Civil and Environmental Engineering | College of Engineering and Computer Science

2012

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

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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,

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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).

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

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

Increases in net ecosystem production also increases deposition of OC to sediments and facilitates the removal of ionic Hg and MeHg from the water column to the sediments (Figure 1). Sediment organic matter has a complex role in affecting Hg and MeHg biogeochemistry, net MeHg formation and its bioavailability to the food web (Figure 1). First, the partitioning of Hg between pore water and the solid phase (K_d) is positively related to sediment organic content. On average, partition coefficients for Hg increase by almost 3 orders of magnitude in coastal sediments as the organic matter content increases from 2 to 15% (Hollweg et al., 2010).

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; Skyllberg, 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 macrofauana

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   (~20–3500 g C m^{-2} 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.

15

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 Hashimoto, 2000). All trophic dynamics were linearly constrained to the algal biomass (i.e., bacterial mass twice and zooplankton one tenth the algal biomass on a dry weight basis). In the model, the DOM concentration also was varied with algal biomass (ratio of 35 for DOM: algal mass). Partition coefficients (dry weight basis) between water and the various biota and the DOM were based on the literature (Kaiser and Benner, 2009; Kim et al., 2008; Mason et al., 1996). It is assumed that only the fraction of MeHg that is <u>not</u> complexed with DOM is 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; Heimburger 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: $Q = U/\mu$.

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

376   *Where*:   R = radius

377   P = membrane permeability

378   C = external Hg concentration

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

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

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 μm) relative to smaller

386   plankton (<1 μm). 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 x 10^{-3} 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

21

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±83,100

486   Hg/OC (ng g C^{-1}) ratio is 8,300 ± 6,000, which is comparable to the ratio observed in surface

487   sediments of Long Island Sound (7,900 ± 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^{-}

496   ^{1}). 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

32

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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5.0 References

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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 blue arrow indicates a decrease. A red arrow indicates an increase. A purple

arrow depicts an unknown direction of change. The color of the boxes depict where in the ecosystem

the process occurs: blue for water column, purple for the sediment-water interface and orange for

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Figure 2. a) Model predictions on the impact of changes in algal biomass on the methylmercury

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Figure 3. a) The modeled concentrations of methylmercury in phytoplankton in different regions of the

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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.

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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.

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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.

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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.

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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.

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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   [a]Note 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.
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1050   [b]For 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   [c]This column reflects the number of waterbody impairments and not the number of unique waters affected.
1054
1055   [d]The number of TMDLs for coastal waters reflect only those for which the state provided information on
1056   waterbody type in the 303(d) listing.
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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
	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

1060   [a]Assigned classification based on presumed productivity.
1061   [b]Literature value or converted to wet-weight concentration assuming 95% water content (Knauer and
1062   Martin, 1972).
1063   [c]Hammerschmidt and Bowman (in review)
1064   [d]Hammerschmidt and Fitzgerald (2006a,b)
1065   [e]Baeyens et al. (2003)
1066   [f]Sunderland et al. (2010)
1067   [g]Balcom et al. (2004)
1068   [h]Balcom et al. (2008)

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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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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
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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.
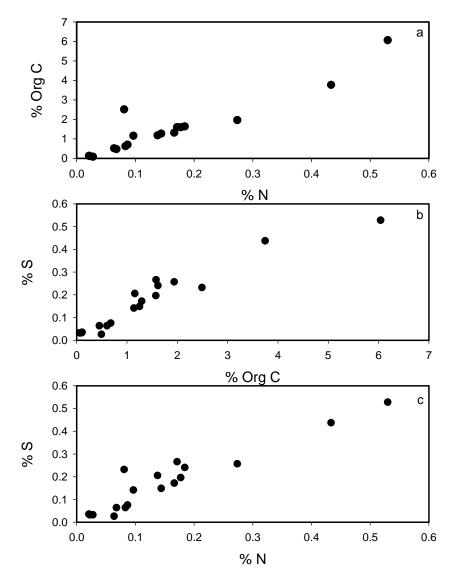
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Figure 5. Concentrations of organic C as a function of N concentration (a), S concentration as a function organic carbon concentration (b) and S concentration as a function of N concentration (c) in Northeast coastal sediment sites.
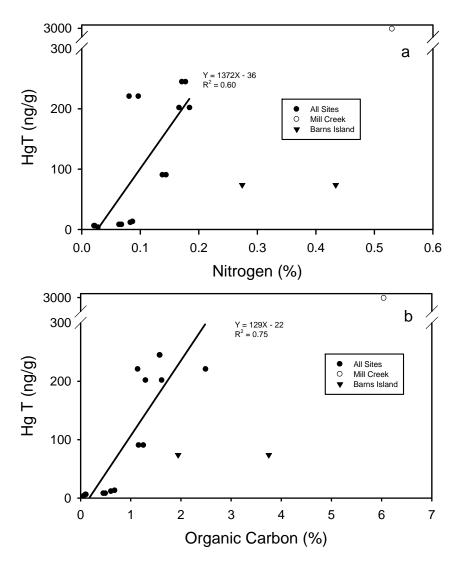
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Figure 6. Total Hg as a function of N concentration (a) and organic C (b) concentration in Northeast
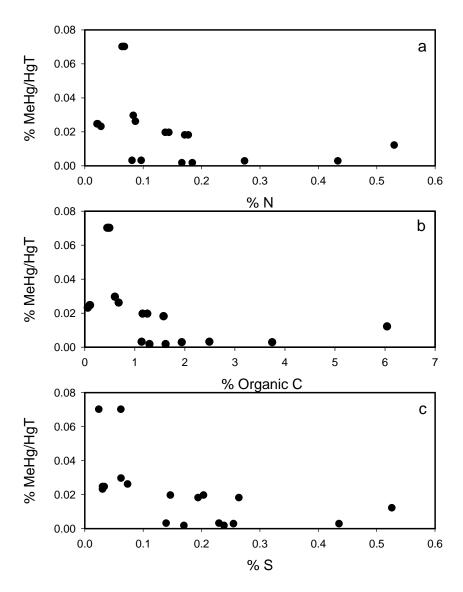coastal sediments. Only closed circles are included in regression analysis.

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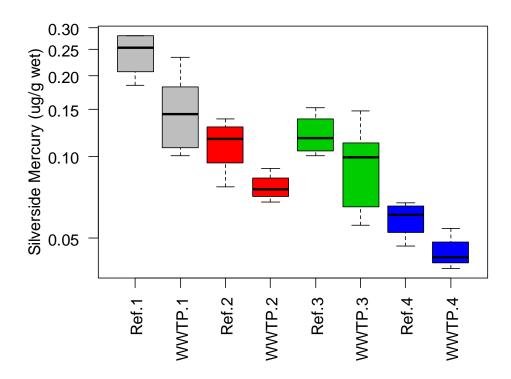(c) in Northeast coastal sediments..

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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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