kim et al., 2008).

179 Increases in net ecosystem production also increases deposition of OC to sediments and
180 facilitates the removal of ionic Hg and MeHg from the water column to the sediments (Figure
181 1). Sediment organic matter has a complex role in affecting Hg and MeHg biogeochemistry, net
182 MeHg formation and its bioavailability to the food web (Figure 1). First, the partitioning of Hg
183 between pore water and the solid phase (K_d) is positively related to sediment organic content in
184 most ecosystems. On average, partition coefficients for Hg increase by almost 3 orders of
185 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 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).

Secondly, 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; Figure 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

208 methylating bacteria and the formation of MeHg (Benoit et al., 2003, 2001, 1999b;
209 Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2008; Hollweg et al., 2009, 2010).

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

223 Past experimental and field studies indicate that bioaccumulation of MeHg in benthic
224 and pelagic fauna decreases with increasing sediment OC (Figure 1). Lawrence and Mason
225 (2001) found that amphipods exposed to Hg in OC-rich sediment accumulated less Hg than
226 those in sediments with lower organic contents. Across sites that vary in Hg and OC supply in
227 the Northern Coastal Shelf region of the Gulf of Maine, benthic-sediment concentration factors,
228 a measure of bioavailability of MeHg to marine organisms, decrease with total OC in sediments

229 (Chen et al., 2009). These observations suggest that production, bioavailability, and/or
230 assimilation of MeHg decreases with increasing organic content of sediments.

231 Increased primary production also will decrease penetration of light in the water column
232 and cause a shift in primary production from benthic to pelagic autotrophs (Paerl et al., 2001).
233 Such a shift will change the pathways whereby MeHg enters the food web (Figure 1). The loss
234 of submerged aquatic vegetation may affect the extent of reducing conditions in estuaries and
235 impact fisheries by loss of habitat. However, and in contrast to the processes by which N
236 loadings are likely to decrease MeHg levels in fish, reduced light penetration associated with
237 increased algal production should limit photodecomposition of MeHg, increasing the amount
238 bioavailable, and thus enhancing bioaccumulation. Photodecomposition is proposed to be an
239 important loss mechanism of MeHg in the surface waters of some coastal ecosystems (Balcom
240 et al., 2004; Monperrus et al., 2007; Whalin et al., 2007; Figure 1). The effects of changes in
241 photodecomposition notwithstanding, the overall consequence of increased nutrient loadings
242 to estuaries should be to decrease fish MeHg concentrations.

243 In this conceptual model we have laid out a number of potential mechanisms by which
244 increased nutrient loading might act to decrease Hg bioavailability, MeHg production and MeHg
245 concentrations in biota (Figure 1). The extent to which these individual mechanisms are
246 important will depend, in part, on the source of ionic Hg and MeHg inputs to diverse marine
247 ecosystems. Moreover, the response of primary production to a change in loading of the
248 limiting nutrient is complex and variable across coastal waters due to factors such as tidal
249 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., this issue, 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 (Figure 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.

2.0 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

292 production. However, such a linear relationship may be confounded by other factors such as
293 changes in the growth rate and size of plankton at the base of a pelagic food chain (see Section
294 2.2). While a wide range of primary production exists among coastal and open-ocean environs
295 (~20–3500 g C m^{-2} y^{-1}; Behrenfeld and Falkowski, 1997), an empirical investigation of such a
296 gradient is made difficult by differences in MeHg loadings to surface waters inhabited by
297 phytoplankton. For example, shallow estuaries highly contaminated with Hg would likely have
298 greater supply of MeHg to surface waters than an oligotrophic surface gyre in the open ocean.
299 One additional factor contributing to this difference is the tight coupling between the water
300 column and sediments in some coastal waters, and the lack of any benthic influence on an
301 oligotrophic open-ocean environment. Note that the benthic influence is also likely small for
302 offshore areas of coastal ecosystems such as the Gulf of Mexico and the Gulf of Maine (Harris
303 et al., this issue; Sunderland et al., this issue). Differences in MeHg inputs/availability can be
304 normalized by calculating a bioaccumulation factor (BAF; L kg^{-1}) for phytoplankton, which is the
305 wet-weight concentration of MeHg in phytoplankton divided by that in filtered water.

306 There is little information on MeHg in marine phytoplankton, but limited data in the
307 literature suggest that biodilution may occur, although other factors also are important. Both
308 the concentration and BAF of MeHg decrease substantially from oligotrophic to mesotrophic
309 marine ecosystems (Table 2), which is consistent with biodilution of MeHg by a greater pool of
310 biomass in mesotrophic waters. While the dissolved MeHg concentrations increase by an order
311 of magnitude from oligo- to mesotrophic systems, the BAFs decrease by at least two orders of
312 magnitude suggesting that there are important changes in partitioning and bioaccumulation.
313 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.

2.2.1 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 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., Shiomoto and

337 Hashimoto, 2000). All trophic dynamics were linearly constrained to the algal biomass (i.e.,
338 bacterial mass twice and zooplankton one tenth the algal biomass on a dry weight basis). In the
339 model, the DOM concentration also was varied with algal biomass (ratio of 35 for DOM: algal
340 mass). Partition coefficients (dry weight basis) between water and the various biota and the
341 DOM were based on the literature (Kaiser and Benner, 2009; Kim et al., 2008; Mason et al.,
342 1996). It is assumed that only the fraction of MeHg that is not complexed with DOM is
343 bioavailable to the food chain (e.g., Mason et al., 1996; Lawson and Mason, 1998). Two cases
344 were considered for this open ocean analysis: 1) conditions where the partition coefficients
345 among water and each of DOM, phytoplankton, and bacteria were the same (10^6 L kg^{-1}) with
346 the trophic transfer of MeHg on a mass basis increasing by a factor of three between
347 phytoplankton and zooplankton; and 2) conditions where the DOM partition coefficient was
348 half (0.5 x 10^6 L Kg^{-1}) and the bacterial coefficient twice (2 x 10^6 L Kg^{-1}) that of the
349 phytoplankton, which was kept at 10^6 L kg^{-1}. Under both cases, MeHg in the water column was
350 complexed with DOM (66% in Case 1, 48% in Case 2 for the base case values) to a greater
351 degree than occurred as inorganic (e.g., Cl^-) complexes (32% in Case 1, 46% in Case 2). The
352 remainder of the MeHg was partitioned among the various biota classes, with similar
353 concentrations for phytoplankton and bacteria in Case 1 (6.3 ng g^{-1}), and 4.6 ng g^{-1} for
354 phytoplankton in Case 2. The bioavailable MeHg concentration was 0.006 ng L^{-1} in Case 1 and
355 0.009 ng L^{-1} in Case 2.

356 Increasing algal biomass and an associated linear increase of DOM, bacteria, and
357 zooplankton led to a decrease of MeHg bioaccumulation in both cases (Figure 2a). Overall, a
358 doubling in algal biomass from the base case (0.025 mg L^{-1} dry weight) results in a 49%

359 decrease in the MeHg concentration of phytoplankton for Case 1 and a 54% decrease for Case
360 2. This relative decrease in MeHg concentration is less than the overall increase of biomass, but
361 is still substantial. In the alternative scenario of decreasing algal biomass, the MeHg
362 concentrations increase (35% for Case 1 and 30% for Case 2). These calculations indicate that
363 changes in algal biomass could have a substantial impact on MeHg levels in pelagic food chains.
364 Empirical evidence and model calculations suggest an increase in the extent of oxygen
365 minimum zones in the ocean (e.g., Duetsch et al., 2011). This change could enhance
366 methylation within these regions given studies which suggest a linear relationship between net
367 Hg methylation and organic matter decomposition rate in the marine water column (Cossa et
368 al., 2011; Heimburger et al., 2010; Sunderland et al., 2009). Thus, we anticipate a proportional
369 increase in the production of MeHg with an increase of algal biomass decomposition upon
370 sedimentation. Increasing the total MeHg concentration to 0.04 ng L^{-1} and the algal biomass to
371 0.05 mg L^{-1} (a doubling of both) yields an algal MeHg concentration of 13.7 ng g^{-1}, a 34%
372 increase over the base Case 1, suggesting that enhanced net production of MeHg may
373 compensate for biodilution effects on MeHg concentrations in algae; similarly, for the opposite
374 scenario.
375 However, it is likely that increases in nutrient loadings will also impact algal species
376 composition, resulting in larger phytoplankton if such loadings alleviate the dominant nutrient
377 limitation (i.e., N is the only limiting nutrient). The impact of algal size on MeHg concentration
378 can be examined with the formulation derived by Mason et al. (1996) for MeHg
379 bioaccumulation into phytoplankton (Figure 2b). The cellular quota (*Q:* mol $cell^{-1}$) at steady
380 state depends both on the relative surface area (*A*) and the volume (*V*) as the rate of uptake (*U*)

381 is dependent on the surface area, and the cellular concentration is defined by the cellular
382 volume (*Q/V*). Growth rate (μ) also is important: $Q = U/\mu$.

383 $$Q = {}^{U}/_{\mu} = 4\pi\, R^2\, PC \qquad (1)$$

384 *Where*: R = radius

385 P = membrane permeability

386 C = external Hg concentration

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

388 $${}^{Q}/_{V} = {}^{U}/_{\mu V} = \frac{4\pi\, R^2\, PC}{{}^{4}/_{3}\,\pi\, R^2} = 3\, {}^{PC}/_{R} \qquad (2)$$

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

401 importance of benthic-pelagic coupling and sediment sources also needs to be considered (see
402 section 2.2.2)
403
404 2.2.2 **Examination of the Impact of Eutrophication on Methylmercury in a Shallow Coastal**
405 **Ecosystem**
406
407 A more detailed examination of the impact of biomass on MeHg bioaccumulation was
408 conducted by Kim et al. (2008) who developed a biogeochemical cycling and bioaccumulation
409 model that included net methylation in sediments that was tied to sediment biogeochemistry,
410 and sediment resuspension/particle settling and diffuse inputs from sediments of both MeHg
411 and nutrients. The authors developed their MeHg bioaccumulation model based on mesocosm
412 experiments that depicted the interactions between the sediment and water column applicable
413 to a shallow estuarine coastal environment (Kim et al., 2004, 2006; Porter et al., 2010).
414 The Kim et al. (2008) model included one phytoplankton and two zooplankton size
415 classes as well as filter-feeding clams. Phytoplankton growth rate was dependent on nutrient
416 concentrations and light levels. Bioavailability of MeHg to the phytoplankton was dependent on
417 DOM concentration and dissolved MeHg speciation, and trophic transfer to invertebrates was
418 based on feeding rates and assimilation efficiencies from the literature. A sensitivity analysis
419 was conducted to quantify the factors having greatest impact on ecosystem dynamics and
420 MeHg bioaccumulation. Of the parameters tested, phytoplankton growth rate was found to
421 have the greatest impact on the overall system dynamics and biota distributions, as well as
422 MeHg concentrations in the food web. A 20% increase in phytoplankton growth rate lead to a
423 47% increase in phytoplankton biomass and an 18% decrease in MeHg concentration in

424 phytoplankton. These results are consistent with the pelagic model discussed above (section
425 2.2.1).

426 The biomass of higher trophic levels also was stimulated by the increased growth rate as
427 were MeHg concentrations (~20% increase in zooplankton MeHg). Note this pattern of
428 biodilution occurring in phytoplankton but not in the zooplankton, contradicts freshwater
429 observations discussed previously. The increase of MeHg concentration in clams was dampened
430 (~4% increase) by other factors that influence bioaccumulation, such as the competition
431 between zooplankton and clams for the same food source in the model; zooplankton biomass
432 increased in response to increasing phytoplankton growth rate considerably more than clam
433 biomass in the model.

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

2.3 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 (Figure 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 samples were

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

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

481 In general, there were strong relationships among OC, N, and S in the Northeast coastal
482 sediments (Figure 5). The mean mass ratios (± 1 SD) of major elements in sediments were
483 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
484 stoichiometry of coastal sediments suggests that inputs of N largely drive the fixation of OC
485 through primary production. The mean OC/N ratio was greater than the Redfield ratio of 6.6
486 and may be attributed to a contribution of allochthonous organic matter from watersheds or
487 preferential loss of N 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 (Figure 5).

For many of the sediment sites, these stoichiometric relationships also extended to total Hg (Figure 6). For most of the sites (8 of 10) the mean Hg/N (ng g^{-1}) ratio is 83,300±83,100; and the Hg/OC (ng g C^{-1}) ratio is 8,300 ± 6,000, which is comparable to the ratio observed in surface sediments of Long Island Sound (7,900 ± 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, 2,960 ng g^{-1}) and exhibited a large Hg/OC ratio (49,000 ng Hg g OC^{-1}). The concentrations at Mill Creek are comparable to highly contaminated deposits previously reported for New York Harbor (40,000 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 (2,800 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 (Figure 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

508 organic C concentrations greater than these values. The highest %MeHg was observed at the
509 lowest sediment S concentrations and decreased with increasing S.

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

524 **2.4. Fish Mercury Response to N Loading**

525 In the previous case studies, measured and modeled MeHg in phytoplankton and
526 sediments are generally consistent with the conceptual model that elevated primary
527 production would result in lower MeHg net production and bioaccumulation at the base of the
528 food web, primarily due to reduced methylation and bioavailability of MeHg, as well as effects

529 of biodilution (Table 2; Figures 1, 2, and 7). Given the strong spatial and temporal
530 heterogeneity of Hg methylation and phytoplankton uptake, and the need to establish a clear
531 linkage with exposure, Hg concentrations in fish can be used as a measure of ecosystem MeHg
532 exposure to humans and wildlife predators (Harris et al., 2007; Sunderland, 2007). Finfish
533 integrate potential changes in food web structure that may occur with changing nutrient status,
534 and have tracked the impact of increased primary production and biodilution in fresh waters
535 (Essington and Houser, 2003; Chen and Folt, 2005). However, this finding has not previously
536 been described in estuarine or marine ecosystems.

537 To address this gap, in the fourth case study we examined Hg and MeHg concentrations
538 in multiple species of fish across a range of spatially distinct estuaries as well as within a single
539 estuary subject to differing nutrient loading. Data for Hg tissue concentration in eight species
540 of fish were compiled from the National Coastal assessment database
541 (http://www.epa.gov/emap/nca/index.html), and peer reviewed literature (Kannan et al., 1998;
542 Adams and Onorato, 2005; Moore et al., 2005; Hammerschmidt and Fitzgerald, 2006a; Adams
543 et al., 2010; Payne and Taylor, 2010; Senn et al., 2010; Stunz and Robillard, 2011; Szczebak and
544 Taylor, 2011). Estuaries and marine embayments from the North Atlantic Coast (11 water
545 bodies), the South Atlantic coast (4 water bodies), and the Gulf of Mexico (14 water bodies)
546 were considered. Whole body results were converted to fillet concentration using the
547 regression equation for all species of Peterson et al. (2005). Average Hg fish burdens were
548 compared to estimated estuary N loads using the SPARROW model (Alexander et al., 2000).

549 Correlation coefficients were low for six fish species (Pearson's correlation coefficient (r)
550 ranging from -0.21 to 0.25). For winter flounder (*Pseudopleuronectes americanus*, r = 0.77, n =
551 5 water bodies) and scup (*Stenotomus chrysops*, r = 0.71, n = 6), there was a positive
552 correlation, inconsistent with the expected decrease in fish Hg burdens with increasing N loads.
553 The lack of relationships between fish Hg concentrations and N loadings was likely affected by
554 extracting data from multiple sources; limited sample size for individual fish species; insufficient
555 data to evaluate confounding factors, such as fish body size; not accounting for differing Hg
556 inputs to the estuaries; inconsistent and limited range of N loading; and not considering the
557 variable response of estuaries to nutrient loadings due to their physical characteristics (Cloern,
558 2001). Future studies having more complete and consistent data sets would aid in determining
559 the overall relationship between nutrient loading and fish mercury biomagnification.

560 We also compared Hg in silverside collected from the effluent drainage waterways of
561 wastewater treatment plants (WWTP) with elevated nutrient concentrations to nearby
562 reference sites in San Francisco Bay, CA (Table 3). San Francisco Bay is TMDL listed for Hg due to
563 historic mining operations and other sources (Davis et al., this issue) and several drainages have
564 TMDL listed for elevated nutrients. Data were obtained from a three-year survey of spatial and
565 temporal patterns in biosentinel fish Hg concentrations. For this analysis 40 to 80 mm
566 Mississippi silverside (*Menidia audens*) were employed as a local biosentinel due to their wide
567 availability, tendency to stay within nearshore margin habitats, and limited movement range.
568 Their diets are largely composed of benthic invertebrates, augmented with zooplankton and
569 riparian insects (Greenfield and Jahn, 2010).

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

577

578 **3.0 Discussion**

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

588 Our model calculations (section 2.2) are limited by the difficulty of making an overall
589 prediction, as changes in nutrient levels can have a marked effect not only on the production
590 and partitioning of MeHg within the sediment and water column, but also on trophic dynamics.
591 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 penetrations and benthic interactions (Cloern, 2001). In San Francisco Bay, 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 (Figure 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

614 in coastal environments (Sunderland et al., 2006). As mentioned, a large number of TMDLs for
615 N have been established for coastal waters in the U.S., and management efforts are underway
616 in North America, Europe and Asia to control N loadings to estuaries to achieve water quality
617 standards. For example, in 2000, wastewater discharges to Boston Harbor were diverted 15 km
618 offshore, decreasing the external load of total N by about 80% (Benoit et al., 2009; Taylor,
619 2010). In five years following the decrease in N loading, harbor-wide concentrations of total N
620 decreased 35%, summer chlorophyll decreased 40%, and dissolved oxygen in bottom water
621 increased by 5%. Increases in benthic invertebrate community densities have also been noted
622 (Bricker et al., 2007; Taylor, 2010). In Long Island Sound, both Connecticut and New York have
623 aggressively pursued N control strategies in wastewater treatment plants to achieve a 30%
624 decrease in N load. These states also are conducting stormwater permitting and non-point
625 source control programs to achieve an additional 10% decrease in N inputs. Similarly, the
626 Tampa, FL, region has been actively controlling N inputs to Tampa Bay resulting in a 60%
627 decrease since the 1970s (Bricker et al., 2007).

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

635 before and following the implementation of nutrient control programs for estuaries to examine
636 responses and the effect on MeHg concentrations in biota.

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

651 As an example, Hg concentrations in surface sediments of New York/New Jersey Harbor
652 decreased 50-80% between the 1960s and the 1990s (Balcom et al., 2010; CARP, 2007), with an
653 associated decrease in Hg concentrations in the water column (Sanudo-Wilhelmy and Gill,
654 1999). Much of the input of Hg (~90%) and MeHg (~55%) to New York/New Jersey Harbor is
655 derived from the Hudson and East Rivers (Balcom et al., 2010; 2008). Inputs of MeHg from the

656 sediment are relatively small (~25%). This pattern suggests that MeHg in the Harbor is likely to
657 respond rapidly to changes of external Hg loadings. The Bay of Fundy is likely to respond
658 similarly (Sunderland et al., 2010). For such ecosystems, large and rapid changes in Hg and
659 MeHg loading could easily overwhelm the effects of changing N loading.

660 However, in contrast, inputs of MeHg from the sediment appear to be the major source
661 to the food web in Long Island Sound (Balcom et al., 2004; Hammerschmidt and Fitzgerald,
662 2006a) and there is a large legacy of Hg contamination in the sediment (Varekamp et al., 2003).
663 For such ecosystems, changes in N loading could have a marked impact on benthic MeHg
664 production. Sediment cores throughout the Sound have shown that concentrations in surface
665 sediment have decreased to a lesser degree (~40%; Varekamp et al., 2003) than found in New
666 York Harbor. At this time, it is not possible to conclude what impacts that decreases in N
667 loading will have on levels of MeHg in estuarine and coastal food chains.

668 Time series investigations would be valuable, overcome some of the limitations
669 associated with spatial studies and provide insight on the mechanisms behind Hg-nutrient
670 interactions. The time scale of the processes is undoubtedly a critical aspect of understanding
671 Hg-nutrient linkages. For example, water column processes could be driven by short-term
672 changes, such as spring algal blooms resulting in seasonal biodilution of MeHg in a temperate
673 estuary, or long-term changes, such as regulatory controls on watershed nutrient loading. In
674 contrast Hg-nutrient interactions that are controlled by sediment processes are likely to be
675 long-term phenomena. Note, it seems likely that, for most estuaries adjacent to developed
676 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.

4.0 Acknowledgements

This publication was made possible by NIH Grant Number P42 ES007373 from the National Institute of Environmental Health Sciences (to CC and RM). Support also was provided by New York State Energy Research and Development Authority (to CTD), the U.S. National Science Foundation (to CRH, and to RM and CG), and the Hudson River Foundation (to RM). The Regional Monitoring Program in San Francisco Bay and the US EPA STAR Fellowship Program (BG). We thank D. Slotton and S. Ayers for field sample collection and mercury analysis in South

699 San Francisco Bay and L. McKee for reviewing portions of the manuscript. We thank P. Balcolm,
700 M. Montesdeoca, I Allen, K.F. Lambert, R. Chemerys, S. Reems, K. Driscoll and M. Hale for their
701 help with this analysis and paper.

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Figure Captions

Figure 1. Schematic diagram illustrating the response 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, grey for the sediment-water interface and white for sediments.

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Figure 3.) The modeled concentrations of methylmercury in phytoplankton in different regions of the Chesapeake Bay, as differentiated by the differences in sediment organic content (% OM)

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

Figure 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.

Figure 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.

Figure 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.

Figure 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*interquartile range/sqrt(n), corresponding to approximately a 95% confidence interval for difference in medians.]

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 2011a, b.

Resource	Contaminant	303(d) Waterbody impairments[c]	Approved TMDLs[d]
Total US waters	Mercury	5,004	6,946
Total US waters	Nutrients[b]	16,075	8,102
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.

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]	Phytoplankton MeHg: % of total Hg	Phytoplankton MeHg: 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
	Bay of Fundy[f]	0.06	0.15	6	3.4
Eutrophic	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 (in review)
[d]Hammerschmidt and Fitzgerald (2006a,b)
[e]Baeyens et al. (2003)
[f]Sunderland et al. (2010)
[g]Balcom et al. (2004)
[h]Balcom et al. (2008)

1085 Table 3. Ammonium and NO_x (NO_3^- + NO_2^-) in four sites exposed to wastewater treatment plant
1086 discharge, and ambient (background) concentrations in South San Francisco Bay.

Source	Site	Average ammonium (mg N/L)	Annual ammonium (metric tons)	Annual NOx (metric tons)
WWTP[a]	East Bay Dischargers Authority*#	20.38	2284	99
WWTP[a]	San Jose/Santa Clara^	0.58	86	1377
WWTP[a]	Palo Alto^	0.30	16	593
WWTP[a]	Sunnyvale^	2.13	37	164
ambient[b]	Lower South Bay	0.08		
ambient[b,c]	South Bay	0.06		

1087 * Combines discharges from six wastewater treatment facilities
1088 # Secondary treatment facility
1089 ^ Advanced treatment facility
1090 a. Averaged across flow class data in McKee and Gluchowski, 2011; annual averages are from 2004-2010
1091 b. Average of 2004-2010 data from the Regional Monitoring Program (SFEI, 2010)
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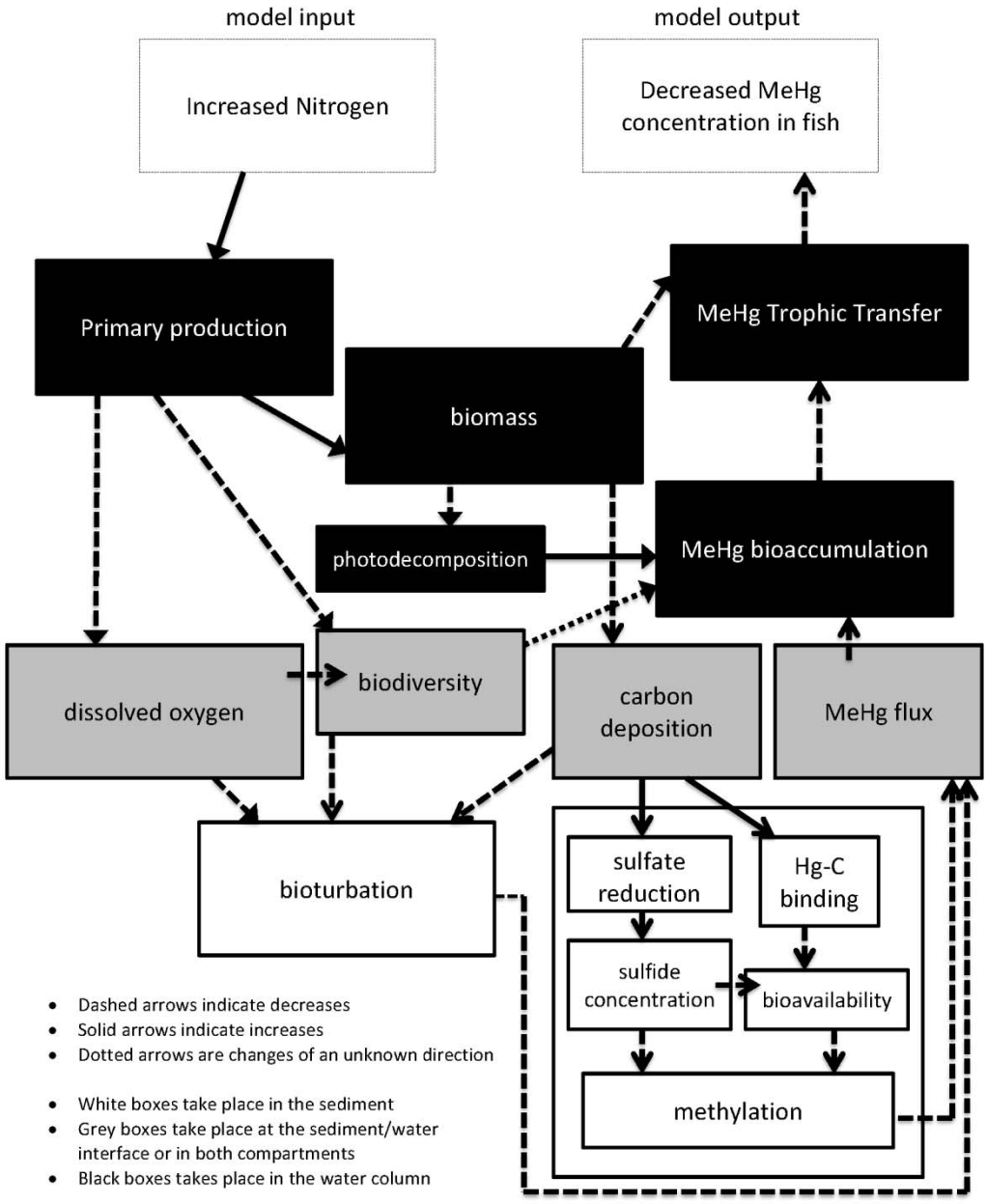

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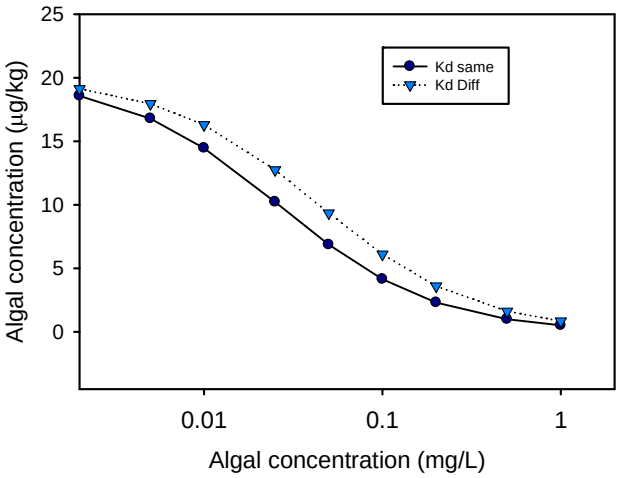

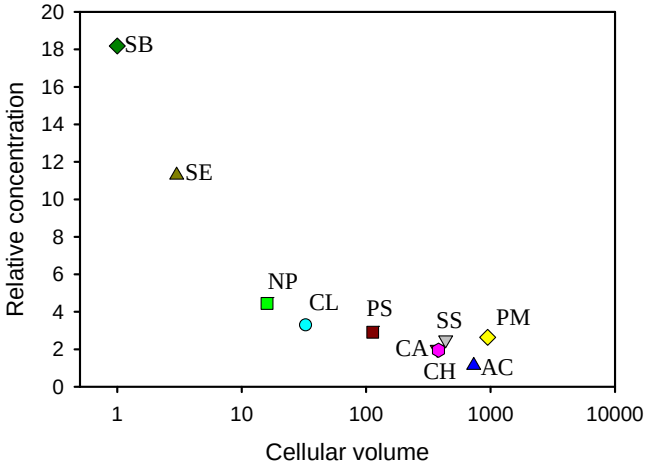

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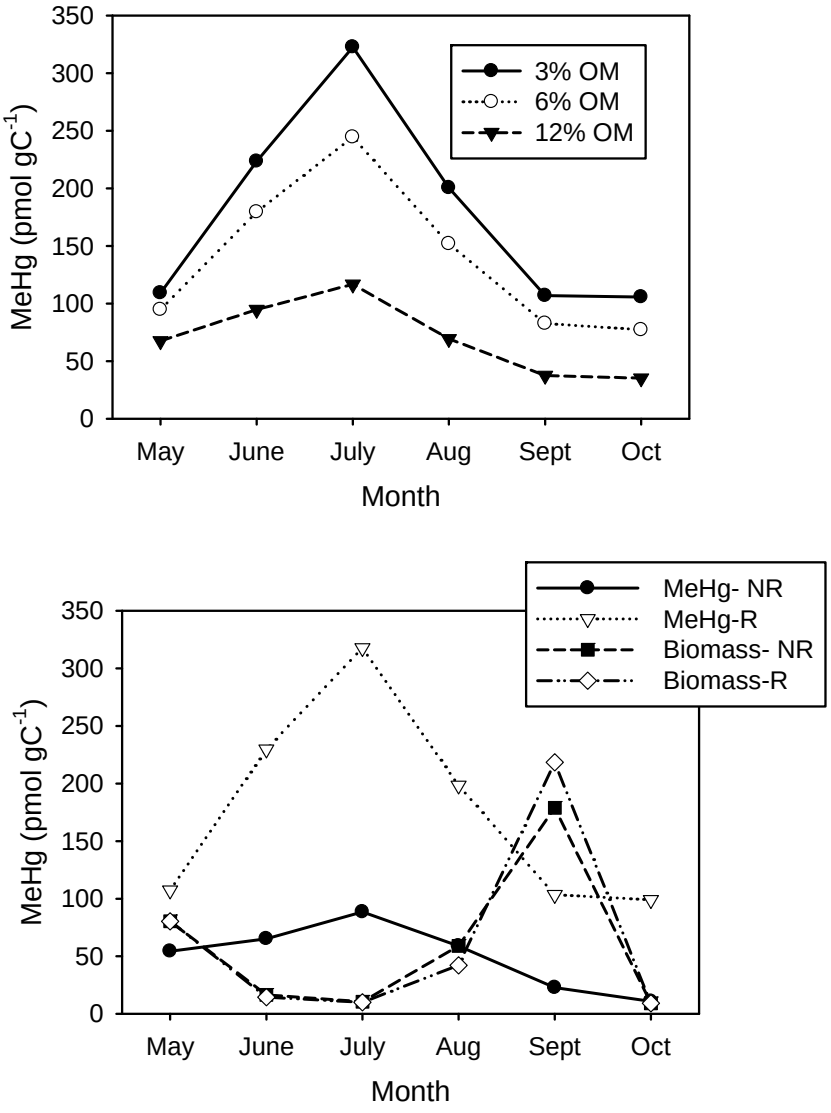

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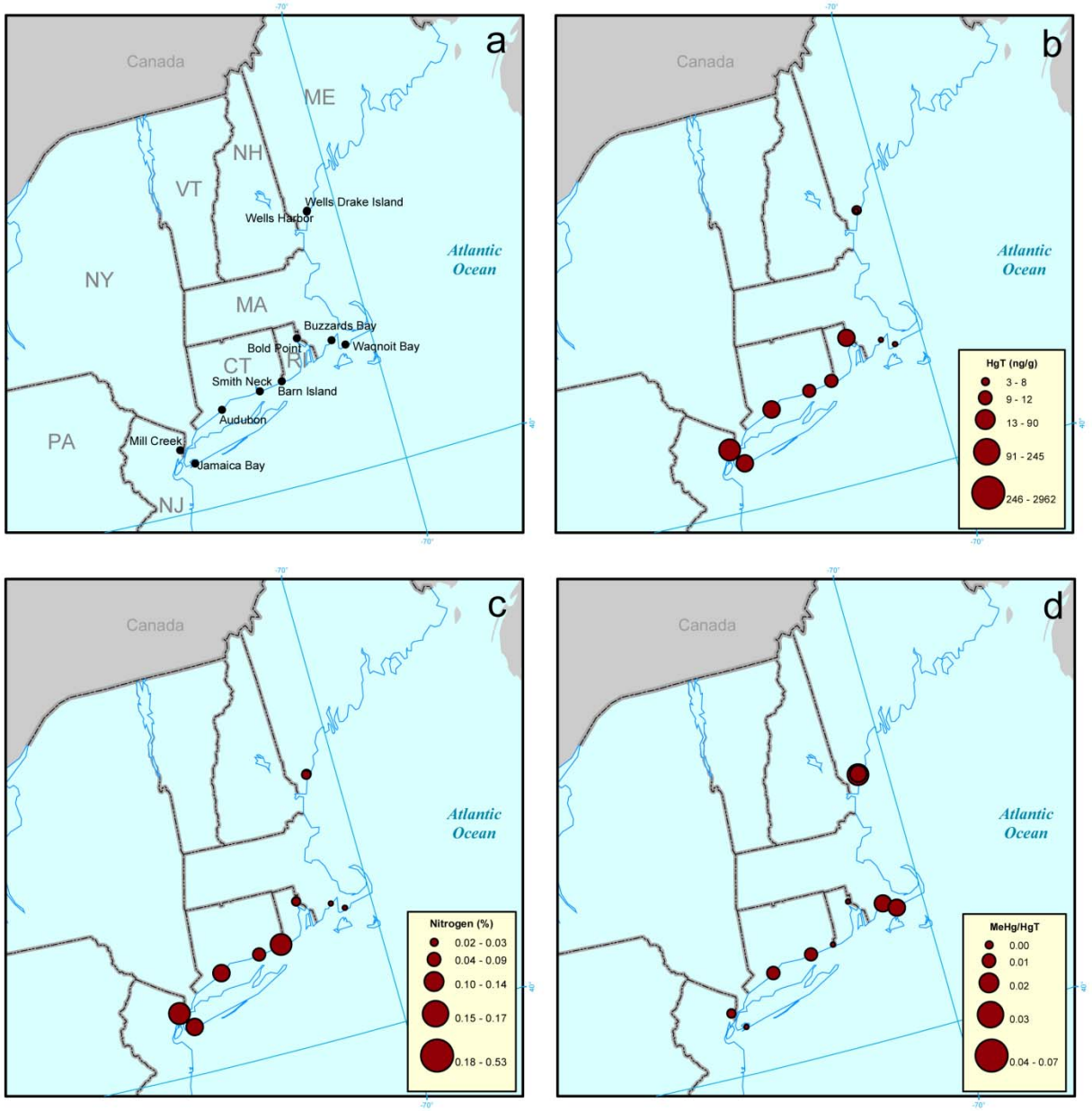

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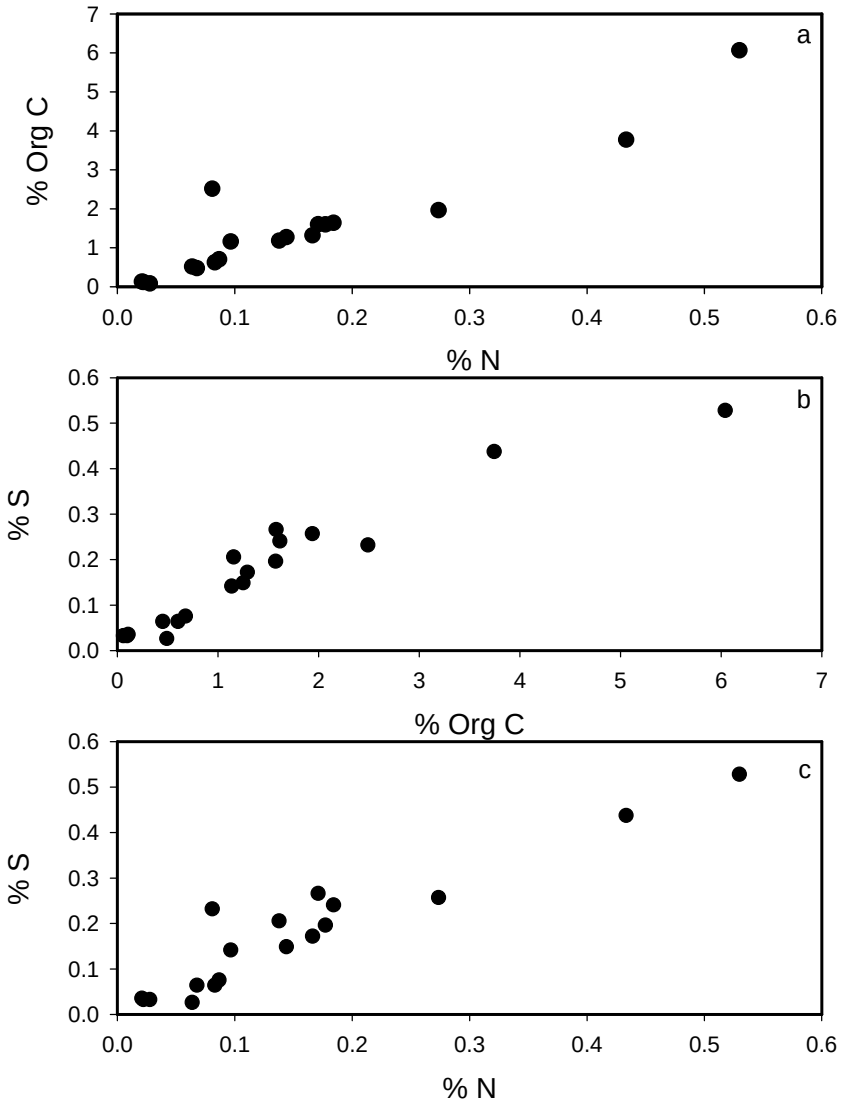

1131

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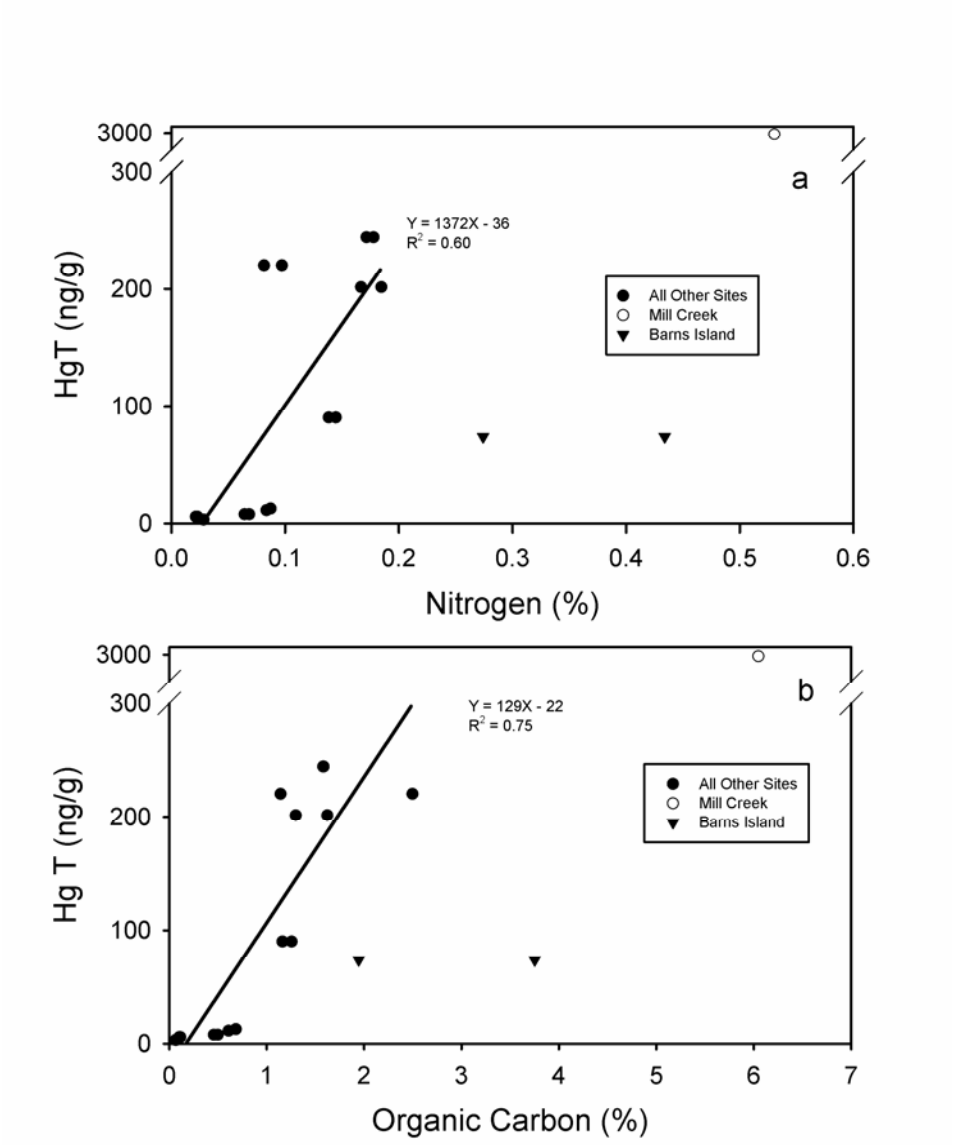

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1138 coastal sediments. Only closed circles are included in regression analysis.

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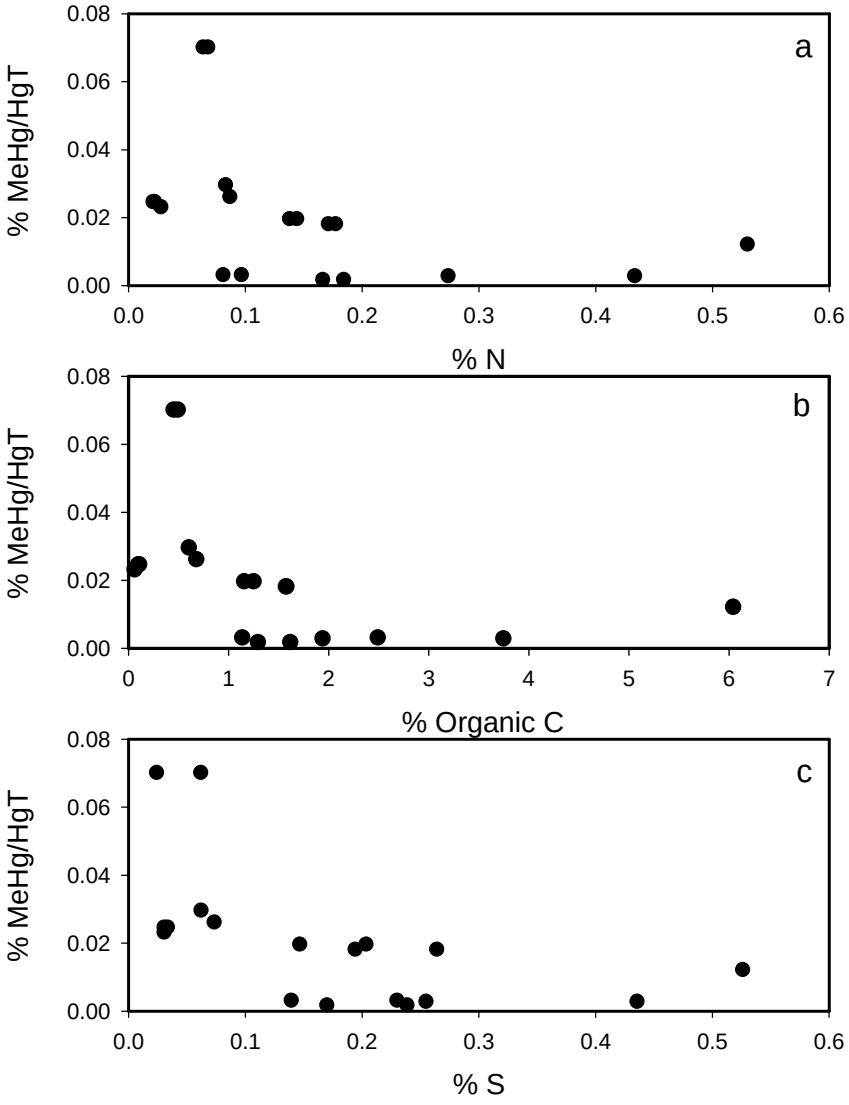
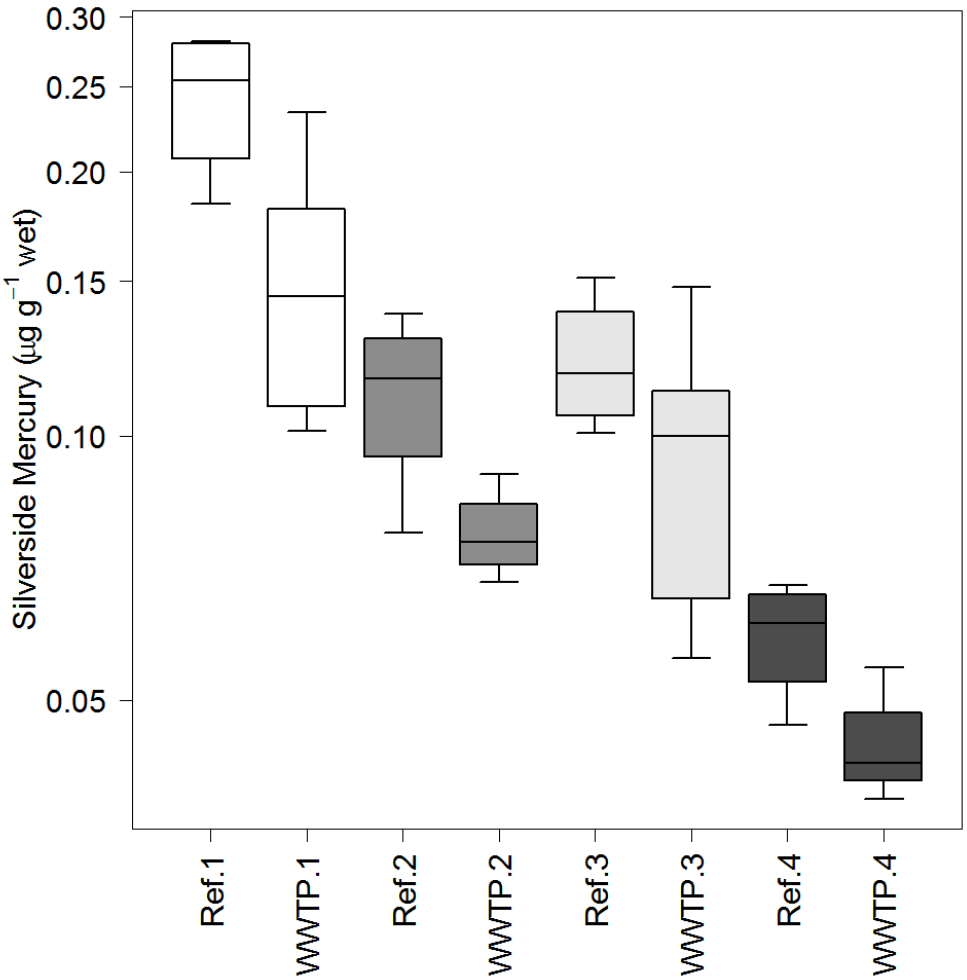


1140

1141 Figure 7. The percent of total Hg occurring as MeHg (%MeHg) as a function of N (a), organic C (b) and S
1142 (c) in Northeast coastal sediments.

1143

1144



1145

1146 Figure 8. Mercury concentrations in silverside in wastewater treatment plant (WWTP) and reference
1147 station pairs in South San Francisco Bay. Station pairs are indicated by corresponding shading. Results
1148 are box and whiskers plots of wet weight mercury concentrations. For each site, the center line
1149 represents the median, the bottom and top of the boxes indicate the first and third quartiles, and the
1150 whisker ends correspond to approximately 95% confidence intervals for difference in medians. Note log
1151 scale Y axis.

1152 [The whisker ends represent ± 1.58*interquartile range/sqrt(n), corresponding to approximately a 95%
1153 confidence interval for difference in medians.]