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

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30 Abstract

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

52 exacerbate problems associated with Hg contamination. Additional focused research and
53 monitoring are needed to critically examine the link between nutrient supply and Hg
54 contamination of marine waters.

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58 **Keywords: eutrophication; coastal ecosystems; marine ecosystems; mercury; nitrogen;**
59 **nutrients**

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68 This research has not involved human subjects or experimental animals.

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78 **1.0 Introduction**

79 **1.1 Background on nutrients (nitrogen), organic carbon and mercury in estuaries**

80 Increases in mercury (Hg) contamination of marine ecosystems, primarily from
81 anthropogenic inputs, have been primarily manifested through elevated concentrations of the
82 more bioaccumulative form methylmercury (MeHg) in food webs. Thousands of estuaries and
83 freshwaters in all states and two territories of the United States are listed by the Environmental
84 Protection Agency as impaired due to high concentrations of Hg in fish (Table 1). However,
85 most studies do not show a linear relationship between Hg inputs and MeHg concentrations in
86 higher trophic level organisms due to many ecosystems factors that can modify the causality.
87 We hypothesize that one such factor, the nutrient status, alters Hg dynamics in marine
88 ecosystems, and this is the focus of this paper.

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

98 The majority of estuaries that have been evaluated in the U.S. show signs of
99 eutrophication—65% of the assessed ecosystems, representing 78% of assessed estuarine area,

100 have been classified as moderately to severely degraded by nutrient over-enrichment (Bricker
101 et al., 2007). In addition to the direct effects of nutrients on ecosystem eutrophication, excess
102 N can potentially have an impact on the cycling and fate of many other contaminants, such as
103 Hg, due to shifts in organic matter production and subsequent impacts on redox status and
104 habitat. Like N, Hg is a global pollutant and can have substantial impacts on coastal ecosystems
105 (Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009; Kim et al., 2008).

106 Increased loadings of nutrients to estuaries lead to more frequent harmful algal blooms,
107 hypoxic and anoxic bottom waters, loss of sea grasses, reduced fish stocks, and changes in
108 trophic dynamics and biogeochemical cycles (Boynton et al., 1995; Hallegraeff, 1993; Paerl,
109 1988, 1995, 1997; Valiela et al., 1990; Valiela and Costa, 1988; Cloern, 2001). The over-
110 enrichment of nutrients in estuaries promotes excessive growth of planktonic algae or
111 cyanobacteria mats, which can shade-out sea grass and other submerged aquatic vegetation
112 that provide critical habitat for fish and other marine organisms. Thus, eutrophication often
113 leads to greater pelagic versus benthic production in estuaries (Paerl et al., 2001; Cloern, 2001).
114 Furthermore, when the algae die and decompose, oxygen in bottom water is consumed. Low-
115 oxygen conditions, or hypoxia, impair habitat of macrofauna, influence the cycling of elements
116 at the sediment-water interface, and can alter the dynamics of microbial processes, such as Hg
117 methylation and MeHg demethylation. The degree of eutrophication an estuary can tolerate
118 without adverse effects depends on the amount of reactive N it receives as well as its physical
119 characteristics, including size, depth, volume of freshwater runoff, and rate of tidal flushing
120 (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

143 freshwater fish decrease under conditions of high nutrient loading and in watersheds with
144 disturbed land cover (i.e., agricultural, urban lands; Chen et al., 2005; Kamman et al., 2004).
145 Note that while freshwater ecosystems with no water exchange are very different from coastal
146 ecosystems, which have more limited and nuanced responses to nutrient loading, exhibit
147 salinity stratification and variable tidal fluxes and ocean inflows, much can be learned from the
148 freshwater literature in the investigation of the effects of nutrient inputs on Hg dynamics in
149 marine ecosystems (Cloern, 2001). For example, in South San Francisco Bay, a phytoplankton
150 bloom caused a three-fold decrease in phytoplankton MeHg concentrations (Luengen and
151 Flegal, 2009) similar to the biodilution phenomenon observed in freshwaters.

152 In this paper we advance the hypothesis that elevated inputs of limiting nutrients (e.g.,
153 N) to coastal waters and the resultant increase in organic carbon (OC) levels in the water
154 column and sediments, decrease Hg availability and ultimately decrease trophic transfer and
155 fish Hg concentrations. We present a conceptual model of how changes in N loading might
156 alter Hg dynamics, net methylation, and fish MeHg concentrations. We follow this with a series
157 of case studies providing information to evaluate this hypothesis and conceptual model. Note
158 that while our analysis is primarily focused on coastal ecosystems which experience the largest
159 impacts of increases in nutrient (Cloern, 2001; Boyce et al., 2010) and Hg loadings, we also
160 make use of observations from the open ocean (section 2.1) and show that comparable factors
161 are important in the pelagic realm (section 2.2.1).

162

163

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 and bioavailability remain constant (Figure 1). As discussed further below
173 (see section 2.2), this hypothesis is valid only if there are not substantial shifts in plankton
174 community composition (e.g., cell size, growth rate) in concert with changes in nutrient
175 loadings. Eutrophication also typically results in loss of ecosystem biodiversity (Carpenter et al.,
176 1998). Changes in phytoplankton species composition and growth rate could impact the
177 concentration of MeHg in primary producers and, as a result, in organisms at the higher trophic
178 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.
184 On average, partition coefficients for Hg increase by almost 3 orders of magnitude in coastal
185 sediments as the organic matter content increases from 2 to 15% (Hollweg et al., 2010).

186 Reduced-sulfur functional groups, on particulate and dissolved organic matter, strongly bind
187 ionic Hg and decrease its availability for formation of MeHg by microorganisms in sediments
188 (Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2009; Skjellberg, 2008). Dissolved organic
189 matter plays a large but opposing role to that of sediment organic matter, helping to partition
190 Hg in sediment pore waters but not directly increasing methylation rates. This mechanism
191 suggests that eutrophication decreases metal bioavailability by increasing sediment OC
192 concentrations and consequent Hg binding. The relationship between Hg concentration and
193 %OC in sediments is linear in many (e.g., Varekamp et al., 2000; Hammerschmidt et al., 2008)
194 but not all (e.g., Hollweg et al., 2009; Mason and Lawrence, 1999) coastal marine systems.

195 Secondly, organic matter is mineralized in anoxic coastal sediments principally by
196 sulfate-reducing bacteria (Capone and Kiene, 1988), which are thought to be the primary group
197 of Hg methylating microorganisms (Compeau and Bartha, 1985; Gilmour et al., 1992; Figure 1).
198 The highest net production of MeHg generally occurs at moderate levels of sulfate reduction
199 (Gilmour et al., 1992). However, with increasing loading of nutrients, organic matter and
200 associated sulfate reduction the production of sulfide increases which changes the speciation
201 of dissolved ionic Hg (Benoit et al., 1999a) and decreases its availability to methylating bacteria
202 and the formation of MeHg (Benoit et al., 2003, 2001, 1999b; Hammerschmidt and Fitzgerald,
203 2004; Hammerschmidt et al., 2008; Hollweg et al., 2009, 2010).

204 Greater respiration of organic matter at the sediment-water interface also reduces
205 levels of dissolved oxygen, which influence the abundance and activity of benthic macrofauna
206 (Dauer et al., 1992; Diaz and Rosenberg, 1995; Montagna and Ritter, 2006; Figure 1).

207 Bioturbation has been shown to increase both MeHg production in coastal sediments (Benoit et
208 al., 2009; Hammerschmidt et al., 2004) and facilitate its mobilization to overlying water
209 (Hammerschmidt and Fitzgerald, 2008). Hence, increased loadings of N and resultant sediment
210 organic matter are likely to decrease both MeHg production in sediments and the biologically
211 enhanced flux of MeHg from sediments (Hammerschmidt and Fitzgerald, 2004). Conversely,
212 higher sulfide concentrations change the speciation of aqueous MeHg from control by dissolved
213 organic matter to complexation with inorganic sulfide ligands. Given the larger diffusion
214 coefficient of the smaller inorganic complexes, such a shift in complexation in anoxic
215 environments could enhance the diffusive flux of MeHg from sediments (Hollweg et al., 2010).

216 Past experimental and field studies indicate that bioaccumulation of MeHg in benthic
217 and pelagic fauna decreases with increasing sediment OC (Figure 1). Lawrence and Mason
218 (2001) found that amphipods exposed to Hg in OC-rich sediment accumulated less Hg than
219 those in sediments with lower organic contents. Across sites that vary in Hg and OC supply in
220 the Northern Coastal Shelf region of the Gulf of Maine, benthic-sediment concentration factors,
221 a measure of bioavailability of MeHg to marine organisms, decrease with total OC in sediments
222 (Chen et al., 2009). These observations suggest that production, bioavailability, and/or
223 assimilation of MeHg decreases with increasing organic content of sediments.

224 Increased primary production also will decrease penetration of light in the water column
225 and cause a shift in primary production from benthic to pelagic autotrophs (Paerl et al., 2001).
226 Such a shift will change the pathways whereby MeHg enters the food web (Figure 1). The loss
227 of submerged aquatic vegetation may affect the extent of reducing conditions in estuaries and

228 impact fisheries by loss of habitat. However, and in contrast to the processes by which N
229 loadings are likely to decrease MeHg levels in fish, reduced light penetration associated with
230 increased algal production should limit photodecomposition of MeHg, increasing the amount
231 bioavailable, and thus enhancing bioaccumulation. Photodecomposition is proposed to be an
232 important loss mechanism of MeHg in the surface waters of some coastal ecosystems (Balcom
233 et al., 2004; Monperrus et al., 2007; Whalin et al., 2007; Figure 1). The effects of changes in
234 photodecomposition notwithstanding, the overall consequence of increased nutrient loadings
235 to estuaries should be to decrease fish MeHg concentrations.

236 In this conceptual model we have laid out a number of mechanisms by which increased
237 nutrient loading might act to decrease Hg bioavailability, MeHg production and MeHg
238 concentrations in biota (Figure 1). The extent to which these individual mechanisms are
239 important will depend, in part, on the source of ionic Hg and MeHg inputs to diverse marine
240 ecosystems. Moreover, the response of primary production to a change in loading of the
241 limiting nutrient is complex and variable across coastal waters due to factors such as tidal
242 exchange, hydraulic residence time, photic depth and the importance of suspension feeders
243 (Cloern, 2001). Depending on the watershed area and associated watershed sources, depth,
244 area, bathymetry and exchange with the open ocean, substantial sources of ionic Hg and MeHg
245 to coastal ecosystems could include atmospheric deposition, riverine inputs, coastal sediments
246 and/or the open ocean (Balcom et al., 2010, 2008; Hammerschmidt and Fitzgerald, 2004; Harris
247 et al., this issue; Sunderland et al., this issue, 2009). For example if ionic Hg and MeHg inputs
248 are largely derived from riverine sources, then the impacts of nutrients on Hg dynamics might
249 be manifested largely through enhanced deposition (removal) from the water column to

250 sediments, biodilution associated with increased primary, secondary and tertiary production or
251 decreases in photodecomposition (e.g., Bay of Fundy, New York Harbor). In contrast, if MeHg
252 supply to the coastal ecosystem largely originates from internal sediments, then increases in
253 sediment organic matter binding of ionic Hg or elevated sulfide limiting MeHg production could
254 be important mechanisms by which increased nutrient loading decrease fish Hg concentrations
255 (e.g., Long Island Sound).

256

257 **1.3 Approaches to test hypothesis**

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

266 In our examination of the nutrient-MeHg conceptual model we utilized modeling and cross-
267 site analysis. We compiled information from three spatial studies to obtain information that
268 would inform aspects of the hypothesis. First, we evaluated phytoplankton MeHg from a suite
269 of marine ecosystems with contrasting nutrient status, including coastal and open ocean
270 environments. Second, an ocean nutrient-production model and a shallow coastal model were

271 applied to illustrate some of the complexities associated with increases in production, driven by
272 changes in nutrient loadings, in the trophic transfer of MeHg. Third, we examined patterns of
273 nutrients and Hg in the sediments at ten coastal sites in the northeastern United States. These
274 sites exhibit a range of nutrient and Hg concentrations in sediments and were used to probe
275 the conceptual model. Finally, we evaluated Hg concentrations in sport fish in response to
276 reactive N loading across estuaries in the Atlantic and Gulf coasts, and forage fish Hg
277 concentrations in San Francisco Bay in response to increases in reactive N loading.

278

279 **2.0 Case Studies**

280 **2.1 Comparison across Marine Nutrient Gradient**

281 Phytoplankton bioconcentrate Hg species from water, with MeHg accumulating
282 primarily in the cytoplasm and ionic forms of Hg bound to cell membranes (Mason et al., 1996).
283 If biodilution of MeHg were to occur in marine ecosystems, then one would expect MeHg
284 concentrations in phytoplankton to decrease with greater N loadings and associated primary
285 production. However, such a linear relationship may be confounded by other factors such as
286 changes in the growth rate and size of plankton at the base of a pelagic food chain (see Section
287 2.2). While a wide range of primary production exists among coastal and open-ocean environs
288 ($\sim 20\text{--}3500 \text{ g C m}^{-2} \text{ y}^{-1}$; Behrenfeld and Falkowski, 1997), an empirical investigation of such a
289 gradient is made difficult by differences in MeHg loadings to surface waters inhabited by
290 phytoplankton. For example, it is reasonable to expect that shallow estuaries highly
291 contaminated with Hg would have greater supply of MeHg to surface waters than an
292 oligotrophic surface gyre in the open ocean. One additional factor contributing to this

293 difference is the tight coupling between the water column and sediments in some coastal
294 waters, and the lack of any benthic influence on an oligotrophic open-ocean environment. Note
295 that the benthic influence is also likely small for offshore areas of coastal ecosystems such as
296 the Gulf of Mexico and the Gulf of Maine (Harris et al., this issue; Sunderland et al., this issue).
297 Differences in MeHg inputs/availability can be normalized by calculating a bioaccumulation
298 factor (BAF; $L\ kg^{-1}$) for phytoplankton, which is the wet-weight concentration of MeHg in
299 phytoplankton divided by that in filtered water.

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

315 **2.2.1 Examination of the Impact of Biomass Changes on Methylmercury in Pelagic Food**
316 **Chains**

317
318 As noted above, increased inputs of nutrients to coastal environments have led to
319 eutrophication and enhanced oxygen depletion (e.g., Rabalais et al., 2002). Nutrient inputs
320 together with changing climate are likely to increase the extent of oxygen minimum zones in
321 the ocean (Deutsch et al., 2011). Investigators have noted that chlorophyll *a* concentrations in
322 the North Pacific near Hawaii have increased substantially in the recent past (200% between
323 1968 and 1985; Venrick et al., 1987) although a recent analysis shows the opposite trend across
324 much of the open ocean (Boyce et al., 2010). Given these dynamics, a simple (partition-based)
325 bioaccumulation model was derived to examine the impact of changes in phytoplankton
326 biomass on MeHg concentrations in open-ocean fish.

327 The base case simulation was developed from literature values (total MeHg 0.02 ng L^{-1})
328 and it was assumed that the MeHg concentration in the water column was not dependent on
329 biomass (see discussion below). The following ecosystem parameters were used in the base
330 case (DOM = $2.075 \text{ mg C L}^{-1}$; algal biomass = 0.025 mg L^{-1} dry weight) (e.g. Shiomoto and
331 Hashimoto, 2000). All trophic dynamics were linearly constrained to the algal biomass (i.e.,
332 bacterial mass twice and zooplankton one tenth the algal biomass on a dry weight basis). In the
333 model, the DOM concentration also was varied with algal biomass (ratio of 35 for DOM: algal
334 mass). Partition coefficients (dry weight basis) between water and the various biota and the
335 DOM were based on the literature (Kaiser and Benner, 2009; Kim et al., 2008; Mason et al.,
336 1996). It is assumed that only the fraction of MeHg that is not complexed with DOM is
337 bioavailable to the food chain (e.g. Mason et al., 1996; Lawson and Mason, 1998). Two cases

338 were considered for this open ocean analysis: 1) the partition coefficients between water and
339 each of DOM, phytoplankton, and bacteria were the same (10^6 L kg^{-1}) with the trophic transfer
340 on a mass basis of a factor of three between phytoplankton and zooplankton; and 2) the DOM
341 partition coefficient was half and the bacterial coefficient twice that of the phytoplankton,
342 which was kept at 10^6 L kg^{-1} . Under both cases, MeHg in the water column was complexed with
343 DOM (66% in Case 1, 48% in Case 2 for the base case values) to a greater degree than occurred
344 as inorganic (e.g., Cl^-) complexes (32% in Case 1, 46% in Case 2). The remainder of the MeHg
345 was partitioned among the various biota classes, with similar concentrations for phytoplankton
346 and bacteria in Case 1 (6.3 ng g^{-1}), and 4.6 ng g^{-1} for phytoplankton in Case 2. The bioavailable
347 MeHg concentration was 0.006 ng L^{-1} in Case 1 and 0.009 ng L^{-1} in Case 2.

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

356 Empirical evidence and model calculations suggest an increase in the extent of oxygen
357 minimum zones in the ocean (e.g. Duetsch et al., 2011). This change could enhance
358 methylation within these regions given studies which suggest a linear relationship between net
359 Hg methylation and organic matter decomposition rate in the marine water column (Cossa et

360 al., 2011; Heimbürger et al., 2010; Sunderland et al., 2009). Thus, we anticipate a proportional
 361 increase in the production of MeHg with an increase of algal biomass decomposition upon
 362 sedimentation. Increasing the total MeHg concentration to 0.04 ng L^{-1} and the algal biomass to
 363 0.05 mg L^{-1} (a doubling of both) yields an algal MeHg concentration of 13.7 ng g^{-1} , a 34%
 364 increase over the base Case 1, suggesting that enhanced net production of MeHg may
 365 compensate for biodilution effects on MeHg concentrations in algae; similarly, for the opposite
 366 scenario.

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

$$375 \quad Q = U/\mu = 4\pi R^2 PC \quad (1)$$

376 *Where:* R = radius

377 P = membrane permeability

378 C = external Hg concentration

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

$$380 \quad Q/V = U/\mu V = \frac{4\pi R^2 PC}{\frac{4}{3}\pi R^2} = 3 PC/R \quad (2)$$

381 So, at the same uptake rate, slower growing organisms will have a greater Q . Overall,
382 the cellular concentration is then defined by the inverse of the product of the relative “radius”
383 (i.e., V/A) and μ . So, while increased eutrophication could be expected to lead to greater MeHg
384 bioaccumulation if methylation were stimulated within the ecosystem, such an increase could
385 be offset by the decrease in cellular quota of large phytoplankton ($> 10 \mu\text{m}$) relative to smaller
386 plankton ($<1 \mu\text{m}$). Such effects have been documented in freshwater phytoplankton (Pickhardt
387 and Fisher, 2007). The cellular volume of phytoplankton can vary over three orders of
388 magnitude and the impact of this effect on concentration is substantial, about an order of
389 magnitude difference (Figure 2b). While these overall simulations suggest that the overall effect
390 of increased nutrient input is a decrease of MeHg in the food web, a more detailed model is
391 needed to examine the complex interactions that exist among food web components, growth
392 rates, bioavailability, and other factors. As the focus of the paper is on coastal ecosystems, the
393 importance of benthic-pelagic coupling and sediment sources also needs to be considered (see
394 section 2.2.2)

395 396 **2.2.2 Examination of the Impact of Eutrophication on Methylmercury in a Shallow Coastal** 397 **Ecosystem** 398

399 A more detailed examination of the impact of biomass on MeHg bioaccumulation was
400 conducted by Kim et al. (2008) who developed a biogeochemical cycling and bioaccumulation
401 model that included net methylation in sediments that was tied to sediment biogeochemistry,
402 and which included sediment resuspension/particle settling and diffuse inputs from sediments
403 of both MeHg and nutrients. The authors developed their MeHg bioaccumulation model based

404 on mesocosm experiments that depicted the interactions between the sediment and water
405 column applicable to a shallow estuarine coastal environment (Kim et al., 2004, 2006; Porter et
406 al., 2010).

407 The Kim et al. (2008) model included one phytoplankton and two zooplankton size
408 classes as well as filter-feeding clams. Phytoplankton growth rate was dependent on nutrient
409 concentrations and light levels. Bioavailability of MeHg to the phytoplankton was dependent on
410 DOM concentration and dissolved MeHg speciation, and trophic transfer to invertebrates was
411 based on feeding rates and assimilation efficiencies from the literature. A sensitivity analysis
412 was conducted to quantify the factors having greatest impact on ecosystem dynamics and
413 MeHg bioaccumulation. Of the parameters tested, phytoplankton growth rate was found to
414 have the greatest impact on the overall system dynamics and biota distributions, as well as
415 MeHg concentrations in the food web. A 20% increase in phytoplankton growth rate lead to a
416 47% increase in phytoplankton biomass and an 18% decrease in MeHg concentration in
417 phytoplankton. These results are consistent with the pelagic model discussed above (section
418 2.2.1).

419 The biomass of higher trophic levels also was stimulated by the increased growth rate as
420 were MeHg concentrations (~20% increase in zooplankton MeHg). Note this pattern of
421 biodilution occurring in phytoplankton but not in the zooplankton, contradicts freshwater
422 observations discussed previously. The increase of MeHg concentration in clams was dampened
423 (~4% increase) by other factors that influence bioaccumulation, such as the competition
424 between zooplankton and clams for the same food source in the model; zooplankton biomass

425 increased in response to increasing phytoplankton growth rate considerably more than clam
426 biomass in the model.

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

438 Not surprisingly, the highest concentrations of MeHg in the food chain were found at
439 the higher methylation rates (i.e., lowest sediment organic content; Figure 3). Again, the effect
440 was dampened for the filter feeders, but overall these results show that the impact of changes
441 in methylation rate, due to differences in sediment organic matter, propagates through the
442 ecosystem and is reflected in the food web (Figure 3a). The linkage between MeHg
443 bioaccumulation and changes in sediment Hg methylation rate is exacerbated when sediment
444 resuspension is invoked as a mechanism linking the two pools. In the absence of sediment
445 resuspension, the transfer of MeHg from sediment to the water column was much less efficient
446 and the overall ecosystem response less dynamic (Kim et al., 2008; Figure 3b). Clearly, the

447 impact of changes in sediment organic matter on bioaccumulation is dependent, in part, on the
448 rate of transfer of MeHg from the sediment to the water column. The results of the model
449 illustrate that all processes (dissolved flux from sediment, resuspension and particle deposition)
450 should be considered when considering the net transfer of MeHg from sediment to the water
451 column (e.g., Sunderland et al., 2010).

452

453 **2.3 Northeastern Atlantic Estuaries**

454

455 The nutrient-MeHg conceptual model also was examined by comparing distributions of
456 nutrients and Hg species in sediment at ten intertidal ecosystems in the northeastern United
457 States (Figure 4). Sediments were sampled in 2008 at locations ranging from Mill Creek in the
458 south, a highly contaminated site in New Jersey to Wells, Maine, in the north. Duplicate
459 samples were collected at all sites, except Waquoit Bay, MA. A total of 19 samples were
460 collected. Sediments were sampled with a 6-cm diameter coring tube, and the top 2 cm of
461 material from nine cores were composited into a single sample. Aliquots of the homogenized
462 sediment composite were freeze dried and analyzed for total Hg, MeHg, and OC, N, and S
463 concentrations.

464 We selected the Northeast sites for analysis because of the contrasting spatial patterns
465 of nutrient and Hg concentrations (Figure 4). In this analysis, we assume that sediment N
466 concentrations are a proxy for N loadings. Relatively high N and OC concentrations in sediment
467 were evident at sites toward the south, including Mill Creek, NJ; Jamaica Bay, NY; Audubon, CT;
468 Smith Neck, CT; Barn Island, CT; and Bold Point, RI. Total Hg concentrations in sediment were

469 exceedingly high at Mill Creek and lower, but still relatively high, at Jamaica Bay, Audubon and
470 Bold Point. Finally, the fraction of total Hg as MeHg (%MeHg) is often a measure of the
471 bioavailability and net methylation of sediment Hg. Northern sites, having the lowest sediment
472 N concentrations, generally exhibited the greatest %MeHg values, including Wells, Waquoit and
473 Buzzards Bays, MA.

474 In general, there were strong relationships among OC, N, and S in the Northeast coastal
475 sediments (Figure 5). The mean mass ratios (± 1 SD) of major elements in sediments were
476 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
477 stoichiometry of coastal sediments suggests that inputs of N largely drive the fixation of OC
478 through primary production. The mean OC/N ratio was greater than the Redfield ratio of 6.6
479 and may be attributed to a contribution of allochthonous organic matter from watersheds or
480 preferential loss of N during sediment diagenesis. In sediments, metabolism of organic matter
481 by sulfate reduction drives the formation of carbon-bonded S and acid volatile sulfide which
482 together largely comprise sediment S concentration. As a result, there is a close
483 correspondence among sediment N, OC and S (Figure 5).

484 For many of the sediment sites, these stoichiometric relationships also extended to total
485 Hg (Figure 6). For most of the sites (8 of 10) the mean Hg/N (ng g^{-1}) ratio is $83,300 \pm 83,100$
486 Hg/OC (ng g C^{-1}) ratio is $8,300 \pm 6,000$, which is comparable to the ratio observed in surface
487 sediments of Long Island Sound ($7,900 \pm 2100$; Hammerschmidt and Fitzgerald, 2004). Of this
488 group of eight sites, sediments in Buzzards Bay and Waquoit Bay had very low organic contents.
489 At the high end of OC concentrations were sites at Audubon and Bold Point. Beyond the eight

490 sites with comparable Hg/OC ratios, the coastal sediments adjacent to Mill Creek were highly
491 contaminated with Hg (mean, 2,960 ng g⁻¹) and exhibited a large Hg/OC ratio (49,000 ng Hg g
492 OC⁻¹). The concentrations at Mill Creek are comparable to highly contaminated deposits
493 previously reported for New York Harbor (40,000 ng Hg g OC⁻¹; Hammerschmidt et al., 2008).
494 The other “outlier” site was Barn Island, where sediments had a relatively high concentration of
495 organic C with relatively low Hg concentration, resulting in a low Hg/C ratio (2,800 ng Hg g OC⁻¹).
496 Barn Island might be considered a “Hg limited” site.

497 Changes of %MeHg along an N, organic C and S concentration gradient generally
498 support aspects of the conceptual nutrient-MeHg model (Figure 7). At the lowest N and organic
499 C concentrations, there appears to be an increase of %MeHg up to concentrations of about
500 0.07% N and 0.5% organic C. The fraction of total Hg as MeHg decreases at sediment N and
501 organic C concentrations greater than these values. The highest %MeHg was observed at the
502 lowest sediment S concentrations and decreased with increasing S.

503 Other studies on the east coast on the U.S. have found patterns similar to those
504 observed in the this study of Northeast coastal sediments, including the Chesapeake Bay and
505 adjoining continental margin, Long Island Sound, and New York Harbor. In Long Island Sound
506 and New York Harbor, potential rates of MeHg production were related inversely with organic
507 matter and sulfide contents of the sediment (Hammerschmidt and Fitzgerald, 2004;
508 Hammerschmidt et al., 2008). In Chesapeake Bay and on the shelf, %MeHg decreased with
509 increasing S in sediments (Hollweg et al., 2009). Except for sites along the continental slope,
510 Hollweg et al. (2009) observed a pattern of decreasing %MeHg with increasing sediment N and

511 OC. However, and in contrast to the Northeast sediment data, they did not observe an
512 apparent increase in MeHg with increasing N at very low sediment N and OC concentrations.
513 The very low sediment N and OC sites in the Northeast sediment study occurred at the sites
514 around Cape Cod (Waquoit Bay and Buzzards Bay), which receive groundwater inputs of Hg
515 (Bone et al., 2007). This behavior may have been a function of unique conditions at these sites
516 or the very low N and organic C concentrations that were not observed in other studies.

517 **2.4. Fish Mercury Response to N Loading**

518 In the previous case studies, measured and modeled MeHg in phytoplankton and
519 sediments are generally consistent with the conceptual model that elevated primary
520 production would result in lower MeHg net production and bioaccumulation at the base of the
521 food web, primarily due to reduced methylation and bioavailability of MeHg, as well as effects
522 of biodilution (Table 2; Figures 1, 2, and 7). Given the strong spatial and temporal
523 heterogeneity of Hg methylation and phytoplankton uptake, and the need to establish a clear
524 linkage with exposure, Hg concentrations in fish can be used as a measure of ecosystem MeHg
525 exposure to humans and wildlife predators (Harris et al., 2007; Sunderland, 2007). Finfish
526 integrate potential changes in food web structure that may occur with changing nutrient status,
527 and have tracked the impact of increased primary production and biodilution in fresh waters
528 (Essington and Houser, 2003; Chen and Folt, 2005). However, this finding has not previously
529 been described in estuarine or marine ecosystems.

530 To address this gap, in the fourth case study we examined Hg and MeHg concentrations
531 in multiple species of fish across a range of spatially distinct estuaries as well as within a single

532 estuary subject to differing nutrient loading. Data for Hg tissue concentration in eight species
533 of fish were compiled from the National Coastal assessment database
534 (<http://www.epa.gov/emap/nca/index.html>), and peer reviewed literature (Kannan et al., 1998;
535 Adams and Onorato, 2005; Moore et al., 2005; Hammerschmidt and Fitzgerald, 2006a; Adams
536 et al., 2010; Payne and Taylor, 2010; Senn et al., 2010; Stunz and Robillard, 2011; Szczebak and
537 Taylor, 2011). Estuaries and marine embayments from the North Atlantic Coast (11 water
538 bodies), the South Atlantic coast (4 water bodies), and the Gulf of Mexico (14 water bodies)
539 were considered. Whole body results were converted to fillet concentration using the
540 regression equation for all species of Peterson et al. (2005). Average Hg fish burdens were
541 compared to estimated estuary N loads using the SPARROW model (Alexander et al., 2000).

542 Correlation coefficients were low for six fish species (Pearson's correlation coefficient (r)
543 ranging from -0.21 to 0.25). For winter flounder (*Pseudopleuronectes americanus*, $r = 0.77$, $n =$
544 5 water bodies) and scup (*Stenotomus chrysops*, $r = 0.71$, $n = 6$), there was a positive
545 correlation, inconsistent with the expected decrease in fish Hg burdens with increasing N loads.
546 The lack of relationships between fish Hg concentrations and N loadings was likely affected by
547 extracting data from multiple sources; limited sample size for individual fish species; insufficient
548 data to evaluate confounding factors, such as fish body size; not accounting for differing Hg
549 inputs to the estuaries; inconsistent and limited range of N loading; and not considering the
550 variable response of estuaries to nutrient loadings due to their physical characteristics (Cloern,
551 2001). Future studies having more complete and consistent data sets would aid in determining
552 the overall relationship between nutrient loading and fish mercury biomagnification.

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

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

570

571 **3.0 Discussion**

572 The data bases, models, and calculations discussed above suggest that changes in
573 nutrient loadings could have substantial effects on MeHg bioaccumulation through a number of

574 interlinked mechanisms. Unfortunately, these case studies provide only limited information
575 with which we can evaluate our conceptual model. The marine nutrient gradient analysis
576 (section 2.1) and the Northeast sediment (section 2.3) results are spatial data limited by the
577 fact that differences in coastal nutrient status are often coincident with variations of Hg
578 contamination, making it difficult to differentiate effects of nutrient and Hg loadings. It seems
579 likely that variations of Hg loadings will alter the extent and the mechanisms to which nutrient
580 inputs affect ecosystem MeHg dynamics.

581 Our model calculations (section 2.2) are limited by the difficulty of making an overall
582 prediction, as changes in nutrient levels can have a marked effect not only on the production
583 and partitioning of MeHg within the sediment and water column, but also on trophic dynamics.
584 In particular, changes in phytoplankton size and growth rate can have a large impact on the
585 overall trophic transfer of MeHg. Our spatial fish analysis (section 2.4) of Atlantic and Gulf coast
586 waters reveals no relationships between fish Hg concentrations and estuary nutrient loading.
587 This lack of relationships is probably not surprising given the relatively coarse analysis
588 conducted and the highly variable responses that estuaries show to nutrient loadings as a result
589 of influences of hydrologic residence time, tidal exchange, light penetrations and benthic
590 interactions (Cloern, 2001). In San Francisco Bay forage fish, concentrations were lower at
591 WWTP discharge locations than nearby reference locations, and WWTP discharge had elevated
592 dissolved nitrogen concentrations compared to ambient concentrations. The finding suggests
593 that estuarine sites with increased anthropogenic nutrient loading will decrease MeHg
594 bioaccumulation in fish, which is consistent with our conceptual model (Figure 1). This is the
595 first published account of spatial variation in fish mercury being associated with WWTP, but it is

596 limited in scope to a single estuary, and the mechanism underlying the correlation is
597 indeterminate. Potential mechanisms include growth dilution of the forage fish or biodilution
598 among primary producers or lower trophic level consumers (Essington and Houser, 2003;
599 Pickhardt et al., 2002). Clearly, further and more comprehensive examination of these factors
600 with both laboratory and field efforts will improve our understanding of the complex linkage
601 between changes in nutrient inputs and MeHg bioaccumulation into fish.

602

603 **3.1 Management implications**

604 Although our conceptual model involves considerable speculation, it may have
605 important implications for efforts to manage nutrient loading to coastal waters
606 (Hammerschmidt and Fitzgerald, 2004) and also organic enrichment from aquaculture activities
607 in coastal environments (Sunderland et al., 2006). As mentioned, a large number of TMDLs for
608 N have been established for coastal waters in the U.S., and management efforts are underway
609 in North America, Europe and Asia to control N loadings to estuaries to achieve water quality
610 standards. For example, in 2000, wastewater discharges to Boston Harbor were diverted 15 km
611 offshore, decreasing the external load of total N by about 80% (Benoit et al., 2009; Taylor,
612 2010). In five years following the decrease in N loading, harbor-wide concentrations of total N
613 decreased 35%, summer chlorophyll decreased 40%, and dissolved oxygen in bottom water
614 increased by 5%. Increases in benthic invertebrate community densities have also been noted
615 (Bricker et al., 2007; Taylor, 2010). In Long Island Sound, both Connecticut and New York have
616 aggressively pursued N control strategies in wastewater treatment plants to achieve a 30%
617 decrease in N load. These states also are conducting stormwater permitting and non-point

618 source control programs to achieve an additional 10% decrease in N inputs. Similarly, the
619 Tampa, FL, region has been actively controlling N inputs to Tampa Bay resulting in a 60%
620 decrease since the 1970s (Bricker et al., 2007).

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

630 Management of wastewater discharge has often lead to a concomitant decrease in Hg
631 loading, as demonstrated by Hg mass balances for the Hudson River and Gulf of Maine and
632 changes in ecosystem Hg (Balcom et al., 2010; Sunderland et al., this issue). For many coastal
633 waters, riverine inputs, atmospheric deposition and the open ocean are important sources of
634 Hg and MeHg. Moreover, it is likely that deposition and riverine sources of Hg have changed
635 over the past decades (e.g., Sunderland et al., this issue, 2010). Therefore, the premise that
636 decreases in nutrient loadings will result in increased MeHg concentrations in the food web
637 must be evaluated in the context of potentially coincident changes of Hg and MeHg inputs. In
638 some ecosystems, continued external input of Hg would be required to sustain sediment MeHg

639 production because relatively fast rates of sedimentation remove Hg from the rapidly cycling
640 pools over a relatively short timescale (years to decades). While in other ecosystems,
641 bioturbation and redistribution of “legacy Hg” buried within the sediment to zones of active
642 methylation may sustain MeHg production for centuries. Moreover, extreme events such as
643 hurricanes can also remobilize Hg and enhance methylation (Liu et al., 2009).

644 As an example, Hg concentrations in surface sediments of New York/New Jersey Harbor
645 decreased 50-80% between the 1960s and the 1990s (Balcom et al., 2010; CARP, 2007), with an
646 associated decrease in Hg concentrations in the water column (Sanudo-Wilhelmy and Gill,
647 1999). Much of the input of Hg (~90%) and MeHg (~55%) to New York/New Jersey Harbor is
648 derived from the Hudson and East Rivers (Balcom et al., 2010; 2008). Inputs of MeHg from the
649 sediment are relatively small (~25%). This pattern suggests that MeHg in the Harbor is likely to
650 respond rapidly to changes of external Hg loadings. The Bay of Fundy is likely to respond
651 similarly (Sunderland et al., 2010). For such ecosystems, large and rapid changes in Hg and
652 MeHg loading could easily overwhelm the effects of changing N loading.

653 However, in contrast, inputs of MeHg from the sediment appear to be the major source
654 to the food web in Long Island Sound (Balcom et al., 2004; Hammerschmidt and Fitzgerald,
655 2006a) and there is a large legacy of Hg contamination in the sediment (Varekamp et al., 2003).
656 For such ecosystems, changes in N loading could have a marked impact on benthic MeHg
657 production. Sediment cores throughout the Sound have shown that concentrations in surface
658 sediment have decreased to a lesser degree (~40%; Varekamp et al., 2003) than found in New

659 York Harbor. At this time, it is not possible to conclude what impacts that decreases in N
660 loading will have on levels of MeHg in estuarine and coastal food chains.

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

675 **3.2 Future studies to evaluate conceptual model**

676 Better understanding of the linkages between nutrient loading and Hg contamination in
677 marine ecosystems is needed for effective management of these two important environmental
678 pollutants. Our analysis of existing datasets and modeling suggest that N inputs to marine
679 ecosystems can interact with MeHg production to decrease its bioavailability. However, our
680 conceptual model would benefit from focused efforts to evaluate pathways and processes of

681 the model as well as entire ecosystem effects. Researchers need to use time-series
682 observations, gradient studies, experimental manipulations and models in coordinated efforts
683 to assess the complexities of nutrient-Hg interactions. There is a particular need to monitor Hg
684 in abiotic and biotic compartments through time as nutrient TMDLs are implemented.

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1002 **Figure Captions**

1003 Figure 1. Schematic diagram illustrating the response coastal processes relevant to transport, net
1004 methylation and trophic transfer of Hg to increases in N loading. The diagram depicts the influence of a
1005 change in a process. A blue arrow indicates a decrease. A red arrow indicates an increase. A purple
1006 arrow depicts an unknown direction of change. The color of the boxes depict where in the ecosystem
1007 the process occurs: blue for water column, purple for the sediment-water interface and orange for
1008 sediments.

1009

1010 Figure 2. a) Model predictions on the impact of changes in algal biomass on the methylmercury
1011 concentration in an open ocean system. Note two values for partition coefficients: Case 1 where
1012 partition are the same for dissolved organic matter, phytoplankton and bacteria with water, and Case 2
1013 where they are different. Unpublished data from Kline and Mason; b) estimation of the concentration
1014 of methylmercury in a range of phytoplankton species using the model for uptake developed by Mason
1015 et al. (1996).

1016

1017 Figure 3. a) The modeled concentrations of methylmercury in phytoplankton in different regions of the
1018 Chesapeake Bay, as differentiated by the differences in sediment organic content (% OM) based on the
1019 biogeochemical model developed by Kim et al. (2008) for a shallow coastal system with tidal
1020 resuspension; b) model results demonstrating the impact of sediment resuspension on methylmercury
1021 accumulation but not on phytoplankton biomass. Note R refers to resuspension and NR refers to no
1022 resuspension conditions. Biomass refers to phytoplankton biomass. Both figures are from Kim et al.
1023 (2008).

1024

1025 Figure 4. Maps of the coastal sediment study sites (a) showing the total Hg concentration (b), %nitrogen
1026 (%N) (c) and percent of total Hg occurring as methyl Hg (%MeHg) (d) in the northeastern U.S.

1027

1028 Figure 5. Concentrations of organic C as a function of N concentration (a), S concentration as a function
1029 organic carbon concentration (b) and S concentration as a function of N concentration (c) in Northeast
1030 coastal sediment sites.

1031

1032 Figure 6. Total Hg as a function of N concentration (a) and organic C (b) concentration in Northeast
1033 coastal sediments. Only closed circles are included in regression analysis.

1034

1035 Figure 7. The percent of total Hg occurring as MeHg (%MeHg) as a function of N (a), organic C (b) and S
1036 (c) in Northeast coastal sediments.

1037

1038 Figure 8. Mercury concentrations in silverside in WWTP and comparison station pairs in South San
1039 Francisco Bay. Station pairs are indicated by corresponding colors. Results are box and whiskers plots of
1040 wet weight mercury concentrations. Note log scale Y axis.

1041

1042

1043

1044 Table 1. Summary of waterbody impairments and Total Maximum Daily Loads (TMDLs) for
 1045 mercury and nutrients in U.S. waters (total and coastal) based on state 303(d) lists submitted to
 1046 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

1047 ^aNote information reflects “assessed waters.” Only a small percentage of coastal
 1048 waters have been assessed. “U.S. coastal waters” includes water classified by as coastal waters, bays or estuaries.
 1049

1050 ^bFor this analysis, nutrient-related impairments and TMDLs include the following impairment categories: algal
 1051 growth, ammonia, noxious aquatic plants, nutrients, and organic enrichment/oxygen depletion.
 1052

1053 ^cThis column reflects the number of waterbody impairments and not the number of unique waters affected.
 1054

1055 ^dThe number of TMDLs for coastal waters reflect only those for which the state provided information on
 1056 waterbody type in the 303(d) listing.
 1057

1058

1059 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

1060 ^aAssigned classification based on presumed productivity.1061 ^bLiterature value or converted to wet-weight concentration assuming 95% water content (Knauer and
1062 Martin, 1972).1063 ^cHammerschmidt and Bowman (in review)1064 ^dHammerschmidt and Fitzgerald (2006a,b)1065 ^eBaeyens et al. (2003)1066 ^fSunderland et al. (2010)1067 ^gBalcom et al. (2004)1068 ^hBalcom et al. (2008)

1069

1070 Table 3. Ammonium and NOx in four sites exposed to wastewater treatment plant discharge,
 1071 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		

1072 * Combines discharges from six wastewater treatment facilities

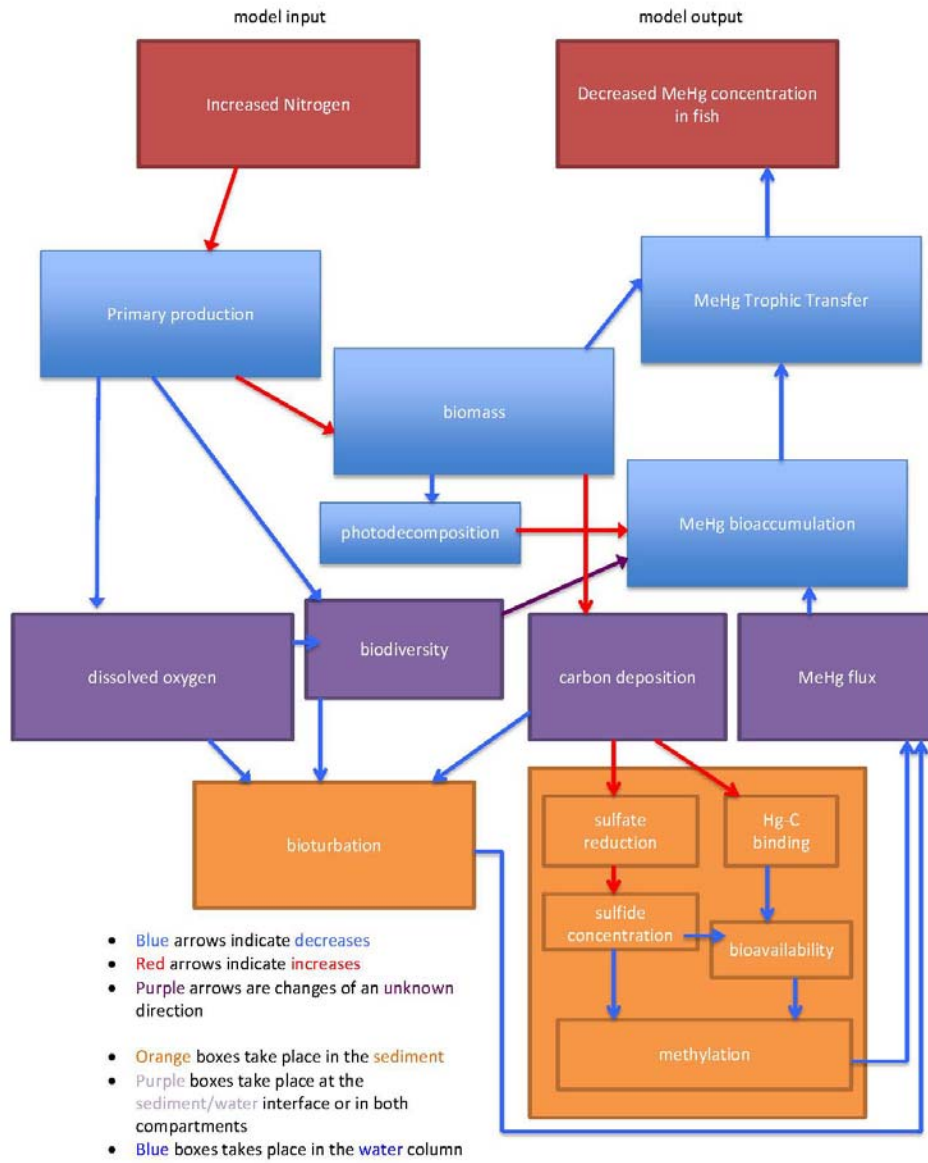
1073 # Secondary treatment facility

1074 ^ Advanced treatment facility

1075 a. Averaged across flow class data in McKee and Gluchowski, 2011; annual averages are from 2004-2010

1076 b. Average of 2004-2010 data from the Regional Monitoring Program (SFEI, 2010)

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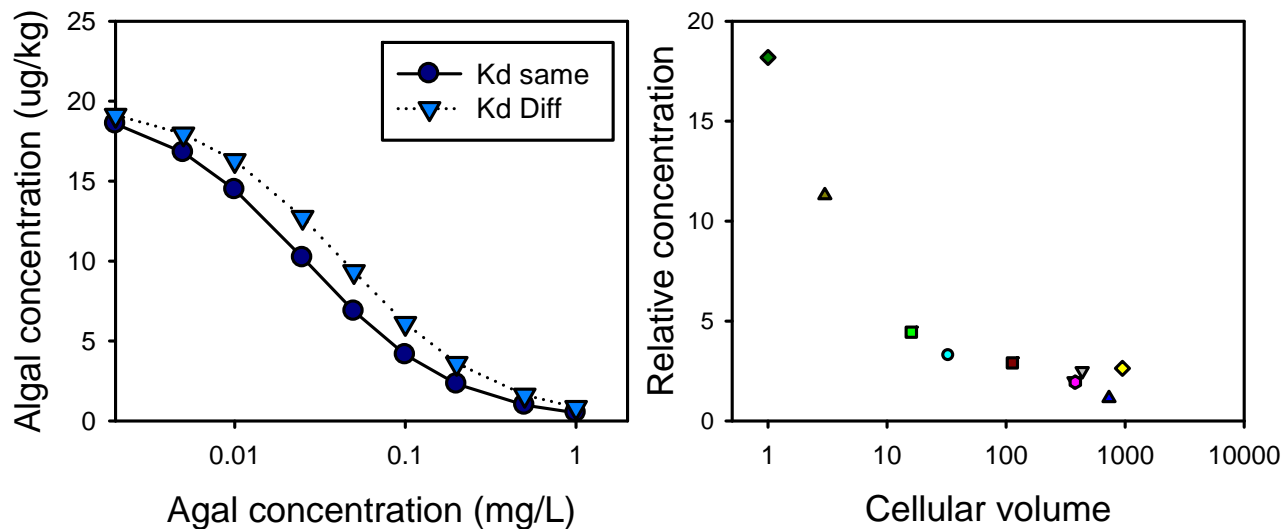


1079

1080 Figure 1. Schematic diagram illustrating the response coastal processes relevant to transport, net
1081 methylation and trophic transfer of Hg to increases in N loading. The diagram depicts the influence of a
1082 change in a process. A blue arrow indicates a decrease. A red arrow indicates an increase. A purple
1083 arrow depicts an unknown direction of change. The color of the boxes depict where in the ecosystem
1084 the process occurs: blue for water column, purple for the sediment-water interface and orange for
1085 sediments.

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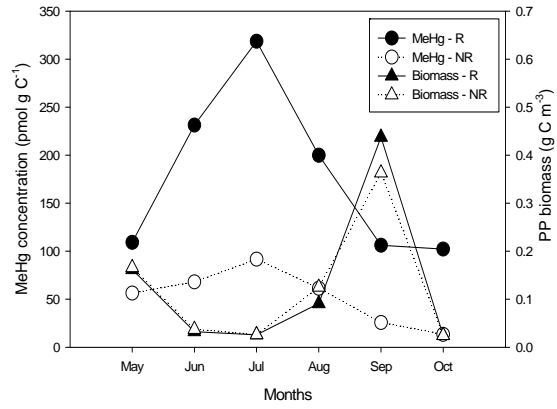
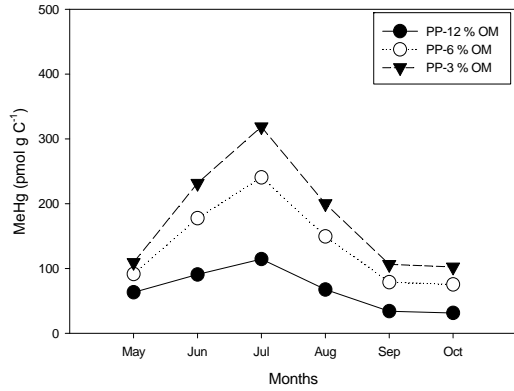


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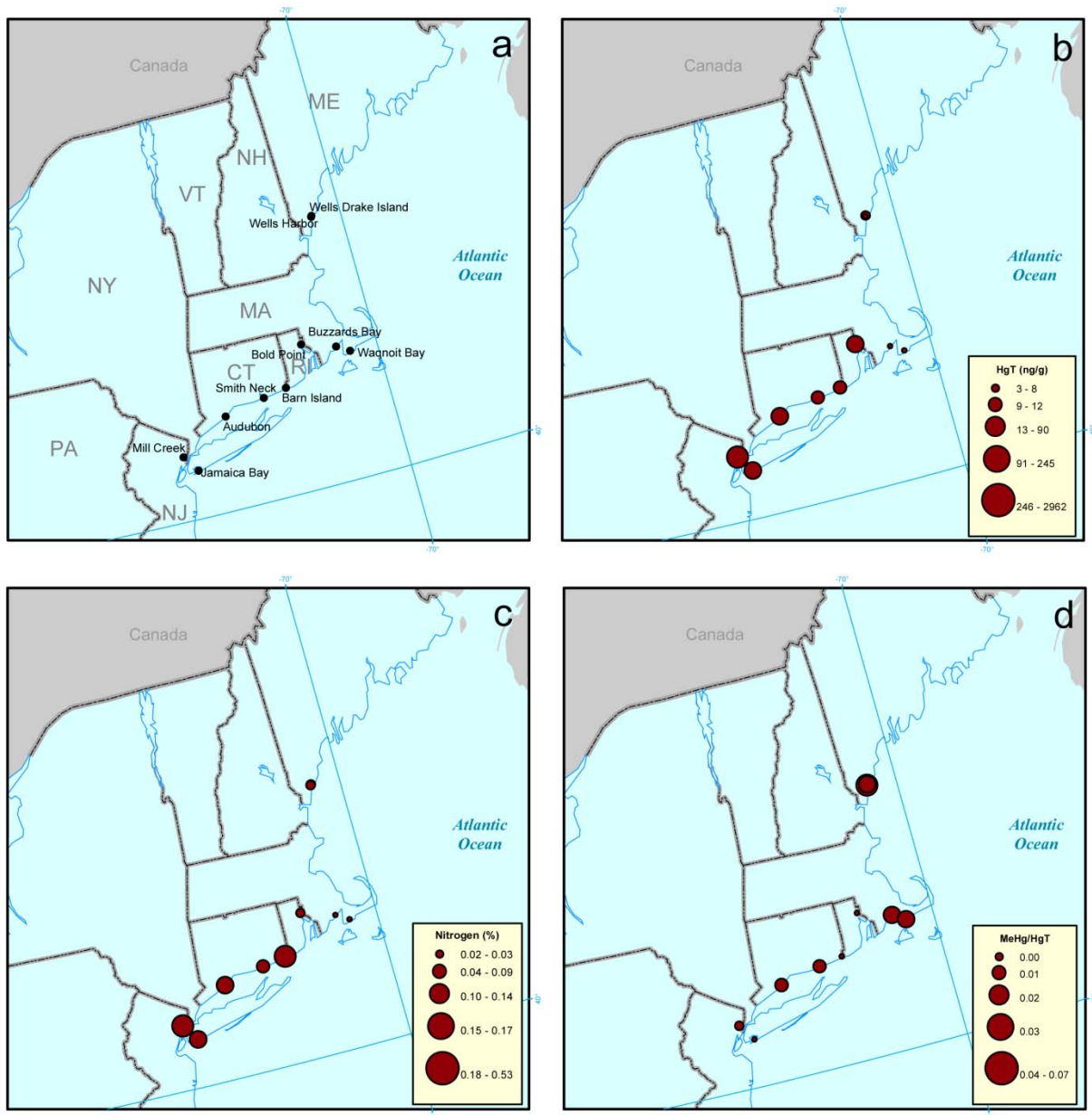
1090 Figure 2. a) Model predictions on the impact of changes in algal biomass on the methylmercury
 1091 concentration in an open ocean system. Note two values for partition coefficients: Case 1 where
 1092 partition are the same for dissolved organic matter, phytoplankton and bacteria with water, and Case 2
 1093 where they are different. Unpublished data from Kline and Mason; b) estimation of the concentration
 1094 of methylmercury in a range of phytoplankton species using the model for uptake developed by Mason
 1095 et al. (1996).

1096



1105 Figure 3. a) The modeled concentrations of methylmercury in phytoplankton in different regions of the
 1106 Chesapeake Bay, as differentiated by the differences in sediment organic content (% OM) based on the
 1107 biogeochemical model developed by Kim et al. (2008) for a shallow coastal system with tidal
 1108 resuspension; b) model results demonstrating the impact of sediment resuspension on methylmercury
 1109 accumulation but not on phytoplankton biomass. Note R refers to resuspension and NR refers to no
 1110 resuspension conditions. Biomass refers to phytoplankton biomass. Both figures are from Kim et al.
 1111 (2008).

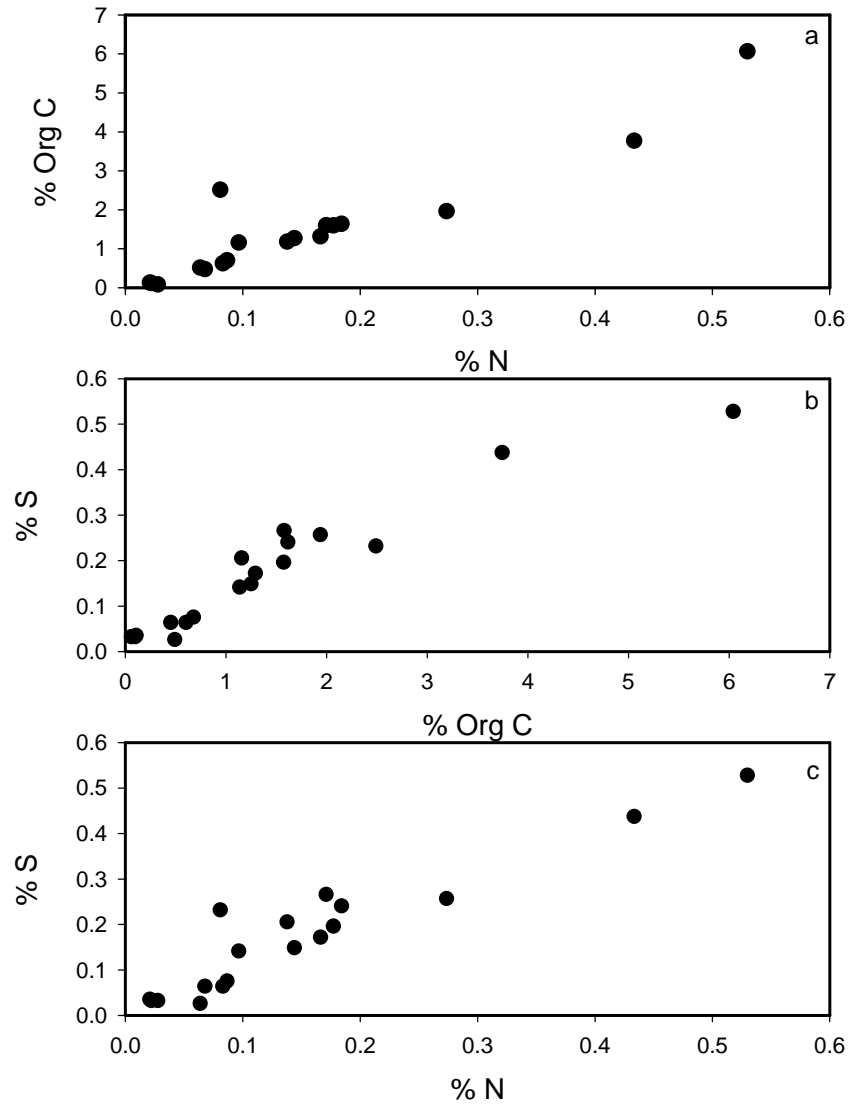
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1114 Figure 4. Maps of the coastal sediment study sites (a) showing the total Hg concentration (b), %nitrogen
 1115 (%N) (c) and percent of total Hg occurring as methyl Hg (%MeHg) (d) in the northeastern U.S.

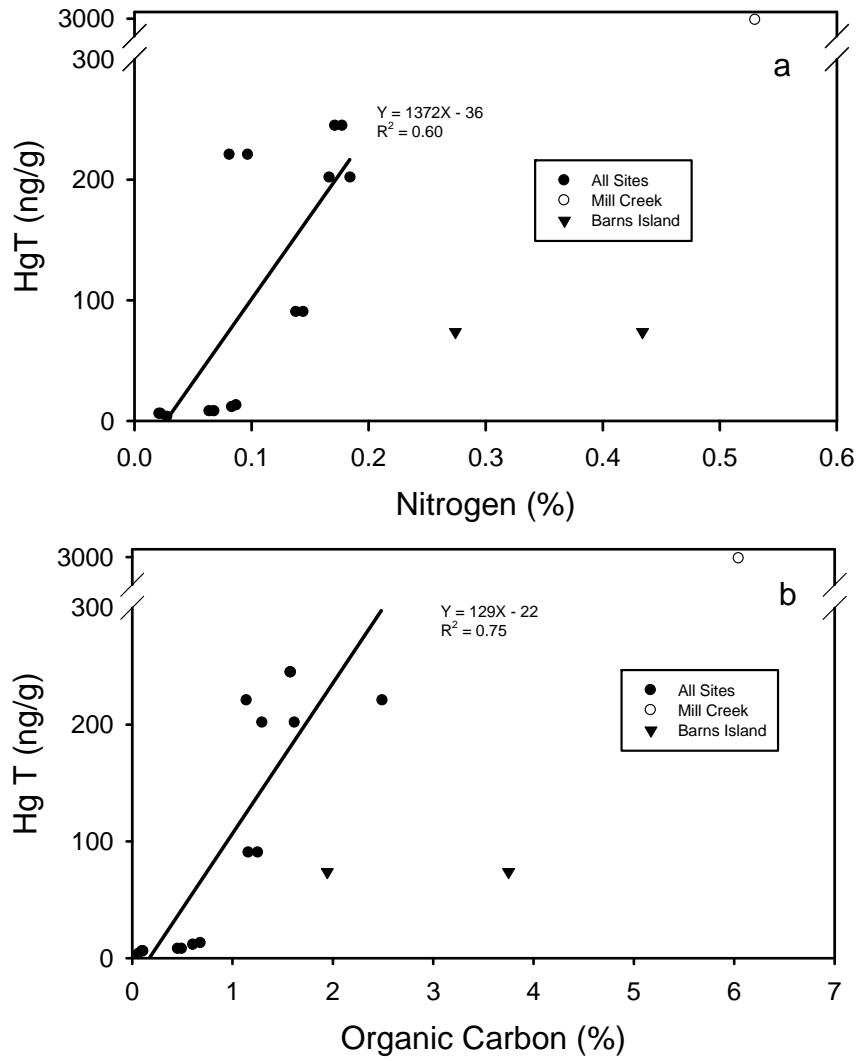
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1118 Figure 5. Concentrations of organic C as a function of N concentration (a), S concentration as a function
1119 organic carbon concentration (b) and S concentration as a function of N concentration (c) in Northeast
1120 coastal sediment sites.

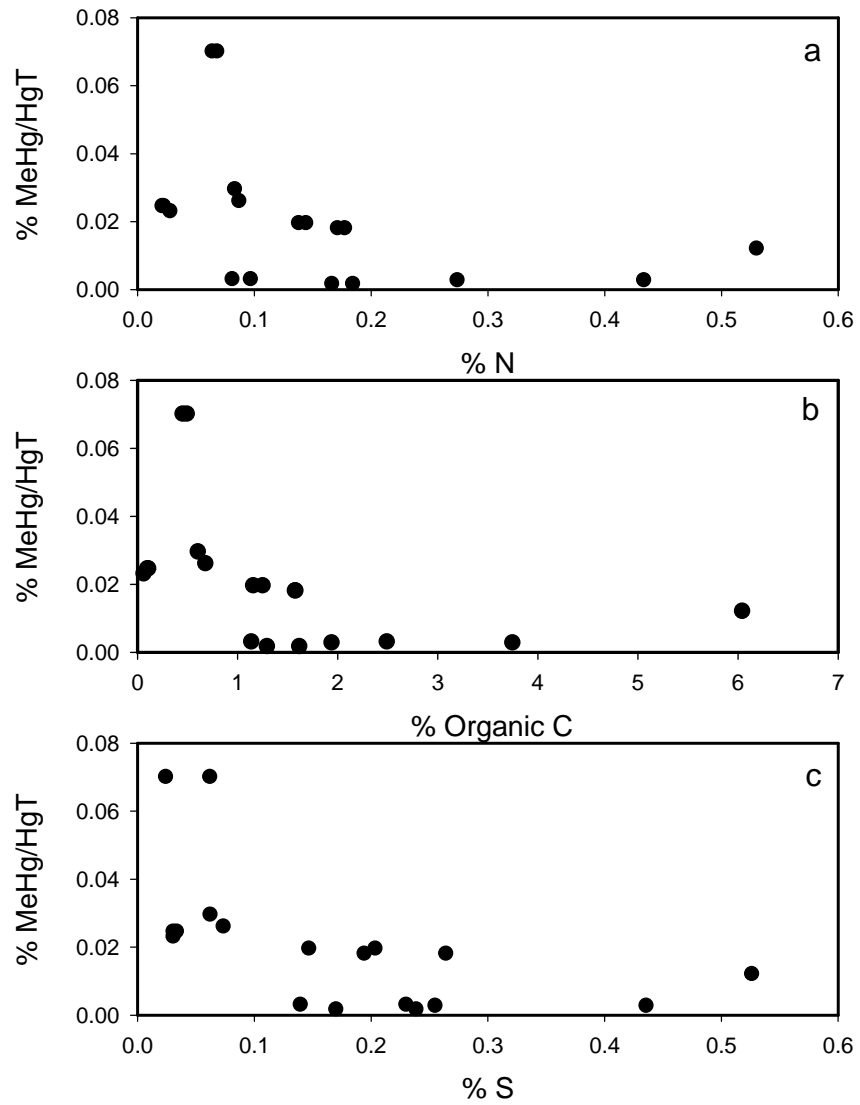
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1123 Figure 6. Total Hg as a function of N concentration (a) and organic C (b) concentration in Northeast
 1124 coastal sediments. Only closed circles are included in regression analysis.

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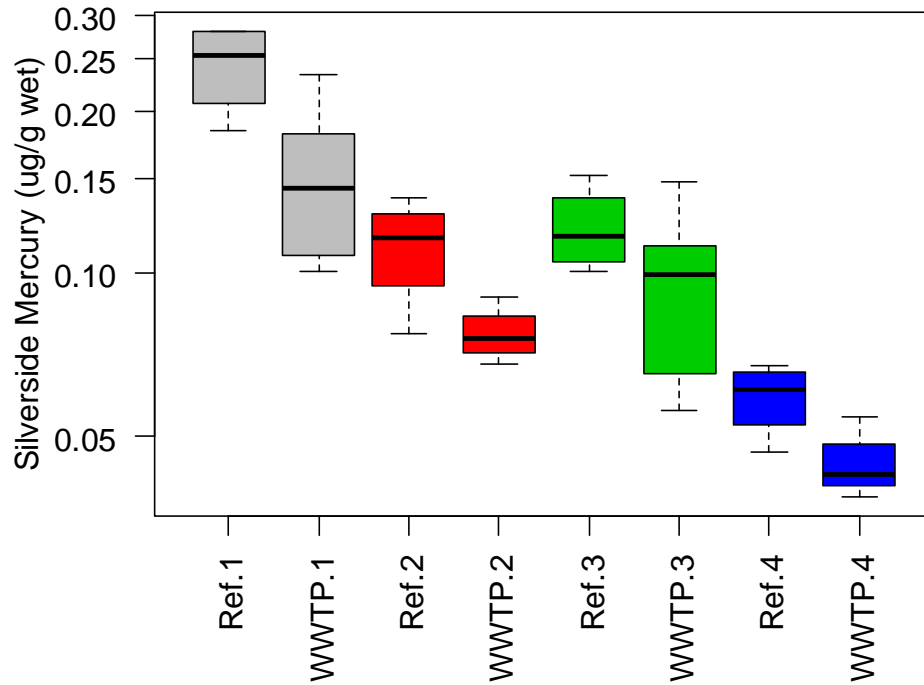


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1127 Figure 7. The percent of total Hg occurring as MeHg (%MeHg) as a function of N (a), organic C (b) and S
 1128 (c) in Northeast coastal sediments..

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1132 Figure 8. Mercury concentrations in silverside in WWTP and comparison station pairs in South San
 1133 Francisco Bay. Station pairs are indicated by corresponding colors. Results are box and whiskers plots of
 1134 wet weight mercury concentrations. Note log scale Y axis.

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