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Abstract

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

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

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

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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,

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

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

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

132 Compared to N, less is known about the dynamics and effects of Hg in coastal and
133 pelagic marine ecosystems. Even less is known about the relationship between changes in N
134 loading and MeHg bioaccumulation in ocean fisheries. In the freshwater literature, however,
135 there are numerous field and experimental studies that show decreases of Hg concentrations in
136 the aquatic food web in response to increasing nutrient inputs. Nutrient enrichment to
137 freshwaters causing algal blooms decreases Hg concentrations in biota through a process
138 referred to as biodilution (Pickhardt et al., 2002). Concentrations of Hg in zooplankton
139 decrease with increasing zooplankton density, resulting in lower fish Hg concentrations (Chen
140 and Folt, 2005). Also, under conditions of high productivity and prey availability,
141 concentrations of Hg in zooplankton and fish may decrease due to growth dilution (Essington
142 and Houser, 2003; Karimi et al., 2007). Field studies have shown that Hg concentrations in

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

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).

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

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

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

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

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

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

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

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

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

1.3 Approaches to test hypothesis

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

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

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

2.0 Case Studies

2.1 Comparison across Marine Nutrient Gradient

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

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

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

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

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

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

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

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

Where: R = radius

P = membrane permeability

C = external Hg concentration

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

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

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

2.2.2 **Examination of the Impact of Eutrophication on Methylmercury in a Shallow Coastal Ecosystem**

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

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

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

In general, there were strong relationships among OC, N, and S in the Northeast coastal sediments (Figure 5). The mean mass ratios (± 1 SD) of major elements in sediments were OC/N ratio = 9.4 ±6.8, S/N ratio = 1.2 ± 0.5 and S/OC ratio = 0.16±0.1. The general nutrient stoichiometry of coastal sediments suggests that inputs of N largely drive the fixation of OC through primary production. The mean OC/N ratio was greater than the Redfield ratio of 6.6 and may be attributed to a contribution of allochthonous organic matter from watersheds or preferential loss of N during sediment diagenesis. In sediments, metabolism of organic matter by sulfate reduction drives the formation of carbon-bonded S and acid volatile sulfide which together largely comprise sediment S concentration. As a result, there is a close correspondence among sediment N, OC and S (Figure 5).

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

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

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

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

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

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

3.0 Discussion

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

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

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

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

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

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

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

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

3.2 Future studies to evaluate conceptual model

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

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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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 sediments.

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

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Table 1. Summary of waterbody impairments and Total Maximum Daily Loads (TMDLs) for mercury and nutrients in U.S. waters (total and coastal) based on state 303(d) lists submitted to and approved by EPA as required by the Clean Water Act. Source: U.S. EPA 2011a, b.

Resource	Contaminant	303(d) Waterbody impairments[c]	Approved TMDLs[d]
Total US waters	Mercury	5,004	6,946
Total US waters	Nutrients[b]	16,075	8,102
US coastal waters[a]	Mercury	196	51
US coastal waters[a]	Nutrients[b]	2,818	199
US coastal waters[a]	Mercury and nutrients[b]	86	10

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

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

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

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

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

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

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

Table 3. Ammonium and NOx in four sites exposed to wastewater treatment plant discharge, and ambient (background) concentrations in South San Francisco Bay.

Source	Site	Average ammonium (mg N/L)	Annual ammonium (metric tons)	Annual 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		

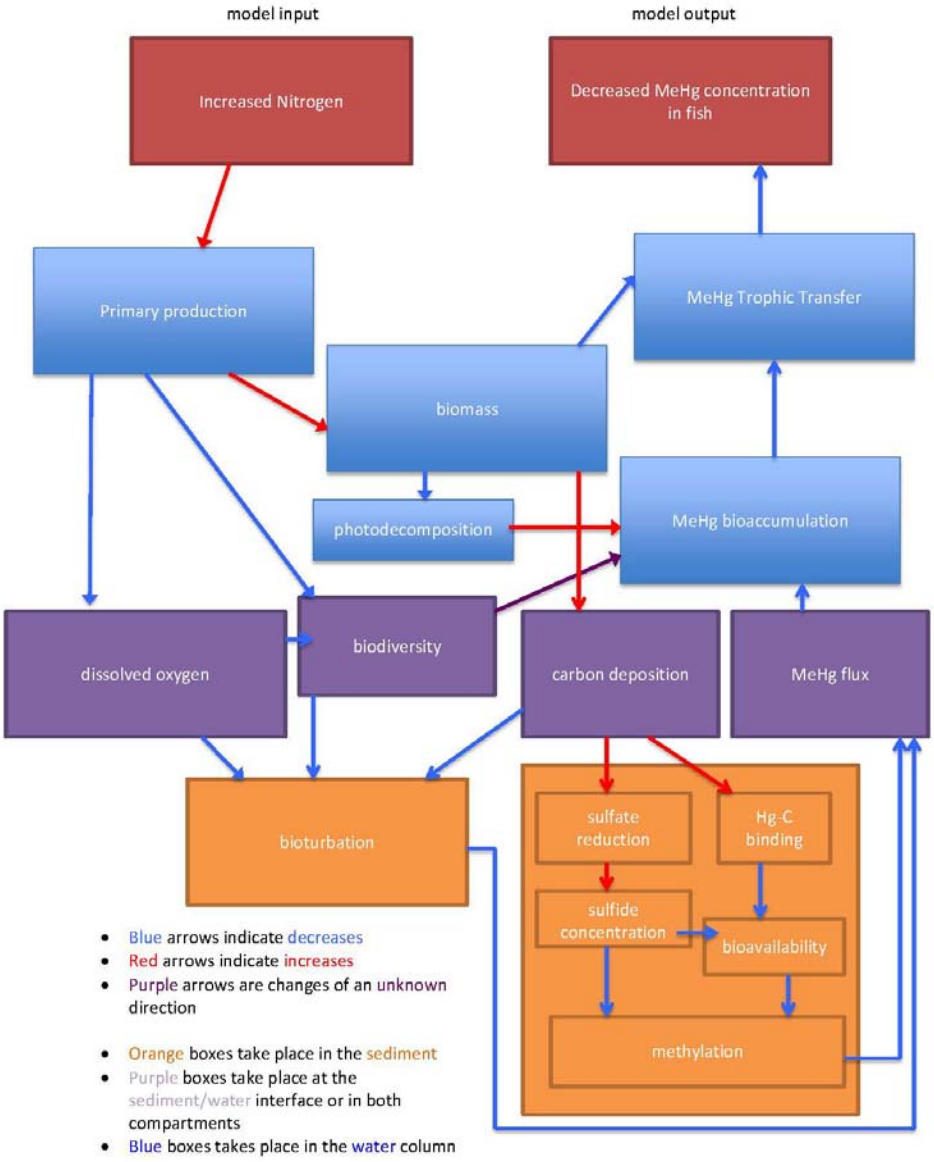
* Combines discharges from six wastewater treatment facilities

Secondary treatment facility

^ Advanced treatment facility

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

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



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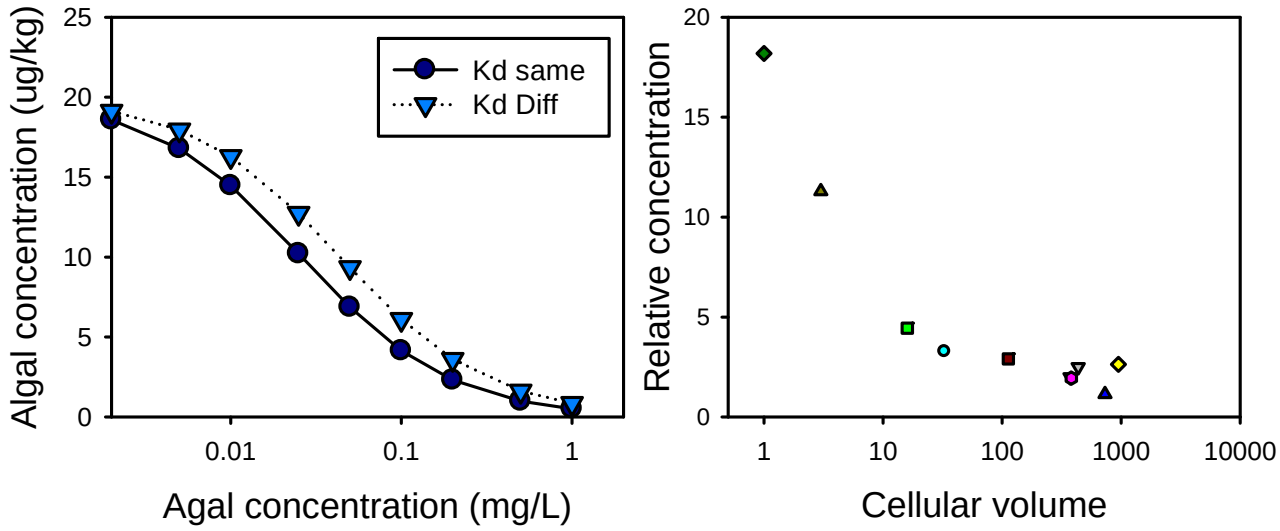

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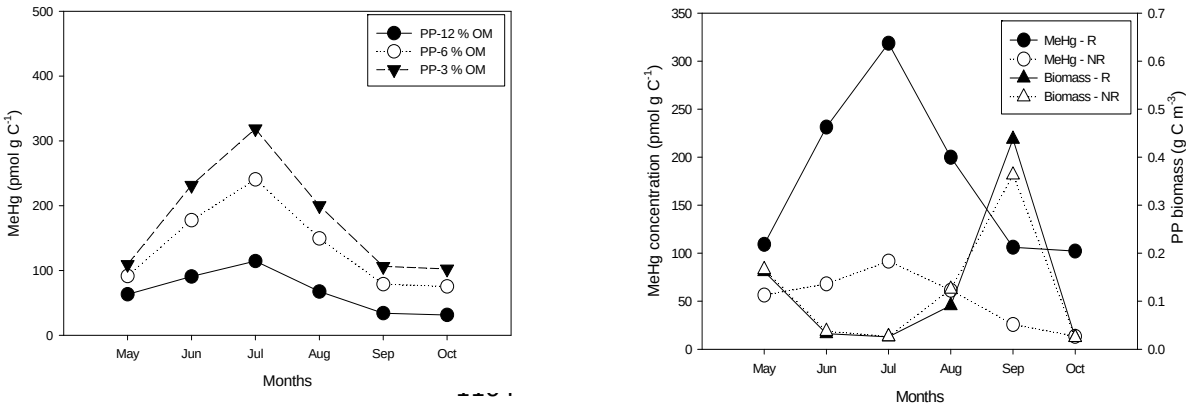

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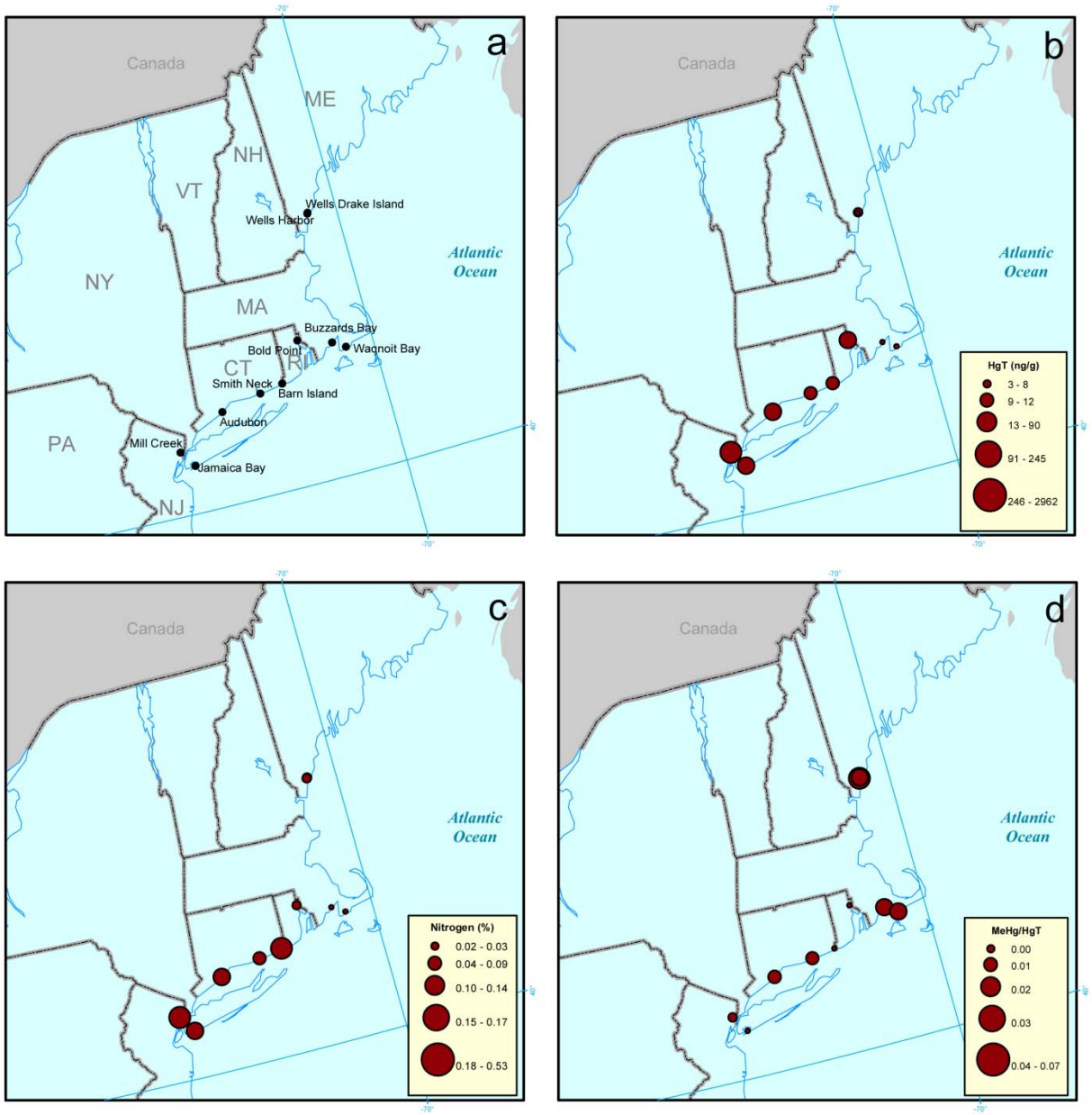

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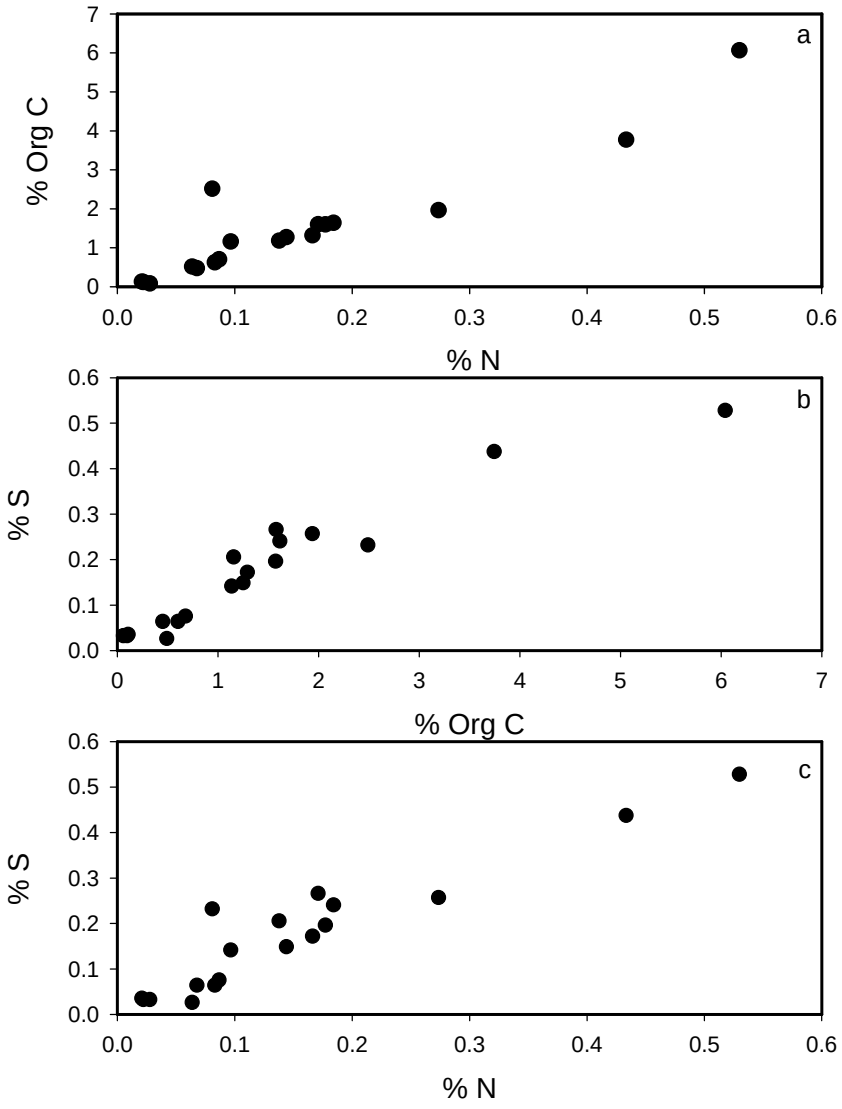

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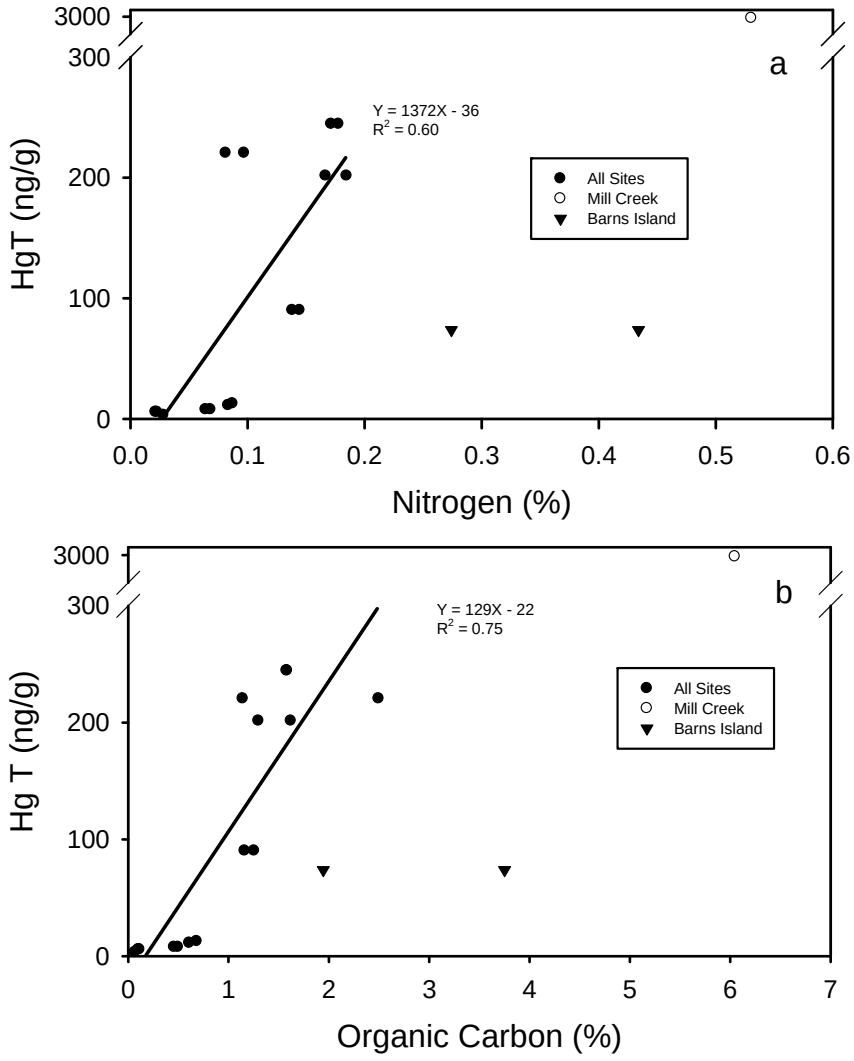

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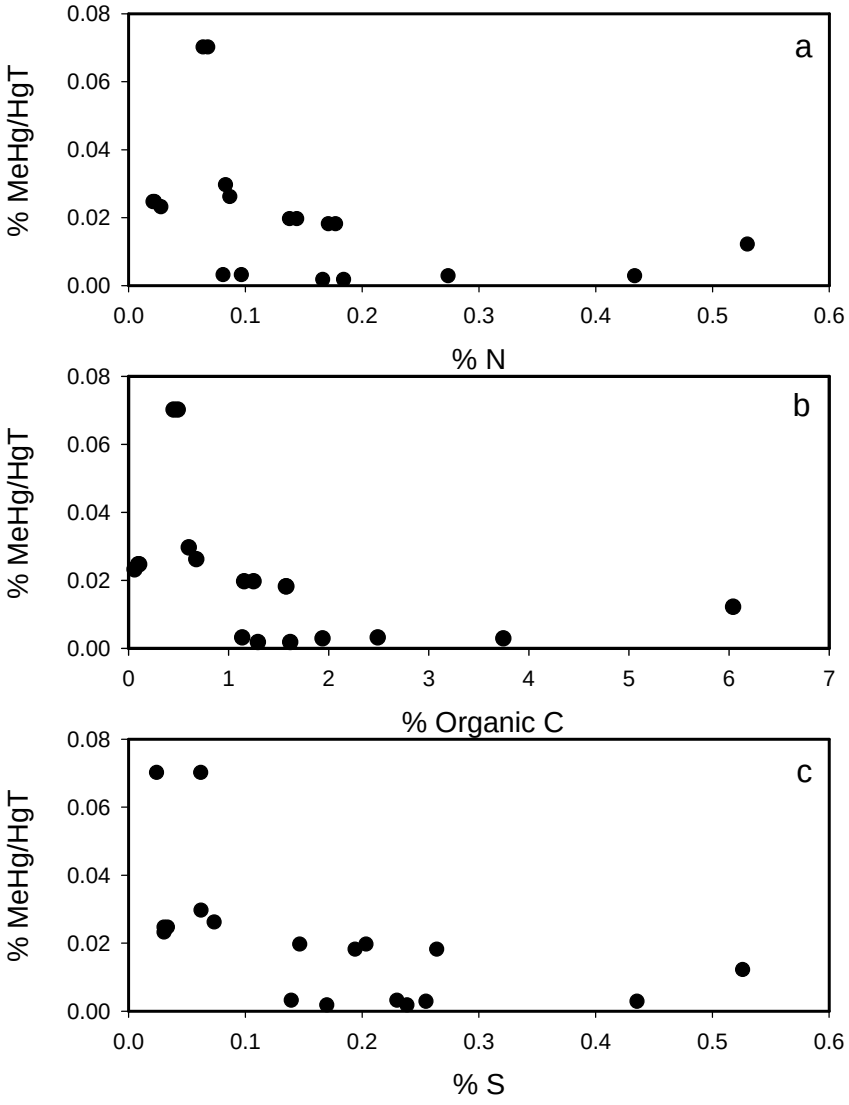

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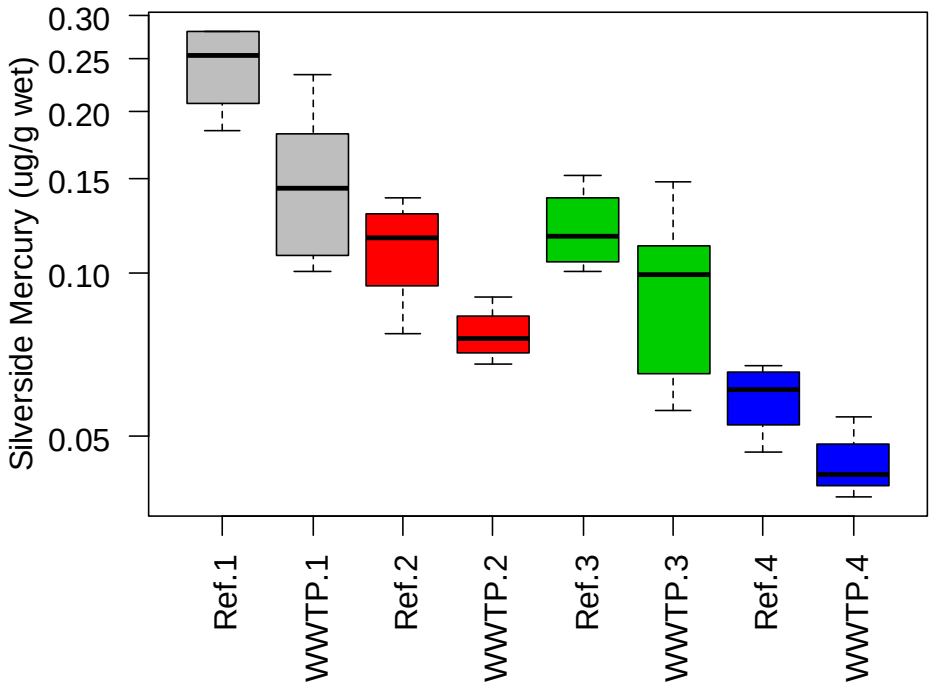

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