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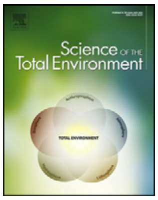

Concurrent photolytic degradation of aqueous methylmercury and dissolved organic matter

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HIGHLIGHTS

- MeHg photodegradation rates were similar in natural waters over a wide range of DOM.
- MeHg concentration was related to labile DOM but percent loss was related to humic DOM.
- Optical measurements of DOM could aid in monitoring in situ MeHg photodegradation.
- Physical characteristics of wetland systems control MeHg concentrations.

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ABSTRACT

Monomethyl mercury (MeHg) is a potent neurotoxin that threatens ecosystem viability and human health. In aquatic systems, the photolytic degradation of MeHg (photodemethylation) is an important component of the MeHg cycle. Dissolved organic matter (DOM) is also affected by exposure to solar radiation (light exposure) leading to changes in DOM composition that can affect its role in overall mercury (Hg) cycling. This study investigated changes in MeHg concentration, DOM concentration, and the optical signature of DOM caused by light exposure in a controlled field-based experiment using water samples collected from wetlands and rice fields. Filtered water from all sites showed a marked loss in MeHg concentration after light exposure. The rate of photodemethylation was 7.5×10^{-3} m^2 mol^{-1} (s.d. 3.5×10^{-3}) across all sites despite marked differences in DOM concentration and composition. Light exposure also caused changes in the optical signature of the DOM despite there being no change in DOM concentration, indicating specific structures within the DOM were affected by light exposure at different rates. MeHg concentrations were related to optical signatures of labile DOM whereas the percent loss of MeHg was related to optical signatures of less labile, humic DOM. Relationships between the loss of MeHg and specific areas of the DOM optical signature indicated that aromatic and quinoid structures within the DOM were the likely contributors to MeHg degradation, perhaps within the sphere of the Hg-DOM bond. Because MeHg photodegradation rates are relatively constant across freshwater habitats with natural Hg–DOM ratios, physical characteristics such as shading and hydrologic residence time largely determine the relative importance of photolytic processes on the MeHg budget in these mixed vegetated and open-water systems.

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1. Introduction

Mercury (Hg) contamination in wetland environments poses significant risks to humans and wildlife because wetland processes convert Hg to monomethyl mercury (MeHg), the form that is more readily concentrated in aquatic food webs (Mergler et al., 2007; Selin, 2009). In fish and wildlife, Hg accumulation has been associated with neurological and behavioral abnormalities, low reproductive success, and direct toxicity (Crump and Trudeau, 2009; Mitro et al., 2008; Wiener et al., 2003). These concerns have led to the listing of Hg as an important pollutant across the world and prompting United Nations Environment Programme (UNEP) international negotiations to address the Hg problem (http://www.chem.unep.ch/mercury/default.htm).

Wetlands are locations of MeHg production and subsequent transport to aquatic systems because they possess the optimal conditions for Hg methylation (Gilmour et al., 1992; St. Louis et al., 1996). Shallow flooded systems of all kinds, including rice agriculture

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and managed wetlands, also possess the optimal conditions for Hg methylation because of their repeated wet–dry cycles and available substrates for microbial activity (Hall et al., 2009; Windham-Myers et al., 2009). In California, shallow flooded habitats have been identified as responsible for a majority of in situ MeHg production in the Sacramento–San Joaquin Delta (Wood et al., 2010a,b). Rice agriculture constitutes a large proportion of the managed flooded lands in California, greater than the acreage of natural and managed non-agricultural wetlands throughout the state (Hill et al., 2006). Globally, rice production also contributes to a significant proportion of the wetland acreage in the lower Mississippi River watershed and much of southern and southeast Asia (USGS, 2000).

Because Hg is a global pollutant and locations where methylation occurs are widespread, it is important to understand the pathways for MeHg removal within aquatic systems to better protect human and ecosystem health (Sellers et al., 1996; Wiener et al., 2003). Photolytic degradation of MeHg, also referred to as photodemethylation, is an important component of the MeHg cycle (Hammerschmidt et al., 2006; Lehnherr et al., 2012; Li et al., 2010; Sellers et al., 2001). In coastal waters where chloride complexes predominate, OH radicals may play the primary role in MeHg degradation (Hammerschmidt and Fitzgerald, 2010). In freshwater systems, MeHg is more strongly associated with reduced organic functional groups within dissolved organic matter (DOM) that will increase photodegradation rates compared to coastal or ocean waters (Black et al., 2012; Zhang and Hsu-Kim, 2010). Other recent studies used isotopic methods to quantify the contribution of photodemethylation to the MeHg cycle in a number of systems (Bergquist and Blum, 2007; Kritee et al., 2012), but questions remain about the effects that DOM has on Hg-isotope fractionation (Zheng and Hintelmann, 2009, 2010). Despite recent studies focused on mechanisms, photodemethylation remains a poorly defined process in the natural environment.

DOM plays a complex role in both Hg cycling and photolytic reactions in aquatic systems. DOM strongly binds with the reactive inorganic form Hg^{II} (Han et al., 2006; Lamborg et al., 2003; Ravichandran, 2004) and MeHg (Hintelmann et al., 1997; Khwaja et al., 2010; Qian et al., 2002). Because of this DOM plays a role in the cycling and bioavailability of both Hg^{II} (Bergamaschi et al., 2012; Brigham et al., 2009; Choe et al., 2003; Dittman et al., 2010; Gorski et al., 2008; Gerbig et al., 2011; Graham et al., 2012; Schuster et al., 2011) and MeHg (Bergamaschi et al., 2011; Choe and Gill, 2003; Pickhardt and Fisher, 2007; Tsui and Finlay, 2011). DOM also binds with other radical-forming constituents that may participate in photochemical processes (Gu et al., 2011; Gao and Zepp, 1998). Specific components within DOM can release labile organic compounds and nutrients when exposed to light (Dalzell et al., 2009; Engelhaupt et al., 2003; Mopper and Kieber, 2000; Moran and Zepp, 1997). Additionally, photolytic reactions within the DOM can physically alter DOM structure by breaking large macromolecules into smaller components that are more available for bacterial utilization (Cory and McKnight, 2005; Blough and DelVecchio, 2002; Mostafa et al., 2007; Spencer et al., 2009). Alternatively, DOM that is dominated by fresh, low molecular weight structures can lead to the formation of larger DOM molecules and particles during light exposure, further complicating the effects of light exposure on DOM dynamics in natural systems (Stepanauskas et al., 2005).

Recent studies have reported contradictory lines of evidence regarding the role of DOM in photodemethylation. Zhang and Hsu-Kim (2010) implicated DOM binding in promoting photodemethylation. In contrast, Li et al. (2010) suggested that spatial trends in MeHg concentrations in waters from the Florida Everglades may have been related to DOM effectively shading the MeHg from solar radiation, thus maintaining higher MeHg concentrations where DOM was high. Meanwhile, Black et al. (2012) observed only a minor effect of DOM on demethylation rates.

Despite the recent contributions of these studies to our understanding of DOM effects on demethylation, none of the work was performed on unadulterated samples. Previous laboratory-based experiments used model compounds (i.e. glutathione (GSH)), commercially available isolates (Suwanee River Humic Acid (SRHA), International Humic Substances Society, St Paul, MN) and other forms of altered or synthesized DOM. The use of commercial standards, concentrated DOM, or isotope-labeled MeHg is useful in mechanistic studies but can significantly alter the DOM and its reactivity thus limiting the extrapolation of these studies to natural systems (Shubina et al., 2010). For instance, GSH is a good model compound for testing the effects of reduced sulfur groups in organic molecules in a well-constrained manner necessary for mechanistic studies, but it lacks the complexity of interactions within the structure of natural DOM to justify extrapolation to natural systems without corroborative field evidence. Isolates derived from natural DOM, like SRHA, are preferable to model compounds when making inferences about natural systems, but commercial isolates are also limited because they are known to have different properties than natural DOM due to the loss of important structural components in the isolation process (Shubina et al., 2010). Because DOM structure and reactivity is so complex, and dependent on conditions (ie. pH, ionic strength and DOM concentration), studies using natural water samples are necessary to bridge the gap between these valuable mechanistic lab studies and what occurs in natural systems.

Characterizing DOM sources and transformations in natural systems is important for improved understanding of biogeochemical processes, but such information is typically difficult or expensive to obtain. There are many ways to measure DOM properties, but most approaches require solid material, which requires large quantities of water and the isolation process typically alters the DOM and includes only a fraction of the bulk pool. One non-destructive method for the characterization of natural DOM that has received recent attention is optical characterization. The use of absorbance and fluorescence spectroscopy uses the inherent optical properties of DOM structures to infer the presence and relative distribution of organic structure and functional groups within the DOM. Furthermore, optical properties can be measured in situ at time-scales relevant to natural processes (Romera-Castillo et al., 2011). Recently, optical proxies have been used successfully to determine temporal variability in THg and MeHg concentration in dynamic hydrologic settings (Bergamaschi et al., 2011, 2012; Dittman et al., 2009).

In this study, we investigated changes in MeHg concentration and the relationship to changes in DOM and inherent optical properties of surface waters collected from rice fields and exposed to solar radiation in a controlled, field-based, bottle experiment. Our objective was to test whether in situ proxies for dynamic biogeochemical settings could be identified that would provide a way to observe MeHg dynamics in the field at timescales relevant to production and degradation processes. This information would be useful for improving our understanding of Hg cycling in natural systems and aid in making informed management decisions that minimize MeHg exposure both within these systems and in downstream habitats.

2. Methods

2.1. Field procedures

Water samples were collected from five field outlets within the Yolo Bypass Wildlife Area on the morning of July 30, 2008 (Table S1; Fig. S1A). Two were collected at the outlets of domestic (white) rice fields (R20, R66), two at the outlets of wild rice fields (W31, W64), and one was collected from a permanently flooded open-water wetland (PW5). All samples were collected early in the morning to minimize light exposure prior to the experiment. From each field location approximately 10 L of filtered surface water was collected in a polycarbonate carboy by pumping water through an acid-cleaned 0.45 μm filter cartridge using a peristaltic pump (Fig. S1C). The samples were filtered to