Environmental Pollution xxx (2017) 1–10

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Water-level fluctuations influence sediment porewater chemistry and methylmercury production in a flood-control reservoir☆

Chris S. Eckley [a], Todd P. Luxton [b, *], Jennifer Goetz [b], John McKernan [b]

[a] US Environmental Protection Agency, Region-10. 1200, 6th Ave Seattle, WA 98101, USA
[b] US Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA

ARTICLE INFO

Article history:
Received 28 October 2016
Received in revised form
15 December 2016
Accepted 7 January 2017
Available online xxx

Keywords:
Porewater
Mercury methylation
Reservoir
Water-level
DOC

ABSTRACT

Reservoirs typically have elevated fish mercury (Hg) levels compared to natural lakes and rivers. A unique feature of reservoirs is water-level management which can result in sediment exposure to the air. The objective of this study is to identify how reservoir water-level fluctuations impact Hg cycling, particularly the formation of the more toxic and bioaccumulative methylmercury (MeHg). Total-Hg (THg), MeHg, stable isotope methylation rates and several ancillary parameters were measured in reservoir sediments (including some in porewater and overlying water) that are seasonally and permanently inundated. The results showed that sediment and porewater MeHg concentrations were over 3-times higher in areas experiencing water-level fluctuations compared to permanently inundated sediments. Analysis of the data suggest that the enhanced breakdown of organic matter in sediments experiencing water-level fluctuations has a two-fold effect on stimulating Hg methylation: 1) it increases the partitioning of inorganic Hg from the solid phase into the porewater phase (lower log K_d values) where it is more bioavailable for methylation; and 2) it increases dissolved organic carbon (DOC) in the porewater which can stimulate the microbial community that can methylate Hg. Sulfate concentrations and cycling were enhanced in the seasonally inundated sediments and may have also contributed to increased MeHg production. Overall, our results suggest that reservoir management actions can have an impact on the sediment-porewater characteristics that affect MeHg production. Such findings are also relevant to natural water systems that experience wetting and drying cycles, such as floodplains and ombrotrophic wetlands.

1. Introduction

Mercury (Hg) is a pollutant of global concern largely due to its ability to accumulate in fish tissue. Most anthropogenic releases of Hg to the environment are in an inorganic form; however almost all Hg in fish tissue is in an organic form—methylmercury (MeHg). Within the US, thousands of water bodies are currently under fish consumption advisories due to Hg pollution (United States Environmental Protection Agency, 2011).

Understanding the variables influencing MeHg production is key to identifying strategies that can be used to reduce MeHg levels in fish. Most Hg methylation is conducted by anaerobic microorganisms in sediments, peatlands and the hypolimnetic water of lakes (Branfireun et al., 1999; Compeau and Bartha, 1985; Eckley and Hintelmann, 2006). Sulfate reducing bacteria (SRB) have been widely reported to be important producers of MeHg (Ullrich et al., 2001); however, some iron reducing bacteria (Kerin et al., 2006) and methanogens (Hamelin et al., 2011) are also capable of Hg methylation.

The activity, abundance, and structure of the microbial community play an important role in determining MeHg production rates. As a result, MeHg concentration can be highly spatially and temporally variable across landscapes, with wetlands and peatlands typically having enhanced MeHg production (Branfireun et al., 1996; Hurley et al., 1995; Johnson et al., 2015; Stlouis et al., 1994).

The microbial community is influenced by the extent of anoxic conditions, the quantity and quality of organic carbon, and the concentration of electron acceptors such as sulfate and ferric iron

☆ This paper has been recommended for acceptance by Maria Cristina Fossi.
* Corresponding author.
E-mail address: luxton.todd@epa.gov (T.P. Luxton).

http://dx.doi.org/10.1016/j.envpol.2017.01.010
0269-7491/

(Hsu-Kim et al., 2013; Kerin et al., 2006; Ullrich et al., 2001). Microbial activity and methylation rates have also been shown to increase with temperature (King et al., 1999), which may be partially responsible for the seasonal variations in MeHg observed in many systems (Hammerschmidt and Fitzgerald, 2004). However, the extent to which Hg is methylated is also highly dependent on the bioavailability of the inorganic Hg to the methylating organisms. The bioavailable forms of inorganic Hg may include neutrally charged Hg-ligand complexes which can enter bacteria via passive diffusion (Benoit et al., 1999) and/or the active transport of Hg complexes with low molecular weight thiol ligands (Golding et al., 2002; Schaefer et al., 2011). Recent studies have also shown that dissolved organic matter can play an important role affecting the uptake of inorganic bacteria into methylating organisms (Graham et al., 2012). Only a small percent (typically $\leq$5%) of the total amount of inorganic Hg in aquatic systems is in a "reactive" form that is considered available for microbial uptake and methylation (Domagalski, 2001; Marvin-DiPasquale et al., 2009; Singer et al., 2016)

In sediment, bioavailable inorganic Hg is mostly associated with the porewater fraction and is related to the sediment-porewater distribution coefficient (K_d) (Buckman et al., 2015; Marvin-DiPasquale et al., 2009; Schartup et al., 2014). Compared to bulk sediment measurements, porewater Hg concentrations are also more available for benthic invertebrate uptake as well as diffusive flux into the overlying water. Sediment-porewater partitioning of Hg is controlled by the amounts of Hg binding ligands, such as sulfide and thiols, in the solid and in the dissolved phases. These ligands in turn are influenced by several factors such as sediment organic matter, redox conditions and pH (Hammerschmidt and Fitzgerald, 2004; Schartup et al., 2014). Overall, partitioning of sediment inorganic Hg between solid and porewater phases can be an important controlling mechanism on the rate of MeHg production.

Reservoirs have been shown to have elevated MeHg concentrations in water and fish compared to natural lakes and is related to the degree of water-level fluctuations (Brigham et al., 2002; Kamman et al., 2005; Larson et al., 2014; Montgomery et al., 2000; Selch et al., 2007; Sorensen et al., 2005). Newly created reservoirs have been shown to have higher MeHg production due to increased organic material available after flooding terrestrial landscapes (Hall et al., 2005; St Louis et al., 2004); however even decades after the initial impoundment reservoirs can continue to have elevated MeHg levels due to ongoing seasonal water-level fluctuations (Anderson et al., 1995; Bodaly et al., 2007) and/or changes in the foodweb structure (lotic to lentic). Water-level fluctuations are believed to promote the recycling of sulfide in sediment to sulfate when exposed to the air, which can enhance microbial methylation when sediments are re-wetted (Eckley et al., 2015; Evers et al., 2007). In addition, this process may enhance partitioning of sediment-bound Hg into the porewater/aqueous phase where it is more available for microbial uptake; however to our knowledge the influence of this mechanism has not been previously assessed in reservoirs. Despite increased MeHg in reservoirs, Hg dynamics in these systems have been much less studied compared to natural lakes. Because reservoirs are waterbodies that are actively managed, understanding how water level management actions influence Hg cycling provides an opportunity to improve environmental conditions. Many natural systems such as river floodplains and ombrotrophic wetlands also experience seasonal wetting and drying cycles that can impact Hg cycling.

The overarching objective of our study is to identify areas of elevated MeHg production within reservoir sediment and to determine the variables that drive these trends. Specifically, we will test the hypothesis that water-level fluctuations result in an increase in MeHg production within a reservoir and that this is influenced by enhanced sulfate cycling and increased partitioning of inorganic Hg to porewater. A previous study conducted at this site (Cottage Grove Reservoir) identified a subtle, yet statistically significant, increase in sediment MeHg concentrations in the seasonally inundated mudflats of the reservoir compared to the permanently inundated sediments (Eckley et al., 2015). In our current study, we expand on these findings by including the areas along the reservoir shoreline that are seasonally inundated wetlands and by adding porewater measurements and isotopic Hg methylation assays to further explore the mechanisms driving MeHg production. In addition, we assess the potential for sediment Hg concentrations to influence the overlying water concentrations.

2. Methods

2.1. Site description

The Cottage Grove Reservoir in western Oregon (43.69403; −123.07328; Fig. 1) is a flood control reservoir constructed in 1942. The reservoir's watershed includes the historical Black Butte mine (cinnabar ore) approximately 15 km upstream. During its operation from the 1890s to the 1960s, the mine produced approximately 635,000 kg of Hg and over 200,000 m^3 of mine tailings (Ecology and Environment, 1998). Sediment core data suggests that Hg at the historical mine site continues to be transported downstream to the reservoir (Ambers and Hygelund, 2001; Curtis et al., 2013).

In order to have storage capacity to prevent flooding, the reservoir water level is kept low during much of the year that experiences higher rainfall (September through April). During the low pool conditions, over 60% of the reservoir area is exposed sediment, which are seasonally inundated during the summer months. When the water levels are raised to full-pool conditions, vegetated wetland areas that occur mostly near the inlet are inundated with reservoir water. The wetlands are fairly extensive (~36 ha) and cover approximately 8% of the total surface area of the reservoir.

In this study, we're defining the wetlands as the areas that have continuous year-round vegetation that is emergent during full-pool conditions. The vegetation is dominated by reed canary grass and cattails. In comparison the mudflat areas do not have any emergent vegetation above the water surface during full-pool conditions; however during the ~6-months of the year that they are exposed to the air some areas become colonized by short grasses or forbs.

2.2. Field sampling

Sediment, porewater and surface water samples were collected in three distinct areas of the reservoir: the permanently inundated area; the seasonally inundated sediments without vegetation; and the seasonally inundated wetland areas (Fig. 1). Due to the important role of wetlands in MeHg production, this area was sampled the most intensively. Samples were collected during four seasonal conditions: winter low-pool (March 2014; 2015); spring full-pool (June 2014; May 2015); summer full-pool (August 2014); and fall low-pool following drawdown (November 2014) (see Fig. S1 in the Supporting Information (SI)).

Sediment samples were collected using a large bore gravity sediment corer (Aquatic Research Instruments) with polycarbonate core tubes. The samples were collected with ~10 cm of overlying water above the sediment. The sediment cores were capped, and stored in a cooler at 4 °C during transport to the mobile laboratory. Within several hours after collection, the top 8 cm of the sediment cores were extruded in an anoxic glove box filled with ultra-high purity nitrogen gas. For solid phase analysis, cores were sectioned

Please cite this article in press as: Eckley, C.S., et al., Water-level fluctuations influence sediment porewater chemistry and methylmercury production in a flood-control reservoir, Environmental Pollution (2017), http://dx.doi.org/10.1016/j.envpol.2017.01.010