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Methylmercury photodemethylation is inhibited in lakes with high dissolved organic matter☆

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ABSTRACT

Photodemethylation can be one of the primary processes for loss of neurotoxic methylmercury (MeHg) in freshwater lakes. Few studies have quantified seasonal variations in photodemethylation rate constants as a function of dissolved organic matter (DOM). We conducted 1-week irradiation experiments in two seasons to test for spatial and temporal differences in photodemethylation potential in temperate lake waters. Six study lakes in Kejimkujik National Park, Nova Scotia were sampled in summer and fall to include a range of naturally occurring DOM concentrations (4.4–13.4 and 3.9–16.4 mg C L^{-1}, respectively). A negative linear relationship ($R^2 = 0.76$, $p = 0.01$) was found between DOM concentration and photodemethylation rate constant across seasons, indicating that DOM is a strong predictor of MeHg photodemethylation independent of seasonal effects. The two highest carbon lakes (BDW and PEB) had significantly higher energy-normalized photodemethylation rate constants in summer compared to fall corresponding with lower DOM concentrations in summer relative to fall. Additionally, there were negative linear relationships between MeHg photodemethylation and DOM photomineralization (R^2s = 0.58–0.72) and DOM photobleaching (R^2s = 0.83–0.90). This key finding suggests that competition for photons within DOM structures may reduce the potential for MeHg photodemethylation in high carbon waters and that this relationship persists across seasons.

1. Introduction

Methylmercury (MeHg) contamination through bioaccumulation and biomagnification in aquatic food webs is an issue in many remote ecosystems far from direct pollution sources (Evers et al., 2007; Wyn et al., 2010; Kidd et al., 2011; Lehnherr, 2014). Understanding why some ecosystems are more sensitive to contamination following atmospheric mercury deposition and quantifying this effect is key to mercury fate modeling and mitigating mercury contamination in food webs. Once MeHg is in the water column it may be degraded through photodemethylation processes (Sellers et al., 1996) and the balance between MeHg formation and degradation is an important factor controlling the availability of MeHg to the base of the food web (primary producers) in the water column.

In water columns, abiotic photodemethylation can be responsible for the majority (58–80%) of the MeHg loss in low nutrient freshwater arctic ponds (Hammerschmidt and Fitzgerald, 2006; Lehnherr et al., 2012) and temperate lakes (Sellers et al., 1996). The process of photodemethylation is also important in high carbon and nutrient-rich systems such as temperate California wetlands (Black et al., 2012; Fleck et al., 2014) and temperate-tropical Florida Everglades (Li et al., 2010). Biological demethylation has not been detected in aerobic lake waters (Hammerschmidt and Fitzgerald, 2010; Klapstein et al., 2016) and rather tends to occur in areas of methylation, such as in sediments that have high organic content and little to no available oxygen (Gilmour et al., 1992; Marvin-DiPasquale and Oremland, 1998; Benoit et al., 1999). Solar radiation varies vertically within a lake, and consequently, MeHg loss through photodemethylation decreases dramatically with depth through freshwater lake columns (Sellers et al., 1996; Krabbenhoft et al., 2002) and this consistent pattern is due to the decrease in transmitted solar radiation (Scully and Lean, 1994; Morris et al.,

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1995), particularly the ultraviolet (UV) wavebands (Lehnherr and St Louis, 2009). The attenuation of UV wavelengths by dissolved organic matter (DOM) occurs rapidly in temperate lakes (Scully and Lean, 1994) with extinction of UV-A in high carbon lakes of Kejimkujik National Park, Nova Scotia occurring within the top 30 cm of the water column (Haverstock et al., 2012). Due to its variable photoreactivity, DOM is a key variable controlling other photoreactions such as photodemethylation of MeHg in freshwaters.

The purpose of this study was to determine how MeHg photodemethylation varies across a series of lakes and two seasons in response to both DOM concentration and photoreactivity. Photoreactivity, as used in this study, indicates the ability to absorb photons and lose chromophoric structures within the DOM (photobleaching) and possibly DOM itself (photomineralization). Recent studies have highlighted the importance of DOM-MeHg complexation in the photodegradation of methylmercury in freshwaters (Zhang and Hsu-Kim, 2010; Fleck et al., 2014; Tai et al., 2014; Qian et al., 2014; Jeremiason et al., 2015) but that the potential for photodemethylation is higher in waters with more photobleached or less photoreactive DOM (Klapstein et al., 2016). Concurrently, solar radiation necessary for photodemethylation is limited due to radiation attenuation by DOM in high carbon systems (Lehnherr and St Louis, 2009; Fernández-Gómez et al., 2013; Zhang et al., 2016). Thereby, DOM plays two roles in controlling MeHg photodemethylation: DOM will form complexes that enable photodemethylation, but DOM will also attenuate radiation. In high DOM waters the proportion of DOM that is associated with MeHg (DOM-MeHg) will decrease and these MeHg-free DOM structures may be critical in regulating photodemethylation reactions.

We hypothesized that photodemethylation rate constants would decrease with increasing DOM concentration due to an increase in the ratio between DOM and DOM-MeHg complexes. An increase in that ratio would result in increased competition for photons in the photochemical reactions involving solely DOM versus those with DOM-MeHg. At low DOM concentrations photoreactions likely involve a larger proportion of photoreactive DOM-MeHg, whereas DOM structures that are not associated with MeHg(I) will be less prevalent and contribute less to photoreactions in these waters (Fig. 1a). Conversely, at higher DOM concentrations DOM may inhibit photodemethylation by dominating the photon absorbance in these waters, and resulting in DOM phototransformations, including photomineralization and photobleaching, that do not involve MeHg (Fig. 1b). Photodemethylation will still occur in high DOM waters but at a limited rate because a smaller proportion of the photoreactions will involve DOM-MeHg. To test these hypotheses, we used water collected from 6 lakes in both the summer and fall and exposed the water samples to the full natural solar radiation spectrum during each collection season. These findings present a simplified framework for predicting energy-normalized photodemethylation rate constants among similar freshwaters using basic DOM characteristics such as concentration and optical properties.

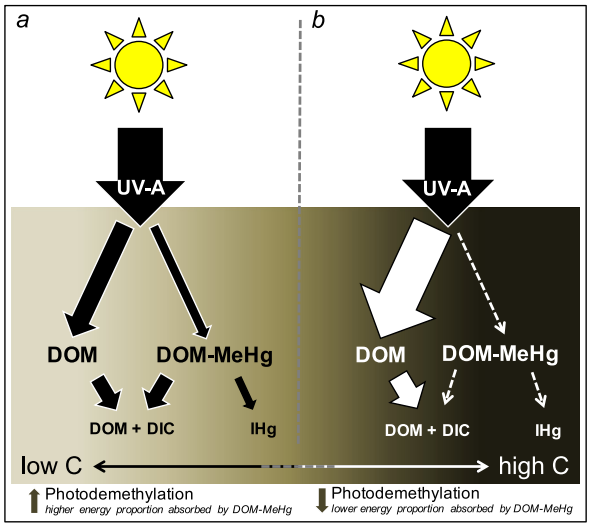

Fig. 1. Conceptual figure displaying photoreactions involving dissolved organic matter (DOM) and methylmercury (MeHg) with regard to the relative use of photons resulting in photodemethylation and the production of inorganic mercury (IHg) compared to photobleaching and photomineralization reactions within the DOM. At low carbon (C) concentrations, photodemethylation occurs because DOM structures and compounds that are associated with MeHg will facilitate photoreactions in these waters. At high C concentrations, more photoreactive DOM structures and compounds will receive a greater proportion of the incoming energy and this will inhibit photodemethylation by these MeHg-free DOM structures dominating the resultant photoreactions. A smaller proportion of the photoreactions will involve DOM-MeHg structures in higher C freshwaters.

2. Materials & methods

2.1. Sampling sites for freshwater of varying DOM

Six lakes in Kejimkujik National Park (Nova Scotia), a biological mercury hot spot (Evers et al., 2007; Wyn et al., 2010; Little et al., 2015), were sampled to include a range of DOM concentrations (3.9–16.4 mg C L^{-1}) (O'Driscoll et al., 2005). Mercury bioaccumulation in organisms may peak around 8 mg C L^{-1} (French et al., 2014) and therefore we included lakes with DOM concentrations both below (low C lakes) and above (high C lakes) this ecological threshold. Sample sites included: Big Dam East (BDE), Puzzle (PUZ), North Cranberry (NCR), Peskawa (PES), Big Dam West (BDW), and Pebbleloggitch (PEB) lakes. Water was collected from BDW in spring (mid-May), all 6 lakes in summer (last week of June), and all 6 lakes in fall (last week of September). Bulk water samples were collected from the side of a plastic canoe in the middle of each lake at 30 cm depth using triple-rinsed (with Milli-Q and lake water) HDPE containers (>10 L).

2.2. Experimental design

In spring, experimental treatments included 0.45 μm filtered (polyethersulfone membrane) and unfiltered water from one lake (BDW lake) to test the effect of particulates on photodemethylation rate constants. In summer and fall, experiments included water collected from six lakes (BDE, PUZ, NCR, PES, BDW, and PES lakes) and filtered to 0.45 μm to quantify temporal and spatial differences in DOM on photodemethylation rate constants.

Polytetrafluoroethylene (PTFE) bottles were used for all irradiations in the experimental design to minimize losses in UV radiation due to absorption by the container walls (measured attenuation was 16–30% in the 320–400 nm region depending on bottle wall thickness) and the incoming UV-A was corrected for wall attenuation to determine the intensity reaching each sample. In spring and summer the bottles were 2 L and allowed for a 75% headspace whereas in fall the bottles were 1 L and maintained a headspace of 50% by volume. Each 500 mL sample of lake water was spiked to have a concentration increase of 3 ng L^{-1} MeHgOH (Strem Chemicals, Inc.), swirled in the PTFE bottle to mix, and left capped in the dark at room temperature to equilibrate for 12 h before being placed outside after sunset. These steps were considered to allow for ambient temperature equilibrium to occur prior to the solar radiation exposure and provide time for the spiked MeHg to bind