JOURNAL OF ENVIRONMENTAL SCIENCES XX (2018) XXX–XXX

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Assessing the utility of dissolved organic matter photoreactivity as a predictor of *in situ* methylmercury concentration

Sara J. Klapstein[1,2,3,*], *Susan E. Ziegler*[1], *David A. Risk*[2], *Nelson J. O'Driscoll*[3]

1. *Environmental Science Program, Memorial University of Newfoundland, St. John's, NL A1C 5S7, Canada*
2. *Department of Earth Sciences, St. Francis Xavier University, Antigonish, NS B2G 2W5, Canada*
3. *Department of Earth and Environmental Science, Acadia University, Wolfville, NS B4P 2R6, Canada*

ARTICLE INFO

Article history:
Received 18 June 2017
Revised 8 February 2018
Accepted 9 February 2018
Available online xxxx

Keywords:
Methylmercury
Dissolved organic carbon
Photoreactions
Kejimkujik National Park
Freshwater lakes

ABSTRACT

Methylmercury (MeHg) bioaccumulation is a growing concern in ecosystems worldwide. The absorption of solar radiation by dissolved organic matter (DOM) and other photoreactive ligands can convert MeHg into less toxic forms of mercury through photodemethylation. In this study, spectral changes and photoreactivity of DOM were measured to assess the potential to control photoreactions and predict *in situ* MeHg concentration. Water samples collected from a series of lakes in southwestern Nova Scotia in June, August, and September were exposed to controlled ultraviolet-A (UV-A) radiation for up to 24 hr. Dissolved organic matter photoreactivity, measured as the loss of absorbance at 350 nm at constant UV-A irradiation, was positively dependent on the initial DOM concentration in lake waters (r^2 = 0.94). This relationship was consistent over time with both DOM concentration and photoreactivity increasing from summer into fall across lakes. Lake *in situ* MeHg concentration was positively correlated with DOM concentration and likely catchment transport in June (r = 0.77) but not the other sampling months. Despite a consistent seasonal variation in both DOM and Fe, and their respective correlations with MeHg, no discernable seasonal trend in MeHg was observed. However, a 3-year dataset from the 6 study lakes revealed a positive correlation between DOM concentration and both Fe (r = 0.91) and MeHg concentrations (r = 0.51) suggesting a more dominant landscape mobility control on MeHg. The DOM-MeHg relationships observed in these lakes highlights the need to examine DOM photoreactivity controls on MeHg transport and availability in natural waters particularly given future climate perturbations.

Introduction

The amount of methylmercury (MeHg) available for uptake at the base of the food web is partially controlled by the balance between methylation and demethylation reactions (Xun et al., 1987). While more is understood about drivers of methylation processes, the MeHg demethylation mechanisms are not well constrained in natural waters. MeHg can be demethylated both biotically and abiotically, however, in water columns of freshwater lakes the primary pathway for demethylation has been identified as photodemethylation by solar radiation (Sellers et al., 1996). Photodegradation experiments have

* *Corresponding author. E-mail:* sara.klapstein@acadiau.ca (Sara J. Klapstein).

https://doi.org/10.1016/j.jes.2018.02.025
1001-0742/

Please cite this article as: Klapstein, S.J., et al., Assessing the utility of dissolved organic matter photoreactivity as a predictor of *in situ* methylmercury concentration, J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2018.02.025

evaluated MeHg photodemethylation rate constants both at water body surfaces (Lehnherr et al., 2012; Sellers et al., 1996) and within lake water columns with relatively low dissolved organic matter (DOM) concentration (Krabbenhoft et al., 2002; Lehnherr and St Louis, 2009; Sellers et al., 1996) using bottle incubations at various depths. Rate constants of this photochemical process have been quantified for several specific ecosystems (ranging from 0.006 to 0.015 E/m^2 for photon flux from 330 to 700 nm) (Black et al., 2012). However, less attention has been given to the photochemically active components themselves, such as the chromophoric portions of DOM and dissolved ions present within these ecosystems (Fleck et al., 2014; Klapstein et al., 2016), and specifically how these constituents interact with solar radiation and mercury. When considering the fate of MeHg in freshwater lakes, it is important to consider how MeHg may be influenced by indirect or direct reactions with dissolved entities.

DOM serves many functions in freshwater lake ecosystems. Along with being a significant carbon pool, DOM is a microbial energy and nutrient source (De Lange et al., 2003), contains binding sites for cations such as mercury and other metals (O'Driscoll and Evans, 2000; Ravichandran, 2004), and is photoreactive, meaning some portions of DOM (including complexes with Fe) will absorb solar radiation, particularly ultraviolet (UV) radiation and visible wavebands, resulting in visibly brown or dark waters (Bertilsson and Tranvik, 2000; Osburn et al., 2009; Granéli et al., 1996). A study from 65 sites across North America has shown that more than 85% of the between-lake variation in UV attenuation may be attributed to bulk DOM concentrations alone (Morris et al., 1995). The depth of penetration for UV radiation has been shown to vary substantially between low carbon temperate lakes (35%–150% of the mixed layer depth throughout a year; DOM = 1.09 mgC/L); 41–41°N) and higher carbon lakes (4%–8% of the mixed layer depth; DOM = 4.80–5.28 mgC/L) (Morris and Hargreaves, 1997). Even though both UV-A (320–400 nm) and UV-B (280–320 nm) radiation have been shown to be important drivers of the photomineralization of DOM (Morris and Hargreaves, 1997), in high DOM lakes (DOM = 3.3–12.3 mgC/L) the flux of UV-A and particularly UV-B radiation in water columns can be quickly quenched in surface waters (Haverstock et al., 2012). Dissolved organic carbon (DOC), the portion of DOM commonly quantified, concentrations correlate with concentrations of total mercury, and are repeatedly reported in the literature. However, sometimes this relationship is positive and sometimes negative (Kim and Zoh, 2013; Li et al., 2010; Meng et al., 2005; Ravichandran, 2004). This inconsistency suggests the relative importance of catchment transport and photodemethylation controls on lake MeHg concentrations varies. The relationship between *in situ* lake water photochemical characteristics, such as DOM photoreactivity, and MeHg concentrations would enable a better understanding of the relative importance of these controls.

Seasonal variations in DOM photoreactivity and effects on MeHg photodemethylation are difficult to assess *in situ* because of the dynamic nature of the aquatic environment. The uncertainty in this research area was initially due to the challenge of separating DOM photoreactions that are *intra*-molecular (MeHg bound directly to DOM subjected to photoreactions) versus *inter*-molecular (MeHg not bound directly to DOM subjected to photoreactions). However, in recent years there is some consensus that photodemethylation is likely intramolecular and MeHg must be bound with photoreactive DOM to photodegrade (Jeremiason et al., 2015; Qian et al., 2014; Tai et al., 2014). Therefore the influence of DOM photoreactivity is essential to characterize in mercury sensitive ecosystems such as Kejimkujik National Park and Eastern North American in general (Evers et al., 2007). High carbon freshwaters, like those lakes used in our study, can efficiently attenuate UV radiation and can inhibit or facilitate MeHg photodemethylation by acting as a photoreactive species within the water column (Li et al., 2010; Sellers et al., 1996).

Previous experiments have shown that higher DOM concentrations will inhibit MeHg photodemethylation (Klapstein et al., 2018) and more specifically that the photoreactive nature of DOM can directly impact photodemethylation potential (Klapstein et al., 2016). Therefore, the objective of our study was to assess DOM photoreactivity in relation to *in situ* concentrations of MeHg and the ecological and seasonal attributes of this relationship (summarized in Fig. 1). We quantified the photoreactivity of DOM in water collected multiple times per year from 6 lakes spanning a gradient of DOM concentration in southwestern Nova Scotia through controlled irradiation experiments and measurement of absorption loss at 350 nm and photochemical mineralization of DOC to inorganic carbon. We hypothesized that DOM photoreactivity of lake water would increase over the sampling season due to a reduction of UV radiation entering lakes from summer through to fall and a consequential decrease of *in situ* photochemical transformation of DOM (Fig. 1). We also predicted that higher concentrations of photoreactive DOM would result in a competitive sink for photons and therefore limit the potential for photodemethylation of MeHg in the lakes. As such, we expect that DOM photoreactivity would be positively correlated with MeHg concentration in dystrophic lake waters from Kejimkujik National Park consistent with catchment input controls over photodemethylation controls on MeHg.

1. Material and methods

1.1. Water collection and monitoring

Located in southwestern Nova Scotia, Canada, Kejimkujik National Park (44.399°N, 65.218°W) is a temperate region characterized by mixed coniferous and deciduous vegetation, high wetland cover, and an abundance of freshwater lakes. The bedrock is split between the Meguma Group of the Cambro-Ordovician and South Mountain Batholith, both of which are known to contain mercury and are associated with low alkalinity bedrock and soils (Smith et al., 2005). Six lakes with DOM concentrations ranging from 3 to 26 mgC/L were sampled over a 3-day period in each of summer (late-June; Week 25), late-summer (mid-August; Week 33), and fall (September; Week 40) in 2013. Lakes sampled included: Big Dam East Lake (BDE), Puzzle Lake (PUZ), North Cranberry Lake (NC), Peskawa Lake (PES), Big Dam West Lake (BDW), and

Please cite this article as: Klapstein, S.J., et al., Assessing the utility of dissolved organic matter photoreactivity as a predictor of *in situ* methylmercury concentration, J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2018.02.025