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Factors controlling the photochemical degradation of methylmercury in coastal and oceanic waters

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Abstract

Many studies have recognized abiotic photochemical degradation as an important sink of methylmercury (CH_3Hg) in sunlit surface waters, but the rate-controlling factors remain poorly understood. The overall objective of this study was to improve our understanding of the relative importance of photochemical reactions in the degradation of CH_3Hg in surface waters across a variety of marine ecosystems by extending the range of water types studied. Experiments were conducted using surface water collected from coastal sites in Delaware, New Jersey, Connecticut, and Maine, as well as offshore sites on the New England continental shelf break, the equatorial Pacific, and the Arctic Ocean. Filtered water amended with additional CH_3Hg at environmentally relevant concentrations was allowed to equilibrate with natural ligands before being exposed to natural sunlight. Water quality parameters – salinity, dissolved organic carbon, and nitrate – were measured, and specific UV absorbance was calculated as a proxy for dissolved aromatic carbon content. Degradation rate constants ($0.87\text{--}1.67\text{ day}^{-1}$) varied by a factor of two across all water types tested despite varying characteristics, and did not correlate with initial CH_3Hg concentrations or other environmental parameters. The rate constants in terms of cumulative photon flux values were comparable to, but at the high end of, the range of values reported in other studies. Further experiments investigating the controlling parameters of the reaction observed little effect of nitrate and chloride, and potential for bromide involvement. The HydroLight radiative transfer model was used to compute solar irradiance with depth in three representative water bodies – coastal wetland, estuary, and open ocean – allowing for the determination of water column integrated rates. Methylmercury loss per year due to photodegradation was also modeled across a range of latitudes from the Arctic to the Equator in the three model water types, resulting in an estimated global demethylation rate of 25.3 Mmol yr^{-1} . The loss of CH_3Hg was greatest in the open ocean due to increased penetration of all wavelengths, especially the UV portion of the spectrum which has a greater ability to degrade CH_3Hg . Overall, this study provides additional insights and information to better constrain the importance of photochemical degradation in the cycling of CH_3Hg in marine surface waters and its transport from coastal waters to the open ocean.

Keywords

Mercury; Methylmercury; Photochemical reactions; Demethylation

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1. Introduction

Methylmercury (CH_3Hg) is the toxic organic form of the global pollutant mercury (Hg) that poses a significant risk to human health due to its bioaccumulation in aquatic food webs. The consumption of seafood represents the primary route of CH_3Hg exposure in humans (Mahaffey et al., 2011; Sunderland, 2007; Sunderland and Mason, 2007). Rising Hg concentrations in the surface ocean (upper ~100 m) over the last century, coinciding with increasing industrialization, have resulted in increased concern over elevated CH_3Hg concentrations in the marine life harvested (Amos et al., 2013; Mason et al., 2012). Many studies have identified and quantified sources of CH_3Hg to aquatic systems (Driscoll et al., 2013; Mason et al., 2012), although relatively little research has been conducted on its fate and stability in oceanic waters. The key processes controlling the biogeochemical cycling of CH_3Hg between coastal wetland, estuarine, and open ocean systems need to be better understood before human exposure risks can be accurately assessed. The extent to which it accumulates in the oceans depends on its rate of production (sources, e.g., bacterial methylation) and degradation (sinks, e.g., sunlight-induced demethylation). The stability of CH_3Hg in the water column also controls the extent to which it is transported between marine environments. For example, greater photodegradation would decrease its advection from polluted coastal waters or methylation hotspots to other parts of the ocean.

While Hg methylation and CH_3Hg demethylation can both be microbially mediated, photochemical degradation is the primary abiotic sink of CH_3Hg in the photic zone of many aquatic systems including the ocean (e.g., Mason et al., 2012; Sellers et al., 1996). Understanding the factors that control CH_3Hg photochemical degradation in oceanic waters therefore facilitates our efforts to model its uptake by marine organisms. The extent of degradation is especially important in regions significantly affected by our changing climate such as the Arctic, where decreased sea-ice cover has been correlated with higher degradation rates resulting in potentially lower accumulation of CH_3Hg into the food web (Blum, 2011; Point et al., 2011). Demethylation also represents a potential sink of Hg in the ocean as ionic divalent Hg (Hg(II)) produced during degradation can be photochemically reduced to volatile elemental Hg (Hg^0) (Amyot et al., 1997), which can evade from the surface ocean and thus decrease the total Hg pool.

Methylmercury photodegradation has been attributed to both direct and indirect processes. Direct processes involve the absorption of light by the molecule itself, potentially involving the transfer of energy within a dissolved organic matter (DOM)- CH_3Hg complex, breaking the C-Hg bond (Inoko, 1981; Jeremiason et al., 2015). Indirect reactions involve secondary reactions with photochemically produced transient intermediates such as reactive oxygen species (ROS) (Black et al., 2012; Chen et al., 2003; Fernández-Gómez et al., 2013; Hammerschmidt and Fitzgerald, 2010; Kim and Zoh, 2013; Suda et al., 1993; Sun et al., 2015; Zepp et al., 1987; Zhang and Hsu-Kim, 2010). Recent studies investigating the rate-controlling parameters of CH_3Hg degradation have revealed complex interactions between competing environmental factors. While degradation rates clearly correlate with light intensity and quality (e.g., Lehnher and St Louis, 2009), contradictory lines of evidence have been reported regarding the role of DOM concentration and type (Qian et al., 2014; Tai et al., 2014; Zhang and Hsu-Kim, 2010), photo-reactive trace metals (Black et al., 2012;

Hammerschmidt and Fitzgerald, 2010) and the ROS they produce (Black et al., 2012; Chen et al., 2003; Gårdfeldt et al., 2001; Suda et al., 1993; Zepp et al., 1987; Zhang and Hsu-Kim, 2010).

Both visible and ultraviolet (UV) wavelengths have been shown to play a role in CH₃Hg photodegradation. While the higher energy UVA (320–400 nm) and UVB (280–320 nm) radiation are more capable of degrading CH₃Hg, photosynthetically active radiation (PAR, 400–700 nm) can dominate degradation in some ecosystems due to its greater penetration in the water column (Black et al., 2012; Fernández-Gómez et al., 2013; Hammerschmidt and Fitzgerald, 2006; Lehnherr and St Louis, 2009). Wavelength specific reaction and attenuation rates must therefore be considered in determining the overall importance of photodegradation in an ecosystem.

Dissolved organic matter has been implicated in promoting photodegradation (Black et al., 2012; Chandan et al., 2015; Jeremiason et al., 2015; Qian et al., 2014; Zhang and Hsu-Kim, 2010) as it is known to bind CH₃Hg and thus affect Hg transport, transformation, and bioavailability in natural waters (Ravichandran, 2004). This complexation is thought to enhance degradation through charge transfer from the photosensitized DOM ligand resulting in the cleavage of the C–Hg bond (Tai et al., 2014). This process could facilitate the degradation of CH₃Hg by PAR. Overall, the role of DOM is complex. While it is a major source of photochemically produced reactive intermediates capable of degrading CH₃Hg, it is also responsible for attenuating light in the water column (Jeremiason et al., 2015; Li et al., 2010). Light attenuation decreases the depth at which photodegradation occurs, thus reducing the overall integrated rate in the water column. These competing factors likely explain the variable and minor effects of DOM that some have observed (Black et al., 2012).

Reactive oxygen species, primarily hydroxyl radicals ($\cdot\text{OH}$) and singlet oxygen ($^1\text{O}_2$), have been implicated in the photodegradation of CH₃Hg (Chen et al., 2003; Hammerschmidt and Fitzgerald, 2010; Kim and Zoh, 2013; Pehkonen and Jing, 2001; Suda et al., 1993; Suda and Takahashi, 1992; Suda et al., 1991; Sun et al., 2015; Zhang and Hsu-Kim, 2010). These ROS can be formed through photochemical reactions of DOM (Clark and Zika, 2000), nitrate (NO_3^-) (primarily forming hydroxyl radicals; Zepp et al., 1987), and trace metals such as iron (Fe) (Hammerschmidt and Fitzgerald, 2010; Zepp et al., 1992). While some of these studies conclusively identify the reactive species responsible, others find no positive correlations.

Additionally, major inorganic constituents such as chloride (Cl^-) and bromide (Br^-) could play a role in the photodegradation process through either the complexation of CH₃Hg or the involvement in radical reaction pathways. Chloride complexation has been invoked as an explanation for differences in degradation rates between fresh and salt water (Black et al., 2012; Chen et al., 2003; Sun et al., 2013, 2015; Whalin et al., 2007; Zhang and Hsu-Kim, 2010), with CH₃HgCl species predicted to be more resistant to degradation (Tossell, 1998). Bromide has been shown to form reactive intermediates in photochemistry pathways (De Laurentiis et al., 2012; Zafiriou et al., 1987), possibly facilitating photodegradation and increasing rates in seawater.

Comparing rates between different studies is difficult due to differing experimental conditions and methods of calculating reaction rate constants. Additionally, most studies have focused on freshwater systems despite the majority of human exposure to CH₃Hg coming from seafood consumption (Sunderland, 2007). The objective of our study was therefore to better understand and constrain the variability in CH₃Hg photodegradation rates by studying this process in a range of estuarine and oceanic waters under consistent experimental conditions. Artificial seawater and simulated sunlight were used in preliminary experiments to examine mechanisms under controlled conditions, and natural waters and sunlight were used to determine ambient photodegradation rates. Experiments were conducted using coastal waters from Delaware to Maine, USA, and oceanic waters from the New England shelf, the Arctic, and the Pacific Ocean. Furthering the efforts to understand the role of complexation and reaction precursors in the photodegradation process, the importance of CH₃Hg speciation involving DOM and chloride (Cl⁻) was investigated, as well as the involvement of bromide (Br⁻) in the potential radical reaction pathways. Using the resulting rate constants and corresponding water quality parameters, CH₃Hg loss in the surface water column of three representative water bodies—coastal wetland, estuary, and open ocean—was modeled to examine the impact of photodegradation in each environment. The results of these efforts, detailed below, have improved our understanding of the spatial importance of photodegradation as a sink of CH₃Hg in marine ecosystems.

2. Methods

2.1. Field sites

Water from both coastal and open ocean sites was used for photodegradation studies (Fig. 1). Estuarine field sites were located along the east coast of the United States in Delaware (DE), New Jersey (NJ), Connecticut (CT), and Maine (ME). Water was collected at each site and brought back to the lab in Connecticut, immediately filtered and used for experiments the following day. Delaware water was collected from Slaughter Beach (38.9372 N, 75.30317 W), near the mouth of the Delaware Bay. Berry's Creek (40.82854 N, 74.07994 W), a highly contaminated estuary in NJ with Hg concentrations among the highest found in North America (Cardona-Marek et al., 2007), was selected as another site. In CT, water was collected from Barn Island (41.3400 N, 71.8745 W). For this location, samples were taken from a "low organic carbon" (LOC - sandy bottom) and "high organic carbon" (HOC - muddy bottom) site. Water was also collected from the Eastern Long Island Sound (ELIS; 41.2633 N, 72.0667 W), and the Avery Point campus (41.3161 N, 72.0625 W) in Groton, as well as the Shetucket River (a tributary of the Thames River, upstream from the Avery Point campus; 41.5297 N, 72.0556 W). Surface water from the Western Long Island Sound (WLIS; 5 m depth; 40.9582 N, 73.5593 W) and the southern New England shelf break (NESB; 10 m depth; 40.2283 N, 70.9564 W) was collected aboard the R/V Connecticut. Maine water was collected in Wells from the Webhannet River (43.2951 N, 70.5824 W) and along the oceanfront on Drakes Island Beach (43.3242 N, 70.5512 W).

In addition to the New England shelf break, oceanic waters were also collected from the equatorial Pacific Ocean, as well as the Arctic Ocean and Bering Strait. Arctic surface water was collected on the U.S. Arctic GEOTRACES cruise aboard the USCGC Healy

(WAGB-20) from both the Bering Strait (65.8 N, 168.6 W) and the continental shelf break (76.5 N, 173.0 W). Water from the equatorial Pacific Ocean (17.0 N 154.4 W) was collected aboard the R/V Kilo Moana on the “Metzyme” cruise and was processed and exposed aboard the ship.

2.2. Sample collection and filtration

At coastal sites, surface water was collected in trace metal clean certified 10 L LDPE Cubitainers or acid cleaned 2 L Teflon FEP bottles. Waters were kept cold in the dark while being transported back to CT, and were filtered to 0.2 μm (Meissner 0.45 μm capsule filter followed by a Barnstead 0.2 μm final filter) within 24 h to ensure that solely abiotic reactions would be observed during experiments. Water from the open ocean (shelf break, Pacific, Arctic) was collected from the surface mixed layer (~5 m depth) in Niskin bottles on a trace metal sampling rosette. Arctic waters were immediately frozen and transported back to CT, while Pacific and NESB waters were filtered aboard the ship. Filtered water was stored in 2 L Teflon FEP bottles, which were (unless otherwise noted) amended with 0.5 pM CH_3Hg (as aqueous Cl^- complexes) about 12 h before the start of experiments to ensure equilibration with natural ligands.

2.3. Photodegradation procedure

To accurately determine in situ photodegradation rates, studies were conducted using natural sunlight as a light source. Aboard the R/V Kilo Moana, surface water (both filtered and unfiltered) from the equatorial Pacific Ocean was exposed to ambient sunlight in 500 mL Teflon FEP bottles for up to 7 days, starting on October 5, 2011. A shallow water bath was used to keep samples at the temperature of the surface ocean ($28 \pm 3^\circ\text{C}$). Total UV measurements were corrected for absorption by the Teflon bottles (17% loss).

The remaining exposures were performed (unless otherwise noted) in quartz flasks (250 and 500 mL, Technical Glass Products) under ambient sunlight (Fig. S3) at the University of Connecticut Avery Point campus in Groton, CT. Quartz was chosen for its UV and visible spectral clarity compared to Teflon (Black et al., 2012; Technical Glass Products, 2017). Samples remained outdoors (at $25 \pm 5^\circ\text{C}$) for up to 7 h, typically for three different durations each repeated in duplicate or triplicate. In all studies, dark treatments were kept in matching flasks wrapped with two layers of aluminum foil to account for any potential losses on the surface of the flask, in addition to other abiotic loss processes.

During the experiments at Avery Point and on the Pacific, total UVA + B intensity (280–400 nm) was monitored every 5–15 min using a Solar Light PMA2100 radiometer with a PMA2107 sensor. Full spectrum absolute irradiance measurements were also made with an Ocean Optics Flame UV–Vis spectrometer with a cosine corrector. Actinic scattering effects were not corrected for based on results from Kieber et al. (2007), which showed excellent agreement between integrated irradiances determined with a spectroradiometer and a chemical actinometer designed to quantify light doses within photochemical reaction vessels.

Concentrations of CH_3Hg at the Barn Island HOC site were sufficiently high to allow us to examine the behavior of ambient and added CH_3Hg with respect to photodegradation rate

constants. The CH₃Hg concentration was increased approximately 2 and 10 times by adding an additional 0.5 and 5 pmol of CH₃Hg per liter of water.

The involvement of the halogens Cl⁻ and Br⁻ in the photochemical reactions was investigated in water from the Shetucket River and Avery Point, respectively. Due to potential Cl⁻ interferences on the analysis of CH₃Hg (Bloom, 1989), freshwater was chosen for this experiment, while coastal seawater was selected for the Br⁻ experiment to correlate with our other studies. Chloride concentrations of 34 mM and 0.33 M were chosen, representing low and mid salinity waters, allowing for comparison of rates found at higher salinities (~0.55 M Cl⁻; Broecker and Peng, 1982) in our other studies. Bromide concentrations were increased from about 0.8 mM in seawater (Broecker and Peng, 1982) to 7.1 mM and 64 mM.

2.4. Sample preservation, storage, and analysis

After exposure to natural/artificial sunlight, all samples were acidified to 0.5% (v/v) sulfuric acid (H₂SO₄, trace metal grade, Fisher Scientific) and stored at 4 °C in the dark in acid-cleaned glass bottles (I-CHEM Certified 200 series). Sample and reactions vessels were cleaned with 2% Citranox detergent followed by 1 M HCl, with thorough rinsing with high purity (18 MΩ cm⁻¹) water (Milli-Q, Millipore) in between and following cleaning steps.

Methylmercury was analyzed using the ascorbic acid-assisted direct ethylation method (Munson et al., 2014). Briefly, samples were acidified to a total of 1% (v/v) H₂SO₄ and left to digest overnight before neutralizing with 8 N potassium hydroxide (KOH), buffering with 4 M acetate, adding 2.5% (w/v) ascorbic acid and finally 1% (w/v) sodium tetraethyl borate (NaTEB) to ethylate the CH₃Hg. A Tekran Model 2700 instrument and autosampler automated the purging, trapping, and detection using cold vapor atomic fluorescence spectroscopy (CVAFS). Average method detection limits (MDL) were < 10 fM, and sample concentrations were corrected for matrix spike recoveries. Average spike recovery was 82% with a typical relative standard deviation (RSD) of 10%. Samples utilizing CH₃¹⁹⁹Hg (see Supporting information) were analyzed via isotope dilution (Hintelmann and Evans, 1997) using the Tekran 2700 connected in line with a Perkin Elmer ELAN DRC II Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

2.5. Light penetration modeling

The HydroLight radiative transfer numerical model (Sequoia Scientific, Inc.) was used to compute irradiance with depth in three representative water bodies: coastal wetlands, estuaries, and the open ocean. HydroLight utilizes water quality parameters, as well as atmospheric and bottom boundary conditions, to calculate water absorption and scattering properties. In the open ocean, chlorophyll (Chl *a*) absorption is the primary water column parameter, while in coastal waters chromophoric dissolved organic matter (CDOM), total suspended matter (TSM), and bottom reflectance also play a role. Aside from the chlorophyll profile in the open ocean, which was modeled using data from the Sargasso Sea (Cianca et al., 2012), the parameters used in the calculations (Table 1) were assumed to be uniform in the surface mixed layer. A sensitivity analysis was conducted to determine the impact of chlorophyll concentrations and distributions on the light penetration to better

understand spatial and temporal variability over the largest area of concern for photodegradation, the open ocean. Light regimes and photodegradation rate constants for coastal wetland and estuarine sites were based on local data (Barn Island and Eastern Long Island Sound; Aurin and Dierssen, 2012), while open ocean data was based on the equatorial Pacific Ocean site. The northern hemisphere summer solstice (June 21) was chosen to provide a maximum estimate of CH_3Hg degradation.

Methylmercury loss per year due to photodegradation was modeled across a range of latitudes from the Arctic to the Equator in the three model water types described earlier. To estimate water column integrated fluxes, rates with respect to photon flux (Table 2) and typical concentrations (Table 1) were used in conjunction with annual average daily integrated PAR values at each latitude – $50 \text{ E m}^{-2} \text{ day}^{-1}$ at the Equator, $30 \text{ E m}^{-2} \text{ day}^{-1}$ at mid latitudes, and $10 \text{ E m}^{-2} \text{ day}^{-1}$ in the Arctic (Frouin et al., 2012).

2.6. Data analysis

Rate constants were calculated from the slopes of semi-log plots of $\ln[\text{CH}_3\text{Hg}]$ versus integrated UV irradiance, giving the rate constant plus or minus its standard error. Regression analysis was used to test the statistical significance of the difference between any two slopes, or rate constants. Per day rate constants for experiments conducted at Avery Point were calculated based on a typical peak local daily total UV dose (around the summer solstice) of $1410 \text{ kJ m}^{-2} \text{ day}^{-1}$ (approximate peak values of 50 W m^{-2} total UV, 460 W m^{-2} PAR). A Teflon bottle absorption corrected value of $1040 \text{ kJ m}^{-2} \text{ day}^{-1}$ was used for samples exposed on the Pacific Ocean. Per day rate constants were then converted to cumulative PAR (400–700 nm) photon flux units for better comparison with other studies and for examination of the spatial and temporal variability in rates. Summer solstice values of $69.5 \text{ E m}^{-2} \text{ day}^{-1}$ and $63.1 \text{ E m}^{-2} \text{ day}^{-1}$ were used, which were calculated from HydroLight data at the Avery Point and Pacific sites, representing peak daily intensities expected during sunny conditions.

2.7. Auxiliary parameters

Ancillary data (collection dates, salinity, dissolved organic carbon (DOC) and NO_3^- concentrations, and calculated specific UV absorbance when available) for the above sites are shown in corresponding tables (2, 4, 5). DOC was characterized by UV/VIS spectroscopy using a Hitachi U-3010 spectrophotometer. Absorbance scans were carried out in 1 cm quartz cuvettes, with Milli-Q blank correction, from 200 to 800 nm at 1 nm intervals, within hours of conducting photodegradation experiments. DOC samples were stored in acid cleaned, muffled glass vials, frozen immediately before the start of each experiment. Concentrations were quantified using a Shimadzu TOC-V analyzer. Absorbance values measured at 254 nm were used to calculate the specific UV-absorbance (SUVA) per $\text{mg C L}^{-1} \text{ m}^{-1}$ (Weishaar et al., 2003). Nitrate was also determined using a SmartChem nutrient analyzer, although many samples were under the method detection limit ($0.5 \mu\text{M}$).

3. Results and discussion

3.1. Degradation rate constants

Photodegradation studies using natural sunlight and a wide range of water types yielded rate constants ranging from 0.87 to 1.67 day⁻¹ (Table 2). Fig. 2 shows a sample degradation curve plotted against total integrated UV exposure. “Dark” samples showed no significant degradation. Reaction kinetics appears to be pseudo first order with respect to irradiance, indicating a possible steady state presence of the reactive species responsible for the rate limiting step of the reaction. The rapid degradation relative to the dark controls indicates that there is no significant net abiotic photochemical production of CH₃Hg, in contrast to the results of others (Siciliano et al., 2005), and this appears especially true for studies in the presence of UV light (Black et al., 2012; Lehnher and St Louis, 2009).

The Pacific Ocean site showed significantly slower degradation than Barn Island sites in CT, while the Bering Strait and Shetucket River sites were significantly lower than both the ELIS and Barn Island sites (Table S3). In the Pacific, exposures were repeated with both filtered (0.2 μm) and unfiltered water, with no difference in rate observed (data not shown). While this is not surprising given the low particulate levels, unfiltered samples kept in the dark for a week did show evidence of methylation, but this was not further investigated. Because the rate calculation in this experiment was based on a 24-hour exposure it is possible that the initial degradation rate was faster than the calculated 0.87 day⁻¹, making the rate more comparable to the other sites. In addition, although the attenuation of the total UV radiation by the Teflon bottle was accounted for when calculating the rate constant, the wavelength specific nature of both the light attenuation and the reaction itself make this correction difficult.

Salinity at the sites studied (Table 2) primarily ranged from 31 to 35 ppt, with a lower value of 25.8 in the Arctic due to sea ice melt, and 6.8 at Berry’s Creek and 0.1 in the Shetucket River due to freshwater runoff. A change in salinity can potentially affect demethylation rate constants if CH₃Hg complexation is shifted from being dominated by photochemically active DOM complexes to more stable Cl⁻ complexes that are less susceptible to photodegradation (Tossell, 1998). Nevertheless, no correlation between salinity and degradation rate constant was observed. In addition, variability in ambient NO₃⁻ levels proved to have little impact on rate constants, suggesting that either the role of ·OH in these reactions is limited or that sufficient ·OH is present at all NO₃⁻ concentrations observed. Alternative sources of radicals could also be responsible, such as Fe in the photo-Fenton reaction (Hammerschmidt and Fitzgerald, 2010; Zepp et al., 1992). These results generally agree with our earlier lab based experiments using a solar simulator (see Supplemental materials for details).

DOC concentrations varied from 70 μM in open ocean waters of the Pacific to 380 μM in the salt marsh waters of Barn Island, CT. Despite this range, no significant trends were observed in degradation rate constants. The highest DOC concentration observed was paired with the third highest rate, while the second lowest DOC concentration was paired with the highest rate. Based on estimates of reduced sulfur ligand concentrations in DOM and binding strengths with CH₃Hg in similar waters (Hollweg et al., 2010; Lamborg et al., 2004), organic

complexation likely dominates CH_3Hg speciation at all of these DOC concentrations; therefore, uniform speciation could explain the lack of variability in degradation rate constants. Consistent rate constants even at higher DOC concentrations, despite increased light attenuation, point to the importance of organic matter complexation in the facilitation of photodegradation. SUVA values ($0.7\text{--}3.8 \text{ L mg}^{-1} \text{ m}^{-1}$) give an indication of the aromatic content of the DOM (Weishaar et al., 2003), but again this measurement did not correlate with rate constants. While not proportional to DOC concentrations, calculated SUVA values were lowest in the open ocean and highest in salt marsh waters, pointing to differing sources of the DOC across sample sites.

Rate constants found in this study ($0.0138\text{--}0.0240 \text{ m}^2 \text{ E}^{-1}$) were up to two times greater than the fastest rate constants found in other studies in the literature, many of which focused on freshwater ecosystems (Table 3). Higher values in the literature, more comparable to values in our study, included rate constants of $0.015 \text{ m}^2 \text{ E}^{-1}$ measured in the wetlands of San Francisco Bay (Black et al., 2012) and $0.0120 \pm 0.0023 \text{ m}^2 \text{ E}^{-1}$ in the Florida Everglades (Tai et al., 2014). Comparison across studies is inherently difficult due to differing light regimes, irradiance measurement techniques, experimental setups, and reported units. Methylmercury concentrations used in those studies were often higher than our study by an order of magnitude or more. Our exposures were also done using quartz vessels, possibly explaining the faster rates compared to studies done in Teflon, where correction for attenuation is difficult due to differing bottle thickness and opacity (and therefore light penetration). Some studies including Black et al. (2012) attempted to correct for the potentially higher light levels within the bottles compared to the incident solar irradiance measured. Applying this conversion factor would bring our rate constants in line with many previous studies; however, this factor likely is not appropriate here due to the use of spherical vessels rather than cylindrical bottles. While the incident light fluxes may not capture the total amount of sunlight entering the reaction vessel from all sides, light scattering is also an important process within the water column and cannot be completely ignored.

3.2. Quartz vs. glass flasks

Natural sunlight and water from the ELIS were used to examine the effect of reaction vessel type, and thus light fraction, on CH_3Hg photodegradation rate constants. The decay rate constant in natural sunlight using quartz flasks was $1.42 \pm 0.05 \text{ day}^{-1}$, decreasing 23% to $1.10 \pm 0.12 \text{ day}^{-1}$ when using comparable borosilicate glass (Pyrex/Kimax) flasks (Table 4). Teflon bottles were not used for comparison due to their lower UV transmittance (Black et al., 2012) and greater observed differences in clarity between bottles. While the visible and UVA radiation intensity was only 3% and 4% lower in glass compared to quartz, the UVB intensity dropped 36%, primarily accounting for the lower rate in glass flasks. Based on the predicted role of UVB intensity in the overall photodegradation rate determined by Black et al. (2012) (36%), this drop in UVB intensity would account for a 13% decrease in the rate constant. The attenuation in UVA and visible light intensities accounts for an additional 2%. The total predicted decrease based on light attenuation by the glass flasks (15%) is smaller than our observed reduction (23%), but falls within the expected range when considering the standard error in our rate constants. These results highlight the importance of UVB radiation

in the reaction, as well as the importance of using spectrally clear reaction vessels (or making careful corrections for wavelength-specific light attenuation) when performing CH₃Hg photodegradation experiments; therefore, as was used in the determination of reaction rate constants in this study, quartz is the preferred material for photodegradation studies.

3.3. Concentration dependence

The relatively high concentration of CH₃Hg (~0.85 pM) in the Barn Island HOC waters allowed for a study comparing the degradation of ambient CH₃Hg (no addition of CH₃Hg standard) to that of amended samples (Table 5). Additional CH₃Hg (0.5, 5 pM) was added to investigate a potential artifact of higher concentrations used in the degradation experiments. Degradation rate constants were not significantly different between the low and high concentrations ($p = 0.550$), indicating that ambient and added CH₃Hg behaved the same, agreeing with the findings of others (Black et al., 2012; Lehnher and St Louis, 2009). Earlier studies done in WLIS and SB water (Table S2) showed a two-fold increase in degradation rates between 0.5 pmol added CH₃Hg and 2 pmol added CH₃¹⁹⁹Hg; however, these CH₃Hg additions were not allowed to equilibrate before exposure. It is known that several hours are required for CH₃Hg to come to equilibrium in terms of complexation with natural ligands in solution (Hammerschmidt and Fitzgerald, 2010; Lamborg et al., 2003). The enhanced rate could therefore be indicative of a greater stability of the CH₃Hg equilibrated with natural ligands, highlighting the importance of pre-equilibrating any added standard additions before beginning experiments examining transformations of CH₃Hg.

3.4. Effect of chloride, bromide and nitrate

Previous studies have shown varying importance of Cl⁻ in the degradation of CH₃Hg. In this study, increasing the Cl⁻ concentration from ambient to 0.33 M resulted in a slight (8%) but significant ($p = 0.018$; Table S3) increase in the degradation rate constant (Table 6). Although the increase was larger at 34 mM Cl⁻, the change was not significant ($p = 0.200$) due to greater variability between replicates. Chen et al. (2003) also indicated that the presence of Cl⁻ leads to faster degradation. In contrast, Tai et al. (2014) found no significant difference in rate constants under Cl⁻ concentrations from 0 to 1 M. Sun et al. (2015) on the other hand showed an 18% decrease in photodegradation rates with Cl⁻ concentrations between 0.3 and 1.1 mM, which is the expected result based on theoretical calculations of Tossell (1998) where Cl⁻ complexes with CH₃Hg were predicted to be more stable. As discussed earlier DOM is predicted to dominate CH₃Hg complexation in the waters tested, possibly minimizing the predicted effects of Cl⁻. Our preliminary studies (described in the Supporting information) using buffered Milli-Q water also showed no significant impact of added Cl⁻ on degradation rate constants (Table S1). Overall, these differing results suggest a minor influence of Cl⁻ on the rate of decomposition, which varies depending on experimental conditions.

Increasing the Br⁻ concentration from its ambient level in seawater (~0.8 mM) to both 7 and 60 mM increased the rate constant by about 60%, but the difference was only marginally significant due to variability between replicates ($p = 0.068, 0.077$). These results indicate that Br⁻ ions could play an important role in potential radical reaction pathways involved in

the degradation of CH_3Hg ; however, as in the case of Cl^- , variable results suggest that other factors likely control the decomposition rate. Salinity dependent reaction rate constants would be expected if Br^- played a crucial role in the reaction due to the change in Br^- concentration across salinity gradients.

Early experiments (see Supporting information for more details) also investigated the effect of NO_3^- concentrations on CH_3Hg degradation. While its presence enhanced degradation in buffered Milli-Q water (Table S1), no significant change in rate constants was observed upon its addition to natural waters from the Western Long Island Sound and New England continental shelf break (Table S2). Although lab based studies have shown $\cdot\text{OH}$ formed from the photolysis of NO_3^- to be capable of degrading CH_3Hg (Chen et al., 2003; Zepp et al., 1987), our experimental results, along with the lack of a trend observed between degradation rate constants and ambient NO_3^- concentrations, suggest that NO_3^- levels do not control photodegradation rates in natural waters.

3.5. Water column integrated rates

To estimate the importance of photodegradation in different marine ecosystems—coastal wetland, estuary, and open ocean—we must take into account not only the measured rate constants, but also the incident solar irradiance and the attenuation of light with depth. Light attenuation, controlled by absorption and scattering within the water column, varies with wavelength so wavelength specific rate constants must be used in such an analysis. Several studies have determined the relative importance of UVB, UVA, and PAR wavelengths in the photodegradation of CH_3Hg (Black et al., 2012; Lehnher and St Louis, 2009; Li et al., 2010; Poste et al., 2015). The percent contribution of these wavelength regions ranged from 7 to 36% for UVB, 40–85% for UVA, and 0–42% for PAR (Table 7). UV radiation generally accounted for at least 70% of the total degradation. Based on similar experimental conditions and water types, we chose to use the wavelength dependence determined by Black et al. (2012) in our calculations. They determined for surface waters that UVB accounted for 36% of the total degradation rate, UVA accounted for 40% of the rate, and PAR accounted for the remaining 24%. These contributions are also comparable to the relative importance of UVB estimated in our study comparing glass and quartz reaction vessels.

Using the HydroLight software, light penetration was calculated down to the depth with 1% of the incident solar irradiance. In coastal wetland water with the characteristics outlined in Table 1, UVB, UVA, and PAR penetrated 0.13 m, 0.27 m, and 1.92 m respectively. Light penetration was 1.63 m, 3.14 m, and 8.72 m in estuarine waters. Offshore, light penetration was 33.3 m, 106.5 m, and 110.0 m. The 10% irradiance depths were about 50% shallower than the depths listed above.

The degradation rate constant as a function of depth was calculated for the three ecosystems (Fig. 3) using the light penetration results and the reaction wavelength dependence determined by Black et al. (2012). In addition to the much deeper occurrence of significant photodegradation in the open ocean, there are differences in the relative importance of each type of radiation in the degradation rate. Calculations show that UV radiation plays a larger role in open ocean waters compared to coastal waters. In coastal wetlands UV accounts for

29.5% of the CH₃Hg loss, increasing to 47.9% in estuarine waters and becoming a dominant 73.5% in ocean waters. Despite the greater importance of UVB and UVA radiation at the surface these short wavelengths are attenuated the fastest, especially in coastal waters with higher levels of CDOM, chlorophyll, and suspended particulate matter; therefore, visible light often plays a larger role than its corresponding degradation rate constant would suggest. These results are consistent with previous studies that have suggested that most of the CH₃Hg degradation is due to PAR, primarily because these studies were completed in turbid shallow waters, such as the salt marsh studies of Black et al. (2012) and the lake and wetland studies of others (Fernández-Gómez et al., 2013; Poste et al., 2015). Regardless, the model results indicate that the previous conclusions about the dominant role of PAR in CH₃Hg degradation do not extend to the open ocean.

The degradation rate of CH₃Hg was integrated through the photic layer (defined as the depth to 1% of the incident PAR) in each water column (Table 8). The total loss of CH₃Hg was 93.7 pmol m⁻² day⁻¹, 119.0 pmol m⁻² day⁻¹, and 304.1 pmol m⁻² day⁻¹ in wetland, estuarine, and ocean waters. Despite the higher concentrations in estuarine (0.1 pM) and wetland (0.5 pM) waters, photodegradation represents a larger overall sink of CH₃Hg in the open ocean (0.02 pM) due to the significantly greater light penetration. Calculating average rate constants and half-lives for the photic layers of each of these three systems also reveals a faster turnover of CH₃Hg in the open ocean versus coastal waters. In wetland waters, the average half-life of CH₃Hg with respect to photodegradation was 7.1 days, decreasing to 5.1 and 3.7 days in estuarine and pelagic waters. Such a short residence time for CH₃Hg in the surface ocean indicates that it must be produced in situ or transported vertically within the water column rather than being transported offshore from coastal waters, as this time scale is much shorter than can be explained by transport due to water mass advection.

The modeled changes in degradation with latitude in each of the model systems (Table 9) are proportional to the local light flux. Like the average daily integrated PAR values, a five-fold (or greater) difference in degradation rates is expected between equatorial and polar waters.

Local variations in light penetration and CH₃Hg concentrations, not included in the model, further add to the variability in CH₃Hg losses between ecosystems. Large variability in the water quality parameters will result in significant changes in light penetration and thus CH₃Hg degradation. In addition, the magnitude of CH₃Hg loss depends on water column concentrations, which vary greatly (by an order of magnitude) both spatially and temporally especially in coastal wetlands and estuaries. An order of magnitude in variability is feasible when moving between regions with differing factors influencing concentrations, such as watershed inputs (including pollution point sources) and in situ methylation. Concentrations chosen for flux calculations were chosen based on averages of measurements made during this study, ranging from 0.02 pM in surface ocean waters (e.g., equatorial Pacific) to 0.1 pM for estuaries (e.g., Long Island Sound) and 0.5 pM for coastal wetlands (e.g., Barn Island, CT) (Table 1).

To determine a global CH₃Hg flux due to photodegradation, offshore rates were scaled by the latitude dependent average daily PAR values (Frouin et al., 2012) and ocean surface area (Allen and Gillooly, 2006). Polar seas were corrected for average ice cover and

concentration, with $6.65 \times 10^6 \text{ km}^2$ and $7.9 \times 10^6 \text{ km}^2$ of ice in the Arctic and Antarctic in 2016 (NSIDC). The estimated global demethylation rate is $25.3 \text{ Mmol yr}^{-1}$, which is over 20 times greater than the value previously estimated by Mason et al. (2012) (1.2 Mmol yr^{-1}). Scaling the rates for the Arctic and utilizing the same conditions (surface area, CH_3Hg and chlorophyll concentration) used by Soerensen et al. (2016) our estimated degradation rate is $0.48 \text{ Mmol yr}^{-1}$, a factor of 10 greater than their prediction ($0.05 \text{ Mmol yr}^{-1}$). The difference is likely partially attributable to Soerensen et al. restricting photodegradation to the polar mixed layer ($\sim 20 \text{ m}$) when it likely occurs much deeper in the water column based on the results of the HydroLight model. In addition to using a constant CH_3Hg concentration (0.02 pM) and degradation rate constant ($0.0138 \text{ m}^2 \text{ E}^{-1}$) for these predictions, the same light attenuation used for the Pacific site is applied across the global oceans.

While little variability in the rate constant was observed across the water types studied, changes in CH_3Hg concentration would proportionally change its flux. Despite higher CH_3Hg concentrations in many parts of the ocean including coastal waters, the deeper light penetration and relative expanse of open ocean waters still results in their predicted dominance in the global CH_3Hg photodegradation flux. While it is reasonable to surmise that degradation is greatest in the region with the lowest surface concentrations, concentrations alone cannot be used to estimate the importance of photodegradation as they are also dependent on processes such as advection and the rate of CH_3Hg formation. Chlorophyll concentrations, the primary HydroLight parameter influencing light penetration in the open ocean, also vary temporally and spatially across the oceans. Increasing or decreasing the chlorophyll concentration by a factor of two compared to the profile used would result in a 15% decrease or increase in the CH_3Hg flux, respectively. With an average chlorophyll concentration of 1 mg m^{-3} in the surface mixed layer, possible in more productive coastal or upwelling regions of the ocean, the flux would drop by 60% compared to the chosen conditions. Increasing the degradation rate constant to closer match the values determined in coastal water would partially make up for this decrease in flux, however. The variability in CH_3Hg concentrations and light penetration therefore indicates that our estimated global demethylation rate serves only as a first order approximation. To improve the estimation requires a better understanding of the spatial and temporal variability of these factors, as well as a more concrete understanding of the degradation wavelength dependence. Overall, the results outlined here confirm the importance of photodegradation as a sink for CH_3Hg in the open ocean.

4. Conclusions

Photochemical degradation is an important sink of CH_3Hg across a variety of coastal and pelagic ecosystems. This study serves to extend the range of water types in which photodegradation has been studied and provides detailed information about ambient degradation rates under consistent conditions, facilitating comparison between sites. Degradation rates are remarkably similar despite widely differing water characteristics. While the enhancement of CH_3Hg degradation has been attributed to both NO_3^- and DOM through indirect photochemical reactions (Chen et al., 2003; Zepp et al., 1987; Zhang and Hsu-Kim, 2010), no evidence of their direct involvement was found in this study. In coastal waters, the dual role of DOM in both the formation and quenching of reactive species, along

with the attenuation of light, is likely responsible for the consistent degradation rates found in our study.

Light attenuation at the sites studied plays a major role in determining the overall importance of photodegradation as a sink of CH₃Hg. The differences in attenuation between water types play a much larger role in the depth integrated degradation rate than any differences observed in the measured rates at the surface. Due to the higher attenuation of UV radiation in turbid waters, degradation due to PAR dominates at most depths in estuarine and wetland waters. In oligotrophic open ocean waters, however, UVA-induced degradation dominates. The magnitude of CH₃Hg loss is also dependent on its concentration in surface waters. Despite the low concentrations found in the surface mixed layer, the loss of CH₃Hg was greatest in the open ocean due to significantly deeper light penetration.

While in situ photodegradation studies remain the best way to determine accurate rates, this study shows that with an average rate constant along with knowledge of the CH₃Hg concentration, local incident photon flux, and water column light attenuation, estimates of the extent of photodegradation at a particular location could be made without further measurements. These results will further improve our efforts to model the biogeochemical cycling of Hg in aquatic environments, and the fate of CH₃Hg in marine surface waters. Using the predicted geographic variability in rates will also help us to predict and understand potential impacts of climate change on the extent of CH₃Hg photodegradation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2017.08.006>.

Abbreviations

CH ₃ Hg	methylmercury
DOM	dissolved organic matter
PAR	photosynthetically active radiation
ROS	reactive oxygen species

DOC	dissolved organic carbon
SUVA	specific UV absorbance
LOC	low organic carbon
HOC	high organic carbon
LIS	Long Island Sound
ELIS	Eastern Long Island Sound
WLIS	Western Long Island Sound
NESB	New England shelf break

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Fig. 1.
Sampling locations for waters used in this study (Ocean Data View; Schlitzer, 2015).

Fig. 2. Methylmercury (CH₃Hg) photodegradation in coastal seawater (Barn Island HOC, CT), plotted against the accumulated UV radiation during the exposure to natural sunlight for up to seven hours. Dark controls wrapped in aluminum foil are also shown.

Fig. 3. Modeled decrease in situ CH_3Hg photodegradation rate constants with depth for UVB, UVA, and PAR in coastal wetlands (A), estuaries (B), and the open ocean (C). Rates were calculated based on the modeled attenuation of light, the surface rate constant from corresponding sites in this study (equatorial Pacific, Eastern LIS, Barn Island HOC), and the relative importance of each wavelength region from Black et al. (2012).

Table 1

Water quality parameters used in HydroLight calculations based on measurements made in waters from Barn Island, the Long Island Sound and the equatorial Pacific Ocean, as well as from Aurin and Dierssen (2012) and Cianca et al. (2012). Chlorophyll *a* concentration ([Chl *a*]), the absorbance of chromophoric dissolved organic matter at 440 nm (aCDOM (440)), and the total suspended material (TSM) concentration are the primary drivers of light attenuation in the HydroLight model.

Site	Salinity (ppt)	Temp (°C)	Daily integrated PAR (E m ⁻² day ⁻¹)	[Chl <i>a</i>] (mg m ⁻³)	aCDOM (440) (m ⁻¹)	TSM (g m ⁻³)	[CH ₃ Hg] (pM)
Wetland	25	24	69.5	8.5	4.81	15	0.5
Estuary	32	24	69.5	7.1	0.3	2	0.1
Open ocean	36.5	26	63.1	variable	–	–	0.02

Table 2

Photochemical degradation rate constants ($\pm$ standard error) at coastal sites in Delaware (DE), New Jersey (NJ), Connecticut (CT), and Maine (ME), as well as offshore sites in the Arctic and Pacific Oceans. Ancillary data for salinity, dissolved organic carbon (DOC), nitrate (NO_3^-), and specific ultraviolet absorbance (SUVA) are also shown.

Location	Date	Salinity (ppt)	DOC (μM)	NO_3^- (μM)	SUVA ($\text{L mg}^{-1} \text{m}^{-1}$)	Rate Constant ($\times 10^{-3} \text{m}^2 \text{E}^{-1}$)	Rate Constant (day^{-1})
DE - Slaughter Beach	7/29/15	28	226.5	< 0.5	2.2	19.0 ± 1.9	1.32 ± 0.13
NJ - Berry's Creek	5/20/16	6.8	396.5	37.82	3.8	16.0 ± 3.3	1.11 ± 0.23
CT - Bam Island LOC	8/13/15	32	164.8	0.43	2.2	22.2 ± 1.6	1.54 ± 0.11
CT - Bam Island HOC	8/16/15	33	379.4	0.14	3.4	21.9 ± 0.7	1.52 ± 0.05
CT - Avery Point	9/24/16	32.5	92.5	< 0.5	1.9	20.9 ± 2.9	1.45 ± 0.20
CT - Shetucket River	9/24/16	0.1	217.5	2.07	3.3	17.0 ± 0.1	1.18 ± 0.01
ME - Sea Mist	9/6/15	32	170.6	< 0.5	3.3	16.8 ± 2.3	1.17 ± 0.16
ME - Drakes Island Beach	9/7/15	33	93.7	< 0.5	2.3	24.0 ± 3.9	1.67 ± 0.27
Eastern Long Island Sound	5/5/15	31	150	< 0.5	–	20.4 ± 0.7	1.42 ± 0.05
Bering Strait	4/20/16	32.1	59.8	9.12	1.4	15.3 ± 1.7	1.06 ± 0.12
Arctic Ocean	4/15/16	25.8	74.4	0.16	0.7	15.4 ± 2.4	1.07 ± 0.17
Pacific Ocean	10/5/11	35	70	0.05	–	13.8 ± 0.8	0.87 ± 0.05

Table 3

Summary of degradation rate constants from the literature, along with corresponding experimental conditions.

Study	Rate constant ($\times 10^{-3} \text{ m}^2 \text{ E}^{-1}$)	Rate constant (day ⁻¹)	Daily integrated PAR ($\text{E m}^{-2} \text{ day}^{-1}$)	[CH ₃ Hg] (pM)	[DOC] (μM)	Location/water type
Black et al., 2012	3.2 ± 1.0	0.19 ± 0.06	59.6 (320–700 nm)	0.10–6.75	120–941	Monterey Bay, CA
Black et al., 2012	9.9 ± 2.0 (15 max)	0.59 ± 0.01 (0.89 max)	59.6 (320–700 nm)	0.10–6.75	120–941	San Francisco Bay wetlands, CA
Byington, 2007	11.2	0.67–3.5	–	1.33	156–395	San Joaquin Delta, CA
Fernández-Gómez et al., 2013	2.1–5.2	0.031–0.0075	14.5	0.80–3.5	1460–6740 (TOC)	Boreal Lake/Wetland, Sweden
Fleck et al., 2014	7.5 ± 3.5	–	–	1.0–19	710–3020	Freshwater wetland, CA
Hammerschmidt and Fitzgerald, 2006	3.7	0.230	62	23	370	Toolik Lake, Alaska
Hammerschmidt and Fitzgerald, 2010	3.8	0.152 ± 0.023	33 ± 10	6.0–21	30–830	Toolik Lake, Alaska
Lehnher and St Louis, 2009	3.69 ± 0.07	0.170	46.1	4.1 (ambient) – 6.0 (spiked)	1070	Boreal Lake, Canada
Lehnher et al., 2011	4.3	0.2	47	0.140 (ambient) -12 (spiked)	–	Canadian Arctic Archipelago
Poste et al., 2015	3.19–4.56	~0.1–0.2	~30–40	0.1–0.8	325–1000	Boreal Lakes, Norway
Sellers et al., 1996	5.2–13	0.36	21–25	5.5	1190–1470	Experimental Lake 240, Canada
Sun et al., 2015	0.78–12	0.015–0.912	19–100	0.40–0.75 (amended to 12.5)	170–270	Jialing River, China
Tai et al., 2014	12.0 ± 2.3	0.389 ± 0.075	32.4	0.60 (amended to 5.0)	1468.3	Florida Everglades
Whalin et al., 2007	–	0.086–0.432	–	0.1–250	125–242	Chesapeake Bay, continental shelf
This study	13.8–24.0	0.87–1.67	63.1, 69.5	0.02–0.60 (0.5 pM added)	59.8–379.4	coastal and oceanic waters

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Table 4

Photochemical degradation rate constants ($\pm$ standard error) and other ancillary parameters in Eastern Long Island Sound (LIS) water for a comparison study of glass versus quartz reaction vessels under natural sunlight.

Location	Trial	Date	Salinity (ppt)	DOC (μ M)	NO_3^- (μ M)	Rate constant (day^{-1})
Eastern LIS	Quartz	5/5/15	31	150	< 0.5	1.42 ± 0.05
	Glass					1.10 ± 0.12

CH₃Hg photochemical degradation rate constants ($\pm$ standard error) and corresponding ancillary parameters for a concentration dependence study using water from the Barn Island, CT high organic carbon (HOC) site.

Table 5

Location	CH ₃ Hg added (pM)	Date	Salinity (ppt)	DOC (μ M)	NO ₃ ⁻ (μ M)	SUVA (L mg ⁻¹ m ⁻¹)	Rate Constant (day ⁻¹)
CT - Barn Island HOC	ambient	8/27/15	33	487.3	< 0.5	3.3	1.70 $\pm$ 0.26
	0.5						2.5
	5						2.34 $\pm$ 0.96

Table 6

Photochemical degradation rate constants ($\pm$ standard error) illustrating the effect of chloride (Cl^-) additions to river water (Shetucket River, CT) and bromide (Br^-) additions to coastal seawater (Avery Point, CT).

Water	[Br^- or Cl^-] (mM)	Rate constant (day^{-1})
Shetucket River (Cl^- addition)	~0.3	1.18 ± 0.01
	34	1.47 ± 0.17
	330	1.27 ± 0.02
Avery Point (Br^- addition)	~0.8	1.45 ± 0.20
	7	2.24 ± 0.20
	60	2.34 ± 0.27

Table 7

Wavelength dependence of the CH₃Hg photodegradation reaction determined by other studies in the literature.

Study	Water type	Percent contribution (%)		
		UVB	UVA	PAR
Black et al., 2012	San Francisco Bay	36	40	24
Lehnherr and St Louis, 2009	Boreal Lake	7–10	51–69	21–42
Li et al., 2010	Florida Everglades	15	85	0
Poste et al., 2015	Boreal Lake	23	52	25

Table 8

Light penetration (to 1% of the incident solar irradiance) and integrated CH₃Hg flux as a function of wavelength in model coastal wetland, estuarine, and open ocean sites.

Site	Wavelength	Light penetration (m)	CH ₃ Hg loss (pmol m ⁻² day ⁻¹)	% loss
Wetland	UVB	0.13	9.7	10.3
	UVA	0.27	18.0	19.2
	PAR	1.92	66.0	70.5
	Total	–	93.7	100
Estuary	UVB	1.63	19.4	16.3
	UVA	3.14	37.6	31.6
	PAR	8.72	62.0	52.1
	Total	–	119.0	100
Ocean	UVB	33.3	48.0	15.8
	UVA	106.5	175.5	57.7
	PAR	110.0	80.7	26.5
	Total	–	304.2	100

Table 9

Predicted daily and yearly loss of CH₃Hg for the three model water types (coastal wetland, estuary, and ocean) at three latitudes (Arctic (75°), Mid (45°), Equator (0°)) based on annual average PAR fluxes.

Site	Latitude	CH ₃ Hg loss (pmol m ⁻² day ⁻¹)	CH ₃ Hg loss (nmol m ⁻² yr ⁻¹)
Wetland	Arctic	13.5	4.9
	Mid	40.5	14.8
	Equator	67.5	24.6
Estuary	Arctic	17.1	6.2
	Mid	51.3	18.7
	Equator	85.5	31.2
Ocean	Arctic	51.7	18.9
	Mid	155.2	56.6
	Equator	258.7	94.4