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Mercury methylation dynamics in estuarine and coastal marine environments – A critical review

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ABSTRACT

Considerable recent research has focused on methylmercury (MeHg) cycling within estuarine and coastal marine environments. Because MeHg represents a potent neurotoxin that may magnify in marine foodwebs, it is important to understand the mechanisms and environmental variables that drive or constrain methylation dynamics in these environments. This critical review article explores the mechanisms hypothesized to influence aqueous phase and sediment solid phase MeHg concentrations and depth-specific inorganic Hg (II) (Hg_i) methylation rates (MMR) within estuarine and coastal marine environments, and discusses issues of terminology or methodology that complicate mechanism-oriented interpretation of field and laboratory data. Mechanisms discussed in this review article include: 1) the metabolic activity of sulfate reducing bacteria (SRB), the microbial group thought to dominate mercury methylation in these environments; 2) the role that Hg_i concentration and/or speciation play in defining depth-specific Hg_i methylation rates; and 3) the depth-dependent balance between MeHg production and consumption within the sedimentary environment. As discussed in this critical review article, the hypothesis of SRB community control on the Hg_i methylation rate in estuarine and coastal marine environments is broadly supported by the literature. Although Hg_i speciation, as a function of porewater inorganic sulfide and/or dissolved organic matter concentration and/or pH, may also play a role in observed variations in MMR, the nature and function of the controlling ligand(s) has not yet been adequately defined. Furthermore, although it is generally recognized that the processes responsible for MeHg production and consumption overlap spatially and/or kinetically in the sedimentary environment, and likely dictate the extent to which MeHg accumulates in the aqueous and/or sediment solid phase, this conceptual interpretation requires refinement, and would benefit greatly from the application of kinetic modeling.

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1. Introduction

The intent of this critical review is to examine the various proposed mechanisms hypothesized to influence the inorganic Hg(II) (Hg_i) methylation rate (MMR) and methylmercury (MeHg) accumulation in estuarine and coastal marine environments. Whereas a broad

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discussion of marine biogeochemical mercury (Hg) cycling, including discussion of Hg biomagnification and global Hg flux models has been recently published elsewhere (Fitzgerald et al., 2007), we are focusing here on predominantly mechanism-oriented questions with respect to MeHg cycling in sedimentary environments. Although research has also explored methylation dynamics within low-oxygen marine waters (e.g., Mason et al., 1993; Lamborg et al., 2008), there are currently insufficient data to allow assessment of the extent to which a redox-stratified water column adequately serves as an expanded proxy, with respect to MeHg cycling, for redox zonation within sediment porewaters. As such, we leave this question as a promising avenue for further research.

This critical review focuses on the dynamics of Hg_i methylation in environments in which sulfate (SO₄²⁻) availability is a non-limiting factor for microbial MeHg production. In the context of Hg_i methylation research, the significance of SO₄²⁻ availability arises from two early experimental observations, specifically that sulfate-reducing bacteria (SRB) are the dominant methylators of Hg_i in anoxic sediments (Compeau and Bartha, 1985), and that through pollution-derived SO_x emissions, freshwater ecosystems may receive SO₄²⁻ inputs sufficient to permit significant SRB community activity (Gilmour and Henry, 1991). While SRB are not the only methylators of Hg_i (Pak and Bartha, 1998; Warner et al., 2003; Kerin et al., 2006) their increased activity has been well correlated with heightened production of MeHg (e.g., Compeau and Bartha, 1985; King et al., 1999, 2000) in the coastal environment, although examples of poor or inconsistent correlation between SRB activity and MeHg production have also been documented (Marvin-DiPasquale and Agee, 2003; Hines et al. 2006; Han et al. 2007).

The literature discussed in this critical review is presented in terms of proposed mechanisms hypothesized to explain MMR and/or observed MeHg concentration profiles in either the sediment solid phase or sediment porewater. This mechanistic focus is not intended to suggest that a particular mechanism occurs to the exclusion of others, as the actual dynamic processes that enhance or limit Hg_i methylation in sedimentary environments are almost certainly comprised of multiple, interacting components. As a means of organizing the literature on this subject, however, three specific mechanistic questions guide this review. These questions address: 1) whether methylation of Hg_i is controlled or limited by the metabolic activity of SRB; 2) whether methylation of Hg_i is controlled or limited by the availability of either total Hg_i or the geochemical speciation of Hg_i; and 3) as the processes responsible for methylation of Hg_i and demethylation of MeHg frequently overlap both spatially and kinetically as a function of sediment depth, what mechanisms and/or environmental variables influence the depth-dependent balance between MeHg production and consumption in estuary and marine sediment.

Prior to specific discussion of these questions, several key points are first considered. These points represent interpretational issues frequently encountered in the examination and comparison of published field and/or laboratory Hg data. Consideration of these issues has guided the development of this critical review and their presentation here is as a contextual framework for the discussion that follows. The intent of this discussion is therefore to highlight issues that may complicate the interpretation of field data, rather than to specifically link particular issues with the conclusions drawn by specific authors. The connection between the topics addressed in Section 2 (below) and the body of published research on Hg_i methylation is made in Sections 3–6 of this critical review. Thus, the research examined in Sections 3–6 should be considered in the general context of the themes introduced in the following section.

2. Contextual framework

A discussion of Hg_i methylation must either implicitly or explicitly account for processes regulating the demethylation of MeHg. Thus, any

discussion of Hg_i methylation is simultaneously an exploration of gross MeHg generation and the ambient biogeochemical processes that permit net MeHg accumulation (in either the aqueous or solid phase). As experimental determination of methylation rate is often through isotope addition experiments (in which radio-labeled Hg_i is injected into sediment cores and its conversion to labeled MeHg is monitored over time), the duration of an experiment will dictate whether results are interpreted as approximating gross MeHg production rates or net MeHg accumulation rates. In general, experiments limited to <6 h are thought to approximate gross methylation rates (or methylation potential), while rate determinations calculated from either long-term incubations (>6 h) or from in situ porewater profiles are best interpreted as representing net reaction rates. Methylation potential is defined under the assumption that within the time frame of a short-term incubation (which may vary from 1 to 6 h as defined in the literature), the generation rate of MeHg from labeled Hg_i significantly exceeds the loss rate of MeHg via demethylation.

In defining the relationship between Hg_i methylation potential and either aqueous-phase MeHg (MeHg_{aq}) or sediment MeHg concentration, these terms are best correlated spatially when: 1) the only source of MeHg is in situ production; and 2) the turnover rate of MeHg is slow, such that high MMR results in proportionately high MeHg_{aq} and sediment MeHg concentrations (e.g., Drott et al., 2008). Because there are multiple variables, including hydrodynamics of the overlying water (e.g., Merritt and Amirbahman 2008), organic matter input and/or accumulation rate (e.g., Lambertsson and Nilsson 2006), and the relationship between sediment sampling location (i.e., position along a transect) and the dominance of in situ versus ex situ MeHg production (e.g., Mason and Lawrence 1999), that may influence both MMR and MeHg accumulation (in either porewater or sediment), these terms may be more or less strongly correlated depending on how well a particular environment satisfies both of these criteria (Table 1). Moreover, as it is well recognized from field data that the degree of bioturbation or physical mixing of the sediment by benthic infauna strongly influences the presence and persistence of concentration gradients in both aqueous and sediment solid phases (e.g., Fisher and Matisoff, 1981; D'Andrea et al., 2002; Kostka et al., 2002; Benoit et al., 2006), significant bioturbation likely also alters in situ relationships between MMR, MeHg_{aq} and sediment MeHg concentration. Examples of how the relationship between MMR, MeHg_{aq} and sediment MeHg concentrations may vary in different locations are presented in Table 1.

Although data on gross and net Hg_i methylation rates exist for a range of experimental designs, including pure-culture incubations, amended sediment slurries, isotope injection to field-collected sediment cores, and field depth-profiles (as discussed below), it is challenging to directly compare rate data across types of experiments (Table 2). This difficulty arises from the fact that the Hg_i methylation rate appears sensitive to a range of variables including temperature (e.g., King et al., 1999; Merritt and Amirbahman, 2008), ambient Hg_i concentration (King et al., 1999), organic substrate concentration and/or composition (Weber et al., 1998; King et al., 2000), cell culture growth phase (Benoit et al., 2001a), sampling location along a coastal transect (Marins et al., 1997; Canario et al., 2007), and seasonal variation in the physiology of coastal vegetation (Weber et al., 1998). A further complication in comparing rate-related data arises from the fact that site-specific zero-order methylation rates are frequently presented in the literature as the product of the experimentally determined first-order rate constant (k_m) (gross or net) and either the ambient porewater Hg_i concentration (Hines et al., 2006), spike addition concentration of labeled Hg_i (Marvin-DiPasquale and Agee, 2003) or ambient solid phase Hg_i concentration (Hammerschmidt and Fitzgerald, 2006). As the magnitude of these Hg terms may easily vary by >3 orders of magnitude, it is not always possible to use the published literature to directly assess the extent to which Hg_i methylation rates vary along transects or across ecosystems.

Table 1
Examples of relationships between Hg(II) methylation rate (MMR), porewater methylmercury (MeHg_{aq}) and sediment methylmercury (MeHg_{sed}) concentrations as presented for various locations.

Site	Sampling	Terms	Relationship	Strength	Reference
Patuxent River (MD) estuary	Transect ^a	MeHg _{aq} , MeHg _{sed}	Qual. ^b	Not apparent	Benoit et al. (1998)
Everglades (FL)	Transect ^a	MMR ^c , MeHg _{sed}	Qual.	Apparent	Gilmour et al. (1998)
Everglades (FL)	Cores ^a	MMR ^c , MeHg _{aq} , MeHg _{sed}	Qual.	Not apparent	Gilmour et al. (1998)
Lavaca Bay (TX)	Cores ^d	MeHg _{aq} , MeHg _{sed}	Qual.	Apparent	Bloom et al. (1999)
Barn Island Salt Marsh (CT)	Cores ^e	MMR ^f , MeHg _{aq}	Qual.	Not apparent	Langer et al. (2001)
San-Francisco Bay-Delta (CA)	Cores ^g	MeHg _{aq} , MeHg _{sed}	Qual.	Not apparent	Choe et al. (2004)
Hudson River estuary (NY)	Cores	MMR ^f , MeHg _{sed}	Quan. ^h	R ² = 0.47	Heyes et al. (2004)
New England Continental Shelf	Cores	MMR ^f , MeHg _{sed}	Quan.	R ² = 0.34	Hammerschmidt and Fitzgerald (2006)
Patuxent River (MD) estuary	Cores	MMR ^f , MeHg _{sed}	Quan.	R ² = 0.77	Heyes et al. (2006)
Bay of Fundy	Cores	MMR ^f , MeHg _{sed}	Quan.	R ² = 0.16	Heyes et al. (2006)
Gulf of Trieste	Cores ^d	MMR ^f , MeHg _{aq}	Qual.	Not apparent	Hines et al. (2006)
Penobscot River (ME) estuary	Cores ^e	MeHg _{aq} , MeHg _{sed}	Qual.	Apparent	Merritt and Amirbahman (2007)

^a Direct vacuum filtration.

^b Qualitative relationship assessed by inspection of published data.

^c MMR determined by isotope injection experiments reaching 48 h in duration.

^d Centrifugation.

^e Equilibrium dialysis membranes ("peepers").

^f MMR determined by short-term (≤ 6 h) isotope injection experiments.

^g Core squeezing.

^h Quantitative relationship as presented in the original research.

A related complication in comparing published Hg_i and MeHg data arises from the fact that both vertical profiles (i.e., cores collected in one location and depth-sectioned for analysis) and longitudinal transects of surface sediments are employed in the assessment of mechanisms and/or environmental variables that influence MeHg concentrations or Hg_i methylation rates in field data. Whereas both field sampling methodologies provide relevant data for assessing the temporal and spatial extent of MeHg accumulation within sediment and/or porewater, conclusions drawn from the two sampling strategies may not be readily interchangeable. Thus, a vertical profile, while providing no information on a contaminant's areal extent, allows depth-specific comparison of MeHg concentration with analytes including inorganic sulfide (S(-II)), pH and dissolved organic

matter (DOM) that may influence the Hg_i methylation rate or MeHg accumulation in that location. If the site under study is at depositional steady-state (in the sense that deposition dynamics have remained relatively consistent over time), vertical analyte profiles from that location are amenable to diagenetic modeling (e.g., Berg et al., 1998). Longitudinal transects, on the other hand, while providing important areal information on contaminant deposition or sequestration, frequently incorporate degrees of geochemical and hydrodynamic variability that may limit their utility for asking process-level or mechanism-oriented questions. As example, although variables such as sediment organic content (Lambertsson and Nilsson, 2006) or acid-volatile sulfide (AVS) (Hammerschmidt and Fitzgerald, 2004) have been correlated with the potential for MeHg accumulation in coastal

Table 2
Methylation rates as determined for various field environments and laboratory incubations using the isotope addition technique.

Site	Experiment type	Duration	Rate	Reference
Santa Rosa Sound (FL) embayment	Sectioned sediment cores ^a	24 h	80–130 ^b	Devereux et al. (1996)
Skidaway Institute saltmarsh (GA)	Intact sediment cores ^c	12 h	0–60 ^b	King et al. (1999)
Skidaway Institute saltmarsh (GA)	Sediment slurries ^d	12 h	0–567 ^b	King et al. (1999)
NA	Pure culture incubations ^e	4 d	1.05 – 7.53 ^b	King et al. (2000)
San Pablo Bay (CA)	Homogenized core sections ^a	23 h	<0.0003 – 0.014 ^g	Marvin-DiPasquale et al. (2003)
Everglades (FL)	Intact sediment cores ^a	2–4 h	0–0.12 ^g	Gilmour et al. (1998)
Prospect Slough (CA)	Sectioned sediment cores ^a	4–5 h	<0.001 – 0.003 ^g	Marvin-DiPasquale and Agee (2003)
Frank's Tract (CA)	Sectioned sediment cores ^a	4–5 h	0.005–0.02 ^g	Marvin-DiPasquale and Agee (2003)
Long Island Sound	Intact sediment cores ⁱ	4–8 h	0.01–0.15 ^g	Hammerschmidt and Fitzgerald (2004)
Estuary sediments: anoxic/non-sterile	Sediment slurries ^h	1 d	0.034 ^g	Martin-Doimeadios et al. (2004)
Estuary sediments: oxic/sterile	Sediment slurries ^h	2 d	0.002 ^g	Martin-Doimeadios et al. (2004)
Hudson River estuary (NY)	Intact sediment cores ^h	4 h	0.003 ^g	Heyes et al. (2006)
Bay of Fundy	Intact sediment cores ^h	4 h	0.026 ^g	Heyes et al. (2006)
Patuxent River estuary (MD)	Intact sediment cores ^h	4 h	0.011 ^g	Heyes et al. (2006)
Continental Shelf-New England	Intact sediment cores ⁱ	6 h	0.02–0.22 ^g	Hammerschmidt and Fitzgerald (2006)
Gulf of Trieste/Isonzo River estuary	Sediment slurries ^a	1–2 d	0.01–0.07 ^g	Hines et al. (2006)
Ore River estuary, Sweden	Sediment slurries ^f	10 d	0.2–2.3 ^j	Lambertsson and Nilsson (2006)
Kopmanholmen + Skutskar, Sweden	Homogenized core sections ^f	2 d	0.0001–0.0006 ^g	Drott et al. (2007, 2008)

^a ²⁰³Hg.

^b pg ml⁻¹ h⁻¹.

^c With 1 μg Hg(II) added per 12 cm³ sediment volume.

^d With Hg(II) addition increasing from 0–9.55 μg Hg(II).

^e Hg(II) added at 100 ng ml⁻¹.

^f ²⁰¹Hg.

^g d⁻¹.

^h ¹⁹⁹Hg.

ⁱ ²⁰⁰Hg.

^j ng g⁻¹ d⁻¹.

marine sediment, such variables likely co-vary across a transect of depositional environments (Lawrence et al., 1999; Hammerschmidt and Fitzgerald, 2004) in ways that complicate identification of limiting or controlling mechanisms.

Relatedly, with the exception of dialysis samplers or Diffusive Gradient in Thin Film (DGT) devices for aqueous-phase measurements, porewater and solid-phase MeHg data are rarely presented with a depth resolution finer than 1 cm, and are sometimes presented as a bulk value for depth increments as coarse as 3–4 cm (e.g., Benoit et al., 1998; Marvin-DiPasquale et al., 2003; Heyes et al., 2006; Drott et al., 2007). As porewater MeHg concentration profiles may demonstrate sharp gradients within the vicinity of the sediment–water interface (SWI; e.g., Gagnon et al., 1996; Covelli et al., 1999; Choe et al., 2004; Goulet et al., 2007; Merritt and Amirbahman 2008), the numerical averaging involved in low-resolution sampling may improperly influence the mechanism-oriented interpretation of MeHg data. Specific examples of such influence may include when using Fick's first law to calculate the magnitude of the diffusive MeHg efflux or when using thermodynamic modeling with depth-specific ancillary geochemical data to explain porewater MeHg profiles. If the studies noted above that demonstrate steep porewater MeHg gradients within the vicinity of the SWI are representative, then measurements drawn from bulk, integrated sampling will be affected by the depth resolution selected for sampling. The degree to which such spatial averaging has occurred should be taken into consideration in correlating the porewater MeHg concentration with other aqueous phase and sediment solid phase constituents whose measured concentration may also be affected by the depth averaging employed.

It important to note here that all porewater sampling strategies, including dialysis samplers and DGT devices, result in some level of averaging to generate sufficient sample volume for analysis. The issue raised here is, thus, one of degrees and is intended to highlight the general observation that the larger the depth increment over which data averaging occurs, the greater the likelihood that mechanistic interpretations of sediment processes may be influenced by inexact depth-specific attribution of geochemical cause and effect.

3. Metabolism-related influence on mercury methylation rate

In environments such as estuaries and marine sediments where SRB are thought to dominate microbial Hg_i methylation, many researchers have sought specific relationships between the sulfate reduction rate (SRR) and MMR. A potential correlation between SRR and MMR is consistent with the results of sediment assays in which conditions correlated with the most significant MeHg production and accumulation occur under active microbial mediation in anoxically maintained sediment (Martin-Doimeadios et al., 2004). Choi and Bartha (1994) present a strong correlation ($R=0.98$ at salinity=7 psu) between depth profiles of SRR and MMR for sediment cores collected along a salinity gradient in Cheesapeake (NJ) estuary. Although all data are not provided, they observe that the depth profiles of SRR and MMR, in which rates are highest near the SWI and then decrease significantly with depth, are consistent across a salinity gradient of 7 to 20 psu. SRR decreases from 300 nmol g⁻¹ d⁻¹ to <50 nmol g⁻¹ d⁻¹ (all rates with units as presented in the cited research) over 0–10 cm, while MMR decreases from ~25 ng g⁻¹ d⁻¹ to ~5 ng g⁻¹ d⁻¹ over the same depth interval. Choi and Bartha (1994) conclude that in environments where SO₄²⁻ availability is not limiting, the major factor controlling MMR is the availability of nutrients (organic matter) because nutrient availability determines the consequent activity of SRB.

Devereux et al. (1996) examine MMR, SRR, and the distribution of SRB as a function of depth in sediment cores collected from the Santa Rosa (FL) estuary. Porewater S(-II) increases from below detection to ~0.8 mM across the depth profile studied. SRB community structure is analyzed with rRNA probes designed to assess both the activity of specific gram-negative mesophilic SRB and the relative contribution of

probed genera to the overall anaerobic bacterial community (as determined by the universal 16S rRNA probe). Although SRR data are not presented, the authors observe that the highest measured SRR of 3.5 nmol mL⁻¹ h⁻¹ occurs at the sediment depth (3–4 cm) correlated with the highest mean ($n=3$) MMR of ~2.5 ng mL⁻¹ d⁻¹. Microbial community analysis suggests that (1) total rRNA decreases with depth in the sediment, (2) SRB probes account for ≤5% of total microbial rRNA, and (3) some evidence exists for zonal stratification of probed SRB genera as a function of depth. These authors conclude that the observed depth variation in metabolic activity and/or number of SRB, and hence potentially the MMR, may result from depth-dependent gradients in electron donor availability and/or utilization. For SRB, a list of possible electron donors includes low molecular weight organic acids, long-chain fatty acids, hydrogen, aliphatic hydrocarbons and simple aromatic compounds (Devereux et al., 1996).

King et al. (1999) assess the correlation between MMR and SRR in anoxic sediment slurries and intact sediment cores. For sediment-slurry incubations, the researchers observe that increasing incubation temperature increases both SRR and MMR, and that manipulating either organic substrate availability or SO₄²⁻ reduction potential by the addition of inhibitors similarly affects the MMR. Organic substrate addition experiments include acetate and pyruvate, and for both organic substrates the MeHg accumulation rate over 36 h is greater than in control (unamended) slurries. Moreover, the addition of molybdate to the slurry incubations significantly decreases both SRR and MeHg accumulation. Based on their results, King et al. (1999) propose that MMR may be predicted as a linear function of SRR, with the highest measured SRR (30 nmol g⁻¹ h⁻¹) corresponding to a MMR ≈ 1500 pg g⁻¹ h⁻¹. Dissolved S(-II) was not measured in the slurry incubations, although conditions were maintained at a reduction potential between -0.11 and -0.22 V and SO₄²⁻ reduction was occurring at a mean rate of 4.8 nmol g⁻¹ h⁻¹.

Although conditions defined in a continuously agitated slurry reactor are clearly distinct from those describing incubated intact sediment cores, isotope injection experiments utilizing salt marsh sediment cores have further demonstrated that both SRR and MMR decrease in parallel, downward in the core, from near-surface peaks (King et al., 1999). In intact sediment cores (as opposed to the sediment-slurry incubations described above), mean SRR decreases from ~50 nmol g⁻¹ h⁻¹ at the SWI to ~5 nmol g⁻¹ h⁻¹ by 10 cm, with mean MMR decreasing from ~50 pg g⁻¹ h⁻¹ to ~1 pg g⁻¹ h⁻¹ over this same depth increment. Subsequent research with cores collected from the same salt marsh ecosystem demonstrate small differences (factor of 2–3) in absolute SRR and MMR, although all cores replicate a consistent trend with surface or near-surface maxima in both SRR and MMR that decrease with depth in the sediment (King et al., 2001).

The SRR depth profile presented in King et al. (2001) is commonly observed in coastal marine and salt marsh sediments lacking significant bioturbation (e.g. Novelli et al., 1988; Holmer and Kristensen, 1996; Schubert et al., 2000; Kostka et al., 2002), and has been explained as a function of SRB relative abundance as controlled by variables such as organic matter input rate or limitations of dissolved oxygen transfer from the overlying water. This explanation is supported by observations that variation in measured SRR as a function of sediment depth appears reasonably well correlated with absolute SRB numbers (Sahm et al., 1999; Bottcher et al., 2000; Llobet-Brossa et al., 2002), and that the observed decrease in SRB numbers with depth is not necessarily driven by SO₄²⁻ limitation at depth (e.g., Bottcher et al., 2000; Wilms et al., 2006).

In general, if a SRR depth profile is defined as containing a depth zone demonstrating maximum SRR (SRR_{max}), environmental variables such as significant bioturbation or a significantly extended Fe(III) and Mn(III/IV) reduction zone may alternately eliminate a SRR_{max} in the depth profile (e.g. Holmer and Kristensen, 1996; Kostka et al., 2002) or result in its manifestation at greater sediment depth (e.g., Canfield et al., 1993), respectively. In the context of Hg_i methylation,

these observations suggest that the decrease in MMR frequently observed at depth in coastal marine sediments may be driven by the same general environmental variables responsible for the decrease in SRB community metabolism.

Research with pure cultures of various SRB genera has documented that, per cell, acetate-utilizing SRB methylate Hg_i at significantly higher rates than non-acetate utilizing SRB (King et al., 2000). This heightened methylation efficacy is potentially metabolic in origin and has been correlated with the induction of methyl transferase enzymes as a component of complete acetate oxidation (King et al., 2000). The methyl (CH_3^-) group in question may originate from multiple compounds generated or oxidized during organic substrate metabolism (including formate, serine, and pyruvate) (Choi et al., 1994a). Other research has documented contrasting results, with Ekstrom et al. (2003) observing methylation rates (per cell) that are equivalent for incompletely acetate-oxidizing SRB (*Desulfobulbus propionicus* 1pr3) versus completely acetate-oxidizing SRB (*Desulfococcus multivorans* 1be1). Utilization of the acetyl-CoA pathway for methylation (and acetate oxidation) is verified for acetate-oxidizing SRB by the observed inhibition of methylation following chloroform addition (a known inhibitor of the acetyl-CoA pathway). Ekstrom et al. (2003) further observe that those SRB capable of Hg_i methylation under chloroform inhibition (i.e., those strains not relying on the acetyl-CoA pathway for organic substrate oxidation) have the capability of utilizing propionate as a carbon source. Several of the incomplete-oxidizing strains of SRB tested (members of the genus *Desulfobulbus*) rely on a B_{12} -containing enzyme in the propionate metabolism pathway that may function in some as yet unknown capacity with respect to CH_3^- group transfer to Hg_i .

King et al. (2000) supplement pure-culture experiments with sediment-slurry incubations in which SRR and MMR are determined under acetate and lactate addition. Results suggest that when normalized to SRR, MMR decreases in the order acetate > lactate > control sediment (no amendment addition) and that the SRB community varies in relative abundance of different genera under these tested regimes. These observations suggest that MMR may be affected both by overall community metabolism (defining the overall SRR) and by conditions such as the presence and activity of syntrophic bacteria or the growth phase of emergent marsh vegetation that influence the quality and composition of the available SRB organic substrate pool.

Although the acetyl-CoA pathway clearly represents only one of several possible CH_3^- transfer pathways (Ekstrom et al., 2003; Ekstrom and Morel, 2007), the hypothesis that methylation of Hg_i may be enzymatically catalyzed is supported by research noting that: 1) the inhibition of the acetyl-CoA synthase pathway inhibits MeHg synthesis by *Desulfovibrio desulfuricans* LS (Choi et al., 1994a); 2) methylation rates in laboratory assays are significantly higher in the presence of cell extracts containing Co-enriched corrinoid proteins (a likely CH_3^- carrier) than simply in the presence of methylcobalamin (Choi et al., 1994b); and 3) the induction of Co-limited conditions inhibits MeHg production (on a per cell basis) for the complete oxidizer *D. multivorans* (Ekstrom and Morel, 2007).

Other research has observed poor or inconsistent correlation between SRR and MMR. Hines et al. (2006) examine SRR and MMR in sediment cores collected from coastal marine sediments in the Adriatic Sea. They observe that for seasonal sampling, SRR is higher in late summer than early spring, with the greatest seasonal increase occurring in near-surface sediments. Mean surface-sediment SRR increases from ~ 10 – $50 \text{ nmol mL}^{-1} \text{ d}^{-1}$ in March to ~ 75 – $250 \text{ nmol mL}^{-1} \text{ d}^{-1}$ in August. While corresponding MMR also increase with the warming of overlying waters, the rate increase appears significant throughout the depth of the sediment cores. The highest measured mean Hg_i methylation rate constant ($k_m = 0.07 \text{ d}^{-1}$), for example, occurs at a depth of $\sim 5 \text{ cm}$ in August, inconsistent with the sediment depth of maximum seasonal SRR.

Gilmour et al. (1998) assess Hg_i methylation dynamics in surface-sediment transects and sediment cores collected along a trophic gradient in the Florida Everglades. Although the Everglades are more accurately characterized as a freshwater system, research results from this location are a central underpinning of hypotheses that are discussed in Section 4 of this review. As such, and for the sake of completeness, a brief summation of research results from Gilmour et al. (1998) that are relevant to Hg_i methylation are presented here.

For sediment collected along a longitudinal transect, methylation rate is assessed by injecting $^{203}Hg_i$ into bulk, homogenized surface sediment (0–4 cm). For the sediment cores, methylation rate is assessed by $^{203}Hg_i$ injection at 1 cm intervals into the sediment column. For surface sediment, Gilmour et al. (1998) observe MMR that both vary seasonally and increase across the trophic gradient studied. Mean ($n = 2$ – 5) MMR in surface sediments is $\leq 10 \text{ ng g}^{-1} \text{ d}^{-1}$. Corresponding SRR is presented as a range (10 – $60 \text{ mmol m}^{-2} \text{ d}^{-1}$) with little supporting information regarding either seasonal or trophic gradient-related variability. For incubated sediment cores, SRR and MMR appear poorly correlated as a function of depth, with SRR either increasing with depth to a broad subsurface maximum before declining deeper in the core or demonstrating no depth-dependent gradient. In both cores analyzed, MMR increases to a distinct subsurface peak at 3 cm then declines more sharply with depth than the corresponding broad peak in SRR (when present). Peak MMR is $\sim 4 \text{ ng g}^{-1} \text{ d}^{-1}$, with corresponding SRR of ~ 100 – $300 \text{ nmol cm}^{-3} \text{ d}^{-1}$. Results from core incubations in which specific inhibitors of SO_4^{2-} reduction are added are inconsistent in terms of limitations on MMR, leading the authors to conclude that MMR may be controlled by either SO_4^{2-} or S(-II) concentration depending on sampling site and season. The role that S(-II) concentration may play in controlling MeHg production is discussed further in Section 4 and Section 6 of this review.

4. Speciation-related influence on mercury methylation rate

If methylation of Hg_i is predicated on diffusive uptake of dissolved Hg_i (Benoit et al., 1999a), then a relationship should exist between MeHg production and either total dissolved Hg_i or the concentration of a particular dissolved Hg_i species. With respect to MeHg production, this relationship may be presented in terms of a production rate (i.e., d^{-1}) or in terms of a concentration of generated MeHg. As examples, Hammerschmidt and Fitzgerald (2004) assess methylation potential (i.e., gross MeHg production) via isotope injection experiments with sediment cores collected in Long Island Sound (NY). In regressing methylation potential (% methylated d^{-1}) against porewater Hg_i , the fraction of explained variance varies seasonally between March ($R^2 = 0.54$) and August ($R^2 = 0.78$). With the exception of one high Hg_i outlier, the highest porewater Hg_i concentration (175 pM) is correlated with a methylation potential of 0.15 d^{-1} . Samples ($n = 6$) excluded from the regression analysis have S(-II) $\geq 50 \text{ } \mu\text{M}$ and significantly lower methylation potential than predicted based on the porewater Hg_i concentration. In sediment cores collected from the New England continental shelf, Hammerschmidt and Fitzgerald (2006) observe a similar correlation ($R^2 = 0.60$) between porewater Hg_i (reaching 30 pM) and $^{200}Hg_i$ methylation potential (reaching 0.2 d^{-1}). In neither study is an upper limit or plateau reached for Hg_i methylation potential and in all study sites (with the exception of the six omitted samples discussed above), porewater S(-II) is $< 10 \text{ } \mu\text{M}$.

In pure-culture experiments, Benoit et al. (2001a) and King et al. (1999) have also observed strong ($R^2 \geq 0.94$) positive correlations between filtered Hg_i and either the concentration of unfiltered MeHg or MMR, respectively. For 6-day experiments with *D. propionicus* (1pr3), Benoit et al. (2001a) observe that across a Hg_i concentration range of 0– 200 pM , the MeHg concentration ranges from 0 to 65 pM . King et al. (1999) examine MMR in terms of both the concentration of initially added Hg_i and the concentration of aqueous phase Hg_i that

remains available over a 36 h incubation. Results suggest that: 1) rapid sorption of the Hg_i spike to sediment solid phases results in an aqueous-phase Hg_i concentration that is <0.2% of the spike concentration; and 2) for incubations ≤ 12 h, MMR is strongly correlated with aqueous phase Hg_i over the Hg_i concentration range 100–650 pM.

Although it is difficult to define the mechanism behind these linear relationships, – in the case of King et al. (1999) as example, what they have demonstrated is that a decrease in aqueous Hg_i concentration correlates with a decrease in MMR, and, separately, that an additional Hg_i spike following a 24 h incubation increases the MMR – these data do suggest that within a porewater Hg_i range that spans most field Hg_i data, MMR is positively influenced by increasing porewater Hg_i concentration. If such a relationship based on total Hg_i is interpreted mechanistically, however, it may obscure several key issues, including whether: 1) the MMR may actually be driven not by total Hg_i , but by the concentration of a particular Hg_i species, and/or 2) the linear relationship observed between MMR and Hg_i may be indirectly a function of a distinct driving variable such as the quality or production rate of requisite microbial organic substrate.

Addressing the question of whether the speciation of Hg_i may influence MMR, studies have examined whether microbial Hg_i availability and/or MMR may be influenced by the concentration of DOM or other potential complexing ligands, either singly or in combination (e.g., Barkay et al., 1997; Ravichandran et al., 1999; Hintelmann et al., 2000; Miller et al., 2007), the concentration of charged versus uncharged cationic Hg ($Hg(II)$) complexes (Benoit et al., 1999a), pH (Paquette and Helz, 1995), and/or the concentration of aqueous polysulfide species (Jay et al., 2000). Although not likely influencing MMR directly, the speciation of MeHg may also influence fate and transport processes that affect the stability of MeHg complexes and, thus, observed net MMR. Loux (2007) reviews published thermodynamic constants for MeHg speciation and highlights the currently poor resolution of this topic within the literature.

Ravichandran (2004) has reviewed the potential influence of DOM on the solubility, bioavailability, and speciation of Hg_i . In terms of solubility, research has documented the effect of DOM on either inhibiting cinnabar precipitation (Ravichandran et al., 1999) or enhancing cinnabar solubilization (Ravichandran et al., 1998; Waples et al., 2005). Results of these experiments thus highlight the role that DOM may play in controlling the porewater Hg_i concentration under conditions in which cinnabar precipitation could theoretically limit porewater Hg_i (and thus potentially MeHg) concentration and availability. However, because such research has typically been conducted under well-oxygenated (e.g., Waples et al., 2005) and/or agitated conditions (e.g., Ravichandran et al., 1998), it is not clear to what extent these processes are significant under field conditions. Moreover, with the calculated rate of DOM-mediated dissolution of cinnabar decreasing by several orders of magnitude under quiescent conditions (Ravichandran et al., 1998), DOM may not function as the ligand that controls porewater Hg_i concentration at depth in anoxic sediment (e.g., Merritt and Amirbahman, 2007). There is currently little published research specifically addressing the kinetics of ligand-mediated solubilization of Hg_i under field conditions, and a better understanding of this topic would provide valuable insight into the nature of Hg_i -ligand interactions in sediment porewater.

In terms of speciation, extended X-ray absorption fine structure (EXAFS) spectroscopy has documented strong interactions between mercury and the sulfur-rich functional groups in organic matter (Xia et al., 1999). Conditional equilibrium constants for these Hg-sulfur complexes, as reviewed by Gasper et al. (2007) and Ravichandran (2004), may reach 10^{30} , and highlight the potential significance of organic complexation in aqueous Hg_i speciation. Competitive ligand exchange experiments conducted by Hsu and Sedlak (2003) and Hsu-Kim and Sedlak (2005) have demonstrated, however, that: (1) in wastewater effluent and surface water, Hg_i complexes exist that do not dissociate in the presence of glutathione (20–100 μM); and (2) the

unidentified strong complexing ligand has characteristics more consistent with inorganic S(-II) than organic thiolated compounds. The experimental strategy employed by Hsu and Sedlak (2003) and Hsu-Kim and Sedlak (2005) (i.e., Competitive Ligand Exchange-Solid Phase Microextraction) is recognized as the most appropriate strategy for characterization of the Hg-DOM binding environment (Gasper et al. 2007). Integration of evidence presented by Ravichandran (2004), Gasper et al. (2007) and Hsu and Sedlak (2003) and Hsu-Kim and Sedlak (2005) suggests that Hg-DOM complexes may dominate Hg_i speciation in oxygenated waters (including oxygenated porewater), whereas S(-II) dominates Hg_i speciation under reducing conditions. The combined role that DOM and S(-II) may also play in enhancing Hg_i bioavailability is considered further in Section 6.

Benoit et al. (1999a) propose that porewater S(-II) concentration likely influences Hg_i speciation and that the microbial availability of Hg_i is controlled not by total Hg_i , but by the concentration of neutral Hg-S(-II) species, principally HgS^0 . Subsequent ab-initio calculations have suggested that this species likely exists as $Hg(SH)(OH)^0$ (Tossell, 2001). While this alternate neutral Hg-S(-II) species may vary in its diffusivity, pH sensitivity and cellular uptake rate relative to HgS^0 , the following discussion will continue to employ the neutral Hg-S(-II) species as HgS^0 .

The HgS^0 model is based on consideration of sediment MeHg and aqueous phase Hg_i and S(-II) data for surface sediment (0–4 cm) collected along transects in the Patuxent River (MD) estuary and Florida Everglades. For both study sites, although there appears to be little or no gradient in sediment MeHg at $>1 \mu M$ S(-II), chemical equilibrium modeling suggests that Hg_i speciation, in the form of the neutral Hg-S(-II) species $HgS^0 + Hg(HS)_2^0$ explains sediment MeHg concentration. Coefficients of determination for the sum of neutral Hg-S(-II) species versus sediment MeHg concentration are $R^2 = 0.50$ and $R^2 = 0.59$ for Patuxent River and Florida Everglades sediments, respectively.

Goulet et al. (2007) have observed that, based on the manner in which the formation constant for the aqueous HgS^0 complex (i.e., $HgS_{(s)} \rightleftharpoons HgS^0$) was derived, application of the HgS^0 model requires critical evaluation. This formation constant, although defining the basis of the model, was extrapolated from the formation constants of other Class IIB transition metal complexes ($ZnS_{(aq)}$ and $CdS_{(aq)}$) rather than being determined experimentally. Subsequent research has not yet confirmed the accuracy of the formation constant presented by Benoit et al. (1999a) in the model's original formulation. In terms of field data, it is also worth noting that for the Patuxent estuary site, the original data from which the model was derived represent surface sediment transects in which: (1) sampling is as bulk collection integrating the 0–4 cm depth interval; (2) no strong correlation is apparent between sediment MeHg and porewater MeHg; and (3) there is only an inferred correlation between sediment MeHg concentration and MMR (Benoit et al., 1998). As discussed in Section 2 of this critical review, (1) bulk sample collection integrates across a sediment depth interval in which concentration gradients likely exist; (2) the data demonstrate only weak spatial correlation between net sediment MeHg accumulation (as defined by sediment MeHg concentration) and either MeHg production or porewater MeHg concentration; and (3) the data presume but do not demonstrate a predominance of in situ MeHg production along this longitudinal transect. As such, mechanistic interpretations of mercury dynamics grounded in these data should be approached with caution.

Related research has tested the neutral Hg-S(-II) species model, hypothesizing that for a fixed concentration of Hg_i , an increase in porewater S(-II) would correlate with a decreasing fraction of neutral Hg-S(-II) species. This decreasing fraction of neutral Hg-S(-II) species (although not necessarily equivalent to a decreasing concentration of neutral Hg-S(-II) species) might in turn limit either the MeHg production rate or MeHg accumulation in sediments (Benoit et al., 1999b). In laboratory experiments Benoit et al. (1999b) observe that

increasing S(-II) over the range ~1 μM –10 mM results in an observed non-linear decrease in the octanol–water partitioning of Hg_i . These results suggest that Hg_i partitions preferentially into the octanol phase at low S(-II) concentrations and support the presence and activity of a lipophilic Hg–S(-II) species.

The neutral Hg–S(-II) species model has been further assessed through experiments examining the effect that aqueous polysulfide species, generated through the reaction of rhombic sulfur (S^0) with HS^- , have on the solubility of cinnabar ($\text{HgS}_{(s)}$) (Paquette and Helz, 1997; Jay et al., 2000). While these studies have substantively confirmed that the solubility of $\text{HgS}_{(s)}$ increases in the presence of S^0 -generated polysulfides, Jay et al. (2002) have found no correlation between the increased solubility of Hg_i and an increase in MMR. These authors attribute the uncoupling of Hg_i solubilization from methylation to marked increases in the concentration of charged Hg–S(-II) species from polysulfide-mediated speciation. As these species do not readily diffuse through lipid membranes, their increased concentration has been hypothesized to have no direct effect on observed MMR.

Whereas Benoit et al. (1999a) note that its contribution to the sum of neutral species is minimal, the inclusion of $\text{Hg}(\text{HS})_2^0$ in the speciation model suggests a further pH-dependence of modeled data (Schwarzenbach and Widmer, 1963). At pH = 7.0, the charged species HgS_2H^- is dominant over the uncharged $\text{Hg}(\text{HS})_2^0$ species, although depending on the equilibrium constants chosen for the one proton dissociation of $\text{Hg}(\text{HS})_2^0$ (as presented in Benoit et al. (1999a)), the first pK_a for $\text{Hg}(\text{HS})_2^0$ may vary by as much as 0.5 pH unit. With a pK_a of 6.0 (Benoit et al., 1999a), a realistic variation in porewater pH will influence the modeled concentration of $\text{Hg}(\text{HS})_2^0$. Such variation in pH may be observed within the suboxic zone of non-bioturbed coastal marine sediments (e.g., Muller et al., 1997; Komada et al., 1998; Cai et al., 2000; Jourabachi et al., 2005) and is likely attributed to a combination of microbial respiration and abiotic redox reactions. Because the presence of this zone creates a pH gradient with influence on Hg–S(-II) speciation (even for a relatively constant concentration of total dissolved S(-II)), the resultant potential variation in $\text{Hg}(\text{HS})_2^0$ concentration may be important as follows: if diffusive microbial uptake is a function of the availability of neutral Hg–S(-II) species, as is suggested by Benoit et al. (2001b), then whether any particular species dominates the porewater Hg–S(-II) pool is less significant than whether changes in the variables that dictate speciation (such as pH or S(-II)) affect the absolute concentration of a particular neutral Hg–S(-II) species.

Other research focusing on the availability of HgS^0 for methylation has demonstrated a linear relationship between model-derived HgS^0 concentration and measured MeHg (unfiltered) for Hg_i originating from the dissolution of various Hg-bearing rock types (Benoit et al., 2001b). Coefficients of determination between HgS^0 concentration and unfiltered MeHg concentration vary between $R^2 = 0.79$ – 0.81 for separate experiments, with this small difference in R^2 values likely explained by differing inoculum concentrations, and thus cell growth characteristics, in each experiment. Although HgS^0 accounts for $\leq 20\%$ of dissolved Hg_i at the S(-II) concentrations presented in this study (Benoit et al., 2001b), the researchers conclude that MeHg production in aquatic environments is controlled both by microbial activity and the role that Hg–S(-II) speciation plays in heightening diffusive uptake of Hg_i (Benoit et al., 2001b). This research, although noting that the mechanistic linkage between HgS^0 and MeHg concentrations remains unclear, highlights the linked nature of the dominant processes (i.e., metabolic activity and speciation) affecting Hg_i methylation rates in estuarine and coastal marine environments.

Field interpretation of these laboratory experiments has focused on the likelihood that there is an optimum S(-II) concentration for Hg_i methylation (e.g., Heyes et al., 2006; Hammerschmidt and Fitzgerald, 2006; Hines et al., 2006; Lambertsson and Nilsson, 2006; Munthe et al., 2007), with that optimum ($\leq 10 \mu\text{M}$; Benoit et al., 2001b; Benoit et al., 2006) defined by the concentration above which HgS^0 no longer

dominates Hg–S(-II) speciation. In this scenario, speciation is argued to be predominantly a function of S(-II) concentration. Interpretation of field experiments that may allow testing of this hypothesis is often hindered, however, by incomplete provisioning of ancillary chemistry including porewater pH, DOC, S(-II), and Fe(II) concentration profiles. Although there are valid reasons for the absence of key analyte data, including small sample volume, expense, and time constraints on various analytes' stabilities, the resultant inability to define system geochemistry limits the ability to critically compare potential Hg_i speciation models and to validate the existence of an optimum S(-II) concentration in a given system.

Recent research (Drott et al., 2007; Merritt and Amirbahman, 2007, 2008) has examined site-specific profiles of porewater Hg_i and MeHg with an eye toward mechanistic interpretation of field data. These studies provide either/both the spatial resolution and ancillary chemistry required to assess whether correlation exists between Hg_i speciation and the net Hg_i methylation rate. Net Hg_i methylation rates have been determined by either isotope injection (Drott et al., 2007) or diagenetic modeling of porewater MeHg profiles (Merritt and Amirbahman, 2008).

For porewater profiles collected in brackish-water environments (as well as freshwater environments), Drott et al. (2007) report no correlation between the concentration of dissolved S(-II) and either sediment MeHg or neutral Hg–S(-II) speciation as determined by thermodynamic modeling. That is, neither sediment MeHg concentration, nor the concentration of neutral Hg–S(-II) species may be defined as a function of porewater S(-II) concentration (which varies between 0.3 μM –700 μM for brackish-water sites). For these brackish-water sites, correlation does exist ($R^2 = 0.64$), however, between the sum of neutral Hg–S(-II) species ($\text{HgS}^0 + \text{Hg}(\text{HS})_2^0$) and sediment MeHg concentration and (with an important caveat described below) between the concentration of neutral Hg–S(-II) species and the net MMR (as determined by $^{201}\text{Hg}_i$ injection with $t = 48$ h). The correlation between the concentration of neutral Hg–S(-II) species and net MMR ($R^2 = 0.58$) is, however, contingent on the exclusion of surface sediments (0–5 cm and 0–3 cm depth increments) from the regression. Importantly, both the net MMR and the concentration of neutral Hg–S(-II) species are higher in the excluded sediments, but presumably are not well described by the indicated relationship (as discussed by Drott et al., 2007). As the near-surface (excluded) sediments are not uniformly described by either decreased dissolved S(-II) or lower pH relative to deeper sediment increments (U. Skyllberg, personal communication), the increase in total neutral Hg–S(-II) species predicted for this shallow depth zone cannot be attributed to simple variables that vary predictably between distinct sampling sites or sediment depths.

Using steady-state diagenetic modeling, Merritt and Amirbahman (2008) have shown that for a site in the Penobscot River (ME) estuary, the net MeHg production rate is highest at ~2–7 cm depth in mudflat sediments. Whereas this depth increment is generally coincident with the highest fractional concentration of both HgS^0 and $\text{Hg}(\text{HS})_2^0$ species (defined, as per Benoit et al. (1999a), as a percentage of Hg–S(-II) species distribution) when these species are modeled separately, this depth increment is not always coincident with the highest absolute concentration of HgS^0 and/or $\text{Hg}(\text{HS})_2^0$ calculated from the thermodynamic model. Of importance in this observation is that whereas thermodynamic modeling results are supportive of the same framework assumptions (i.e., Benoit et al., 1999a) both with and without the inclusion of the HgS^0 species, speciation models explain the field data best when defined in terms of relative percent contribution of neutral Hg–S(-II) species. Moreover, whereas the concentration of HgS^0 always dominates neutral Hg–S(-II) speciation when included in the model, scenarios modeled either with or without the presence of this species are generally equally robust in their ability to correlate depth-specific net Hg_i methylation rates with the highest relative contribution of neutral Hg–S(-II) species, rendering it difficult to attribute this

correlation to any individual, specific uncharged Hg-S(-II) species. We note that as neither Drott et al. (2007) nor Merritt and Amirbahman (2008) present data from which to assess depth-specific variation in SRR or other measures of SRB community metabolism, it is not possible to examine their data in light of the discussion presented in Section 3 of this critical review.

For the Penobscot River (ME) estuary field data presented above, the highest measured porewater MeHg concentration of 72 pM occurs at a S(-II) concentration of 20 μM (Merritt and Amirbahman, 2008), approximately consistent with the proposed S(-II) optimum at 10 μM (Benoit et al., 2001b; Benoit et al., 2006). However, using laboratory incubated sediment columns collected from the same study site and maintained under varying redox regimes at the SWI, the porewater S(-II) concentration coincident with highest porewater MeHg concentration increases from $\sim 70 \mu\text{M}$ for the column maintained under oxic conditions to $\sim 700 \mu\text{M}$ for the column maintained under stagnant water conditions (Merritt and Amirbahman, 2008). Furthermore, the highest measured porewater MeHg concentration (117 pM) and the highest modeled net MeHg production rate ($16.6 \times 10^{-20} \text{ mol cm}^{-3} \text{ s}^{-1}$) occur in the stagnant water incubation and coincident in depth increment with the sharp increase in porewater S(-II) concentration at the redoxcline. Porewater S(-II) concentrations range from $< 1 \mu\text{M}$ –1.2 mM for this experiment and for all redox manipulations increase with sediment depth as expected. These results do not support the hypothesis that low S(-II) concentrations are the dominant environmental variable correlating with depth-dependent variations in either porewater MeHg concentration or the net rate of MeHg production. Further discussion of the role that the porewater S(-II) concentration may play in affecting either porewater MeHg concentration or net Hg_i methylation rate is presented in Section 6.

5. Demethylation dynamics

Whereas this review has addressed the often observed decline in MMR with sediment depth, Hg_i methylation dynamics within the vicinity of the SWI also warrant further examination. As the processes responsible for methylation of Hg_i and demethylation of MeHg frequently overlap both spatially and kinetically, environmental variables that influence the relative balance between these terms will determine the extent to which MeHg generated within porewaters accumulates in the vicinity of the SWI. Because porewaters may be enriched in MeHg relative to the overlying water (e.g., Covelli et al., 1999; Choe et al., 2004), net MeHg accumulation near the SWI may generate a concentration gradient with implications for MeHg diffusive flux to overlying water.

Research examining the balance between MeHg production and degradation has documented the existence of multiple methylation and demethylation pathways. Although MeHg production and consumption appear to be dominantly microbially-driven processes (Fig. 1), researchers have documented photochemical production of MeHg in lake surface water (Siciliano et al., 2005) and, potentially, on the surface of Everglades periphyton, as inferred from the microbially-inhibited control incubations presented by Cleckner et al. (1999). Results from Siciliano et al. (2005) suggest that both the concentration and size fractionation of DOM influenced MeHg formation, with formation restricted to the smallest DOM size fractions. In terms of abiotic MeHg consumption, photochemical demethylation may also occur (Sellers et al., 1996; Hammerschmidt et al., 2006) as well as demethylation via a S(-II)-mediated transformation of MeHg into dimethylmercury and HgS_(s) (Baldi et al., 1993; Wallschläger et al., 1995). The significance of these abiotic MeHg production and consumption mechanisms remains an open question within estuary and marine environments (e.g., Gagnon et al., 1996; Bloom et al., 1999; Hintelmann et al., 2000; Martin-Doimeadios et al., 2004) and a topic for further research. Likewise, the effect of MeHg speciation on MeHg consumption (either biotic or abiotic) has not been well addressed in

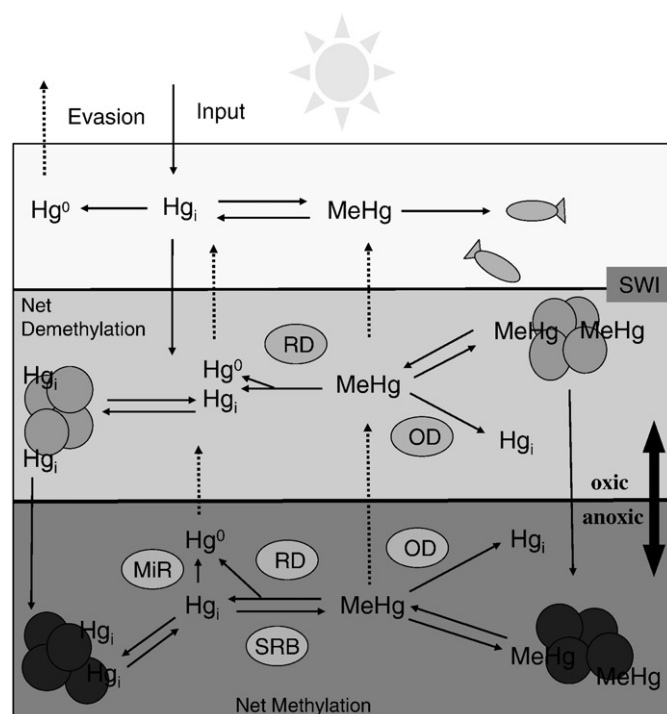


Fig. 1. Conceptual overview of mercury methylation dynamics in estuarine and coastal marine environments. The sedimentary environment is presented with oxic and anoxic regions, with arrows indicating that the boundary between these regions (i.e., the redoxcline) may fluctuate vertically. Hg_i = inorganic divalent Hg; MeHg = aqueous phase methylmercury; Hg_i and MeHg associated with dark circles represent Hg species associated with particulate matter; SWI = sediment–water interface; OD = oxidative demethylation; RD = reductive demethylation; SRB = sulfate reducing bacteria; MiR = *mer*-independent reduction. Solid arrows directed downward represent sedimentation or depositional processes, including atmospheric inputs, sedimentation following sorption to particulate matter, and sediment burial. Dotted arrows directed upward represent diffusional processes, including aqueous phase diffusion and vapor phase volatilization. Other solid arrows represent biogeochemical or geochemical processes including methylation and demethylation, biotic uptake, and sorption/desorption reactions involving sediment particulate matter.

the literature, and, as noted by Loux (2007) may also influence the fate, transport, and/or biological availability of MeHg.

Microbially-mediated demethylation of MeHg has been observed to occur by both reductive and oxidative pathways and may result from either cellular detoxification or metabolic mechanisms across a broad range of microbial genera. Reductive demethylation, in which the end products of MeHg degradation are CH₄ and either Hg(II) or Hg⁰, occurs in aerobic and anaerobic environments, and represents a mercury resistance or detoxification mechanism encoded in plasmid-carried *mer*-operons (Marvin-DiPasquale et al., 2000). *Mer* operons appear to be widely distributed in nature, occurring in gram-negative and gram-positive bacteria (Barkay et al., 2003), and appear to be induced under aqueous phase Hg_i or MeHg concentrations that are relevant to a range of potential contaminant levels. Rasmussen et al. (1997) observe, as example, that *mer*-specified functions (defined in this experiment by luminescence of the *mer-lux* bioassay) are sensitive to both applied Hg_i concentration and cell density in the bioassay. For cell densities $\leq 10^6 \text{ cells mL}^{-1}$, luminescence was induced under Hg_i concentrations as low as 7 pM, suggesting that *mer*-based detoxification mechanism is not limited to highly polluted environments. Ambient Hg_i and/or MeHg concentration does appear to affect the potential for microbial Hg resistance, however, as Schaefer et al. (2004) observe that for two sites with differing surface water concentrations of total Hg_i and MeHg, the site with the higher total Hg_i and MeHg concentrations (Meadowlands, NJ) is enriched in Hg-resistant bacteria containing and expressing *mer* genes relative to

the site with lower total Hg_i and MeHg concentrations (Pine Barrens, NJ). For the Meadowlands site, total Hg_i ranges from 0.5 to 21 nM, and MeHg ranges from 0.4 to 8.0 pM. For the Pine Barrens site, total Hg_i ranges from 1.5 to 27 pM, and MeHg ranges from 0.14 to 0.16 pM.

Complete reductive demethylation via *mer*-operons may be viewed as a two-step process: a *mer*-B gene first encodes for the production of organomercurial-lyase, an enzyme responsible for CH₃⁻ group cleavage and the resultant transformation of MeHg to CH₄ + Hg(II); a *mer*-A gene separately encodes for the production of mercuric reductase and the reduction of Hg(II) to Hg⁰ which may potentially volatilize from surface sediments. In anaerobic environments, the reduction of Hg(II) to Hg⁰ may also occur via *mer*-independent pathways involving respiratory electron transport activity (Wiatrowski et al., 2006). Dissimilatory metal reducing bacteria, including species of the genus *Geobacter*, have demonstrated such Hg(II) reduction ability in the presence of suitable electron donors (acetate) and acceptors (Fe(III)) (Wiatrowski et al., 2006). Abiotic reduction of Hg(II) to Hg⁰ in the presence of reducible Fe(III) citrate has also been demonstrated in laboratory incubations of saturated tropical soils (Peretyazhko et al., 2006). As noted above, the significance of these Hg(II) reduction mechanisms within estuary and marine environments remains an open research question.

Oxidative demethylation, in which the CH₃⁻ group in MeHg is utilized as a C₁ substrate analog, appears to result in the dominant production of CO₂ + Hg(II). CO₂ production from MeHg degradation has been observed in anaerobic incubations of estuary sediments and in anaerobic and aerobic incubations of freshwater sediments and is at least partly mediated by SRB, methanogenic bacteria and aerobes (Oremland et al., 1991). This MeHg loss mechanism has been reported in sediments that span the freshwater to hypersaline continuum (Oremland et al., 1991; Hines et al., 2006) and appears to function across a broad range of sediment Hg_i and/or MeHg concentrations (Oremland et al., 1995; Marvin-DiPasquale et al., 2000; Marvin-DiPasquale et al., 2003), although neither driven nor induced by the sediment MeHg concentration. Experimentally it has been shown that for depth profiles of labeled ¹⁴CH₃Hg, ¹⁴CO₂ production appears generally greater in surface sediments and decreases down core (Oremland et al., 1995). It is important to note that as oxidative demethylation utilizes the CH₃⁻ group, the carbon end product will be determined by the depth-specific dominant respiratory process (Oremland et al., 1991). Thus, while CO₂ production likely dominates in environments defined by the abundance of denitrifiers, dissimilatory metal reducers and SRB, CH₄ production may likely result from oxidative demethylation under methanogenic conditions (Warner et al., 2003). As the end-product of oxidative demethylation is presumed to be Hg(II), this demethylation pathway results in an aqueous phase Hg_i species that may recycle within the sedimentary environment (Barkay et al., 2003).

As with methylation rate assays, potential demethylation rates have been estimated in intact sediment cores and slurry incubations. Depth profiles of demethylation rate, as determined by isotopic injection of ¹⁴CH₃Hg into sediment cores, have demonstrated that while net rates may vary seasonally (Hines et al., 2006), they appear to vary less significantly with sediment depth than either net or gross methylation rates (e.g., Heyes et al., 2006; Hines et al., 2006; Lambertsson and Nilsson, 2006). The latter conclusion is conceptually similar to observations made in slurry incubation experiments assessing wetland sediment methylation and demethylation rates under varying dominant respiratory processes (i.e., Fe(III)-reducing, SO₄²⁻-reducing, and methanogenic conditions) (Warner et al., 2003). In this research, whereas net methylation rates vary significantly over time under the conditions described above, and are generally lower under Fe(III)-reducing versus SO₄²⁻-reducing or methanogenic conditions, net demethylation rates (while not presented on a cell specific basis) appear relatively constant over time and similar in magnitude for all terminal electron acceptor treatments (Warner et al., 2003).

These observations suggest that if MeHg production (*M*) and degradation (*D*) rates are presented in terms of either a $\frac{M}{D}$ ratio or a measure of net methylation potential (NMP) as defined by the difference between gross MeHg production and gross MeHg degradation rates, the depth distribution of these variables (i.e., $\frac{M}{D}$ or NMP) may mirror that of typical MMR. For example, Marvin-DiPasquale et al. (2003) present a $\frac{M}{D}$ ratio depth profile that increases downward from the vicinity of the SWI ($\frac{M}{D} < 1$) to a mid-depth maximum ($\frac{M}{D} > 1$), then decreases again at greater sediment depth. This depth profile is mirrored in the MMR profile presented for the same field sampling site (Marvin-DiPasquale et al., 2003). Lambertsson and Nilsson (2006) present data demonstrating that both the MMR and NMP profiles vary in concert for field sites ranging from a shallow sandy bay with low organic matter content (<1%) to a deep depositional hole with stagnant bottom water circulation and significant organic matter content (>10%). If these sites are viewed as end members along a transect in organic matter concentration, site specific depth profiles reported by Lambertsson and Nilsson (2006) suggest: 1) little gradient in MMR as a function of depth and NMP consistently <0 for the coarse grained sandy bay site; 2) concurrent subsurface maxima (3–5 cm) in both MMR and NMP for sites defined by moderate organic matter accumulation (i.e., sited at intermediate location along the hypothetical transect); and 3) near SWI maxima (≤2 cm) in both MMR and NMP for the organic-rich depositional site. These correlations between MMR and NMP may be visualized as a progressive shoaling of the net MeHg production zone toward the SWI with an increase in sediment organic matter that may facilitate the activity of SRB close to the SWI (Lambertsson and Nilsson, 2006).

Laboratory demonstration of this same phenomenon has documented a shoaling of the zone of maximum net methylation when water overlying incubated estuary sediment cores is allowed to pond (Merritt and Amirbahman, 2008). Results from this experiment suggest that progressive near-surface anoxia, whether induced through limiting dissolved oxygen re-supply from overlying water or via the potential enhancement of anaerobic microbial respiration under high organic matter input (as inferred from data in Lambertsson and Nilsson (2006)), may narrow or eliminate a near surface zone characterized by net demethylation. Elimination of this zone may thus allow significant net MeHg production to occur at or near the SWI (Merritt and Amirbahman, 2008). In near-surface sediments, the influence of relative anoxia on the dominance of methylation versus demethylation activity may conceptually explain variations in MMR and MeHg concentration described in the literature.

6. Discussion and conclusions

Although mechanisms that may control mercury methylation dynamics in estuarine and coastal environments are considered in discrete sections of this critical review, it is likely that, to some degree, all themes discussed herein influence observed field data. To evaluate the significance and likely interdependence of these themes, specifically the activity of SRB, Hg_i concentration and/or speciation and the depth-dependent balance between MeHg production and consumption, this section: (1) highlights the extent to which each mechanism presented in this review is broadly supported in the literature; and (2) discusses analytical work that, while not always specifically conceived to address this topic, contributes toward a better mechanistic understanding of potential controls on mercury methylation dynamics.

For example, as is commonly observed in estuarine and marine sediment, and discussed throughout this critical review, methylation rates at or near the SWI are generally higher than methylation rates at greater sediment depth (e.g., Gilmour et al., 1998; King et al., 1999; King et al., 2001; Langer et al., 2001; Merritt and Amirbahman, 2008). Researchers have attributed this decline in MMR at depth to either S(-II)-mediated inhibition (Gilmour et al., 1998; Langer et al., 2001) or

the effect of diminishing organic substrate quality on the metabolic activity of sulfate reducing bacteria (SRB) (King et al., 1999). S(-II)-mediated inhibition has been alternately defined, as a function of Hg-S(-II) speciation favoring charged aqueous complexes (Benoit et al., 1999a), the ability of S(-II) to sequester Hg_i as HgS_(s) (Choi and Bartha, 1994) thereby limiting porewater Hg_i availability (e.g., Covelli et al., 1999; Langer et al., 2001), S(-II) reactivity with MeHg to form volatile dimethylmercury (Baldi et al., 1993), and/or the potential for S(-II) toxicity to methylating microbes (e.g., Benoit et al., 2001a). Although high S(-II) concentrations may limit microbial access to the trace metals (including Co, Ni, and Zn) required to form metabolic enzymes (e.g., Patidar and Tare, 2004; Ekstrom and Morel, 2007), and cause population shifts in SRB community structure (Icgen and Harrison 2006), there is little consistent evidence for S(-II)-mediated toxicity to SRB at common field concentrations of S(-II) (<1–2 mM) (Hoppe et al., 1990; Sundback et al., 1990; Reis et al., 1992).

Moreover, because examination of field and laboratory research suggests that: 1) it is questionable whether HgS_(s) is stably sequestered and/or microbially unavailable under sulfidic conditions (Morse and Luther, 1999; Ravichandran et al., 1999; Hintelmann et al., 2000; Slowey and Brown, 2007); 2) porewater MeHg concentrations may appear high even in the presence of considerable porewater S(-II) (e.g., King et al., 2000; Langer et al., 2001; Drott et al., 2007; Merritt and Amirbahman, 2008); 3) depth-dependent variation in observed MMR and/or porewater MeHg concentration are apparent even in the absence of porewater S(-II) gradients and/or the presence of sub-optimum S(-II) concentrations (e.g., Korthals and Winfrey, 1987; Marvin-DiPasquale and Agee, 2003; Hines et al., 2004; Hines et al., 2006; Goulet et al., 2007); and 4) the concentration threshold of reactive sulfide (as AVS) specifically correlated with methylation inhibition has been defined at >0.03 μmol S g⁻¹ (Hammerschmidt and Fitzgerald, 2004), >60 μmol S g⁻¹ (Craig and Moreton, 1983) and 1 mM ΣH₂S (Muresan et al., 2007), it is likely that simple correlations involving hypothesized concentration optima (as with S(-II)) may confound clear mechanistic interpretation of observed MeHg field data.

Relatedly, because the S(-II) concentration generally increases with depth in the non-methanogenic zone of coastal marine sediments, but is likely to be low in the depth zone characterized by the highest density of SRB (e.g., Laanbroek and Pfennig, 1981; Sahn et al., 1999; Llobet-Brossa et al., 2002), it is difficult to assess whether an optimal low concentration of S(-II) actively drives methylation or is simply correlated as a function of depth with the zone characterized by both greatest SRB metabolic activity and rapid cycling of labile organic substrate. Because of this potential for co-variation with depth of key variables correlated with mercury methylation dynamics, the conclusions of field studies presenting speciation-based correlations would be strengthened by accounting for variations in depth-specific SRB density, metabolism and community structure as well as porewater geochemistry.

Because depth trends in SRB activity appear to correlate reasonably well with depth trends in SRR (as discussed above), and SRR depth profiles may be affected by the same balance of variables that influence net methylation rates, the hypothesis of SRB community control on near surface Hg_i methylation rate in estuarine and coastal marine environments is broadly supported by the literature. Hg_i speciation, as a function of S(-II) and/or pH and/or DOM concentration likely also plays a role in observed variations in MMR, although the exact nature of the controlling or limiting ligand(s) is difficult to discern and has not yet been adequately characterized in the literature.

As example of this difficulty in identifying ligands that may control or limit MMR, Miller et al. (2007) have observed that for DOM addition experiments conducted with S(-II)-containing estuary porewater and laboratory solutions amended with dissolved S(-II), the octanol:water partition coefficients (*D*_{ow}) of added Hg_i spikes are lower than would be predicted based on the assumption that

complexation with inorganic S(-II) dominates Hg_i speciation. These experimental results suggest that the presence of DOM renders dissolved Hg-S(-II) complexes at much lower concentrations than predicted in earlier work discussed in detail in Section 4 of this critical review. Interactions between Hg_i, S(-II) and DOM are further supported by ultrafiltration experiments suggesting that: 1) small, inorganic Hg-S(-II) complexes appear to co-exist with larger-molecular-weight Hg-DOM complexes; and 2) increasing the DOM concentration over a realistic range for porewater (6–20 ppm; defined in terms of DOC) increases the concentration of Hg-DOM complexes, as defined by their inability to pass through the ultrafiltration membrane (Miller et al., 2007). Although the fraction of Hg_i complexed with DOM is consistent high (>80%) in the absence of dissolved S(-II), when 10 mM S(-II) is added, the fraction of Hg_i complexed with DOM increases from <40% to >60% across the DOM ranged assessed in this experiment. Sunderland et al. (2006) have also observed that across a gradient in total organic matter enrichment, both the fraction of total sediment mercury that is MeHg and, potentially, the net rate of MeHg production appear greater when porewater also contains higher concentrations of S(-II) as well as organic matter. As noted above, these studies further support the conclusion that whereas porewater geochemistry likely influences the production rate of MeHg, the mechanism through which Hg_i, S(-II), and DOM concentrations (as well as pH) contribute to observed field profiles of solid phase or porewater MeHg are likely more complicated than speciation-oriented research has demonstrated to date.

Regarding the balance between MeHg production and consumption, whereas it is widely recognized that: (1) the processes responsible for methylation of Hg_i and demethylation of MeHg overlap spatially and kinetically in sediment, and (2) it is the balance of environmental variables considered in this review that determines the extent to which MeHg accumulates in the aqueous and/or sediment solid phase, this statement defines a conceptual model only. As discussed above, in near-surface sediment the influence of relative anoxia on the dominance of methylation versus demethylation activity may help to conceptually explain variations in MMR and MeHg concentration described in the literature. Further research to test the validity of these conceptual statements is warranted and should include the advancement of kinetic models to more rigorously examine depth-specific net MeHg production and accumulation in field sediment.

Because much of the speciation literature discussed in this critical review is predicated on the assumption that uptake of Hg_i is diffusively controlled, it is also worth considering whether this underlying assumption is a necessary pre-condition for the methylation of Hg_i. Various studies document the ability of aerobic and anaerobic microbes to actively take up Hg_i (e.g., Golding et al., 2002; Golding et al., 2007). Although these studies generally assess uptake and/or toxicity via bioluminescence of the inducible *mer-lux* reporter, and work with microbes (including *Vibrio anguillarum* and *Escherichia coli*) not known to utilize either SO₄²⁻ or Fe(III) as terminal electron acceptors, it is worth a more careful examination of the implications of their work. Golding et al. (2002) have shown, as example, that uptake of Hg_i under anaerobic conditions as determined by luminescence of the *mer-lux* reporter is: 1) not proportional to the concentration of lipophilic Hg_i species; and 2) is enhanced following the addition of yeast extract and low-molecular weight organic acids. These results suggest the presence of Hg_i uptake mechanisms that demonstrate active regulatory control (Golding et al., 2002). Golding et al. (2007) have shown that for Hg_i concentrations reaching 500 pM, the charge on Hg_i complexes has no effect on the uptake rate or toxicity of Hg_i to *V. anguillarum*. Ligands considered in this experiment include NH₄⁺, Cl⁻ and OH⁻, with conditions manipulated to generate cationic, neutral and anionic complexes. Although uncorrelated with charge, the uptake rate and induced toxicity in this study are correlated with the total added Hg_i concentration. Importantly, the authors note that the microbial strains studied are modified by the deletion of intrinsic

mer operons. This deletion allowed examination of Hg₂ bioavailability as it occurs for the majority of microbes lacking such detoxification mechanisms (Golding et al., 2007).

Furthermore, with respect to the question of whether mercury methylation dynamics are controlled by the metabolic activity of SRB, the related question of whether observed trends in diminishing organic substrate quality with sediment depth result in a simple decrease in SRB number with depth (as is often observed) or a combination of diminished number coupled with a decline in cell-specific SO₄²⁻ reduction rates has not been resolved in the literature. This topic therefore remains an area for fruitful examination. Research on this question, as example, has observed sharper gradients in cell-specific SRR within near surface marine sediments (0–5 cm) than at greater depth (5–10 cm) within the same sediment profiles (Sahm et al., 1999; Ravensschlag et al., 2000). Although such data may suggest that the decline with depth in SRR (and potentially MMR) observed in coastal marine sediments is a function of decreasing overall SRB numbers, it is also likely that this overall trend obscures real depth-related differences in SRB community composition with resultant effects on MMR. Because microbial community differences may arise from variation in processes such as the production rate and/or the accessibility of specific organic substrates or co-factors, answering these questions may aid in illuminating the specific controls on MeHg production, accumulation, and consumption in estuarine and coastal marine environments.

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