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Hydrologic indicators of hot spots and hot moments of mercury methylation potential along river corridors

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HIGHLIGHTS

- Flood magnitude, frequency, and duration are relevant to mercury methylation potential (MPP).
- Methylmercury is present in aquatic biota at various trophic levels.
- We estimate MPP from surface sediment by floodplain inundation, 1967–2013.
- Longer floods in the historical record are tied to higher MPP than shorter ones.
- The legacy of 19th Century hydraulic gold mining in CA is one of ongoing toxicity to food webs.

GRAPHICAL ABSTRACT

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ABSTRACT

The biogeochemical cycling of metals and other contaminants in river-floodplain corridors is controlled by microbial activity responding to dynamic redox conditions. Riverine flooding thus has the potential to affect speciation of redox-sensitive metals such as mercury (Hg). Therefore, inundation history over a period of decades potentially holds information on past production of bioavailable Hg. We investigate this within a Northern California river system with a legacy of landscape-scale 19th century hydraulic gold mining. We combine hydraulic modeling, Hg measurements in sediment and biota, and first-order calculations of mercury transformation to assess the potential role of river floodplains in producing monomethylmercury (MMHg), a neurotoxin which accumulates in local and migratory food webs. We identify frequently inundated floodplain areas, as well as floodplain areas inundated for long periods. We quantify the probability of MMHg production potential (MPP) associated with hydrology in each sector of the river system as a function of the spatial patterns of overbank inundation and drainage, which affect long-term redox history of contaminated sediments. Our findings identify river floodplains as periodic, temporary, yet potentially important, loci of biogeochemical transformation in which contaminants may undergo change during limited periods of the hydrologic record. We suggest that inundation is an important driver of MPP in river corridors and that the entire flow history must be analyzed retrospectively in terms of

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inundation magnitude and frequency in order to accurately assess biogeochemical risks, rather than merely highlighting the largest floods or low-flow periods. MMHg bioaccumulation within the aquatic food web in this system may pose a major risk to humans and waterfowl that eat migratory salmonids, which are being encouraged to come up these rivers to spawn. There is a long-term pattern of MPP under the current flow regime that is likely to be accentuated by increasingly common large floods with extended duration.

1. Introduction

Mercury (Hg) contamination of food webs is a global problem with severe consequences for ecosystem and human health (Cristol et al., 2008; Mergler et al., 2007). Anthropogenic sources of inorganic divalent Hg (Hg^{2+}), hereafter referred to as iHg, enter the environment primarily through atmospheric emissions (and deposition) or through point source releases from historical mining. In the environment, iHg can be biogeochemically processed into monomethylmercury (MMHg) that is toxic to biota and becomes bioconcentrated and biomagnified in food webs. Currently there is limited understanding of the production of MMHg along river corridors due to the complex interactions between inundation history and net transport/deposition of contaminated sediment.

Flooding affects redox history and thus supports the activity of bacteria that are responsible for converting iHg to its more toxic, bioavailable form, MMHg. This conversion is based on biologically mediated reactions that are thought to occur in locations and time periods of low oxygen at the sediment-water interface (Beutel et al., 2008). There is currently a well-documented understanding of MMHg production by anaerobic bacteria in laboratory settings, (e.g., Compeau and Bartha, 1985; Gilmour et al., 1992; Kerin et al., 2006), but there are major outstanding uncertainties regarding loci, timing and rates of Hg (II) methylation in natural fluvial systems, especially at the landscape scale. In river basins affected by high levels of iHg contamination, for example due to historical mining, there may be great variability in spatial patterns of total Hg concentrations (THg) in channel boundary sediment (Miller et al., 1999; Miller, 1997; Pizzuto, 2012; Singer et al., 2013), yet the spatiotemporal variability of redox might be a more dominant control over microbial activity. There is limited systematic understanding of where and when MMHg is produced in river corridors. This could, in part, be due to spatial or temporal biases in prior investigations emphasizing particular river reaches or sampling over a limited timeframe, which masks the impact of important hydrologic events (Balogh et al., 2006; Blum et al., 2001; Domagalski, 1998; Domagalski, 2001; Marvin-DiPasquale et al., 2009b). It could also be due to a lack of attention to less obvious locations in the watershed, such as river floodplains, that exhibit suboxic conditions only temporarily, associated with large inundation events or within hyporheic flow (Briggs et al., 2015; Hinkle et al., 2014). Thus, the zone of potential Hg methylation may expand and contract vertically and laterally with flood cycles (Creswell et al., 2008).

It is conventionally assumed that MMHg production mainly occurs in wetland environments or in lakes (Benoit et al., 2003; Coleman Wasik et al., 2015; Grigal, 2002; Krabbenhoft et al., 1995; St. Louis et al., 1994), where oxygen levels are relatively low such that anaerobic sulfate-reducing bacteria (SRB) and iron reducing bacteria (FeRB) primarily responsible for Hg methylation can thrive (Gilmour et al., 1992; Gilmour et al., 2013). However, there are limits to this view of Hg methylation. The following have been shown in prior work. 1) The percentage of wetland area within a basin may be a poor predictor of MMHg concentrations in certain river basins (Tsui et al., 2009a), suggesting the importance of other Hg methylation zones along some rivers. 2) There is, in some basins (but see Grigal, 2002), a tenuous relationship between lowland wetland area and MMHg in local pore water within sediments, suggesting the prevalence of upstream MMHg production in some lotic settings (Marvin-DiPasquale et al., 2009b). 3) High MMHg concentrations have been found in non-migratory algae, benthic macrointvertebrates, and fish in parts of river basins well upstream of lowland floodplains/wetlands (Buckman et al., 2015; Donovan et al., In Review; Donovan et al., 2016; Tsui et al., 2009a). 4) Cycles of wetting and drying have been shown to increase Hg concentrations within fish in lake systems (Sorensen et al., 2005), suggesting that non-permanent wetland areas may be important sites for conversion of iHg to MMHg. 5) MMHg production has been shown to be driven by flood events that infrequently inundate large areas adjacent to the channels (Balogh et al., 2006).

Thus, it is possible that upland riverine environments play an important role in MMHg production, which has been largely overlooked. Clearly, there are relevant factors affecting mercury methylation on the landscape scale that have not been well documented or quantified. The extension of streamflow from river channels into floodplains is understood to influence oxygen availability and affect biogeochemical processing of phosphorus, nitrogen, and sulfur (Baldwin and Mitchell, 2000), so it follows that the so-called flood pulse (Junk et al., 1989; Tockner et al., 2000) should also play a role in Hg biogeochemistry. In fact, recent research has suggested that the hyporheic zone along stream channels may control MMHg production (Bradley et al., 2012; Hinkle et al., 2014), but there is very limited research on this topic. Spatial and temporal variability in streamflow directly affects the extent, timing, and persistence of inundated surfaces along a river. Sequences of flood events generate complex inundation histories banks, terraces, and floodplains that have the potential to alter local redox conditions and thereby affect the microbial conversion of iHg to MMHg (Benoit et al., 1999; Benoit et al., 1998; Gilmour et al., 1992; Schaefer and Morel, 2009; Wallschlager et al., 1998), potentially increasing or decreasing the likelihood of MMHg introduction into aquatic food webs. In summary, the infrequent extension of flooding from channels into floodplains dramatically reduces oxygen supplies within sediment as pore spaces become filled with water rather than air (typically decreasing pore oxygen content by > 3 orders of magnitude). Subsequently, oxygen becomes limited due to lack of replenishment from the atmosphere, thus stimulating anaerobic bacterial processes (Briggs et al., 2015). Therefore, the frequency and duration of floods and their spatial extent in the landscape may be critical to riverine Hg biogeochemistry.

This paper addresses the spatial and temporal dimensions of MMHg production potential at the landscape scale within a large, Hg-contaminated watershed. We use hydraulic modeling over a decadal timeframe to infer the frequency and duration of land surface inundation across this watershed, which we interpret as a proxy for temporary suboxic conditions conducive to MMHg production potential (Podar et al., 2015). We aim to infer the past history of mercury dynamics by identifying locations in a large drainage basin that may be considered 'hot spots' of MMHg production due to frequent inundation, as well as particular flood events that may be considered 'hot moments' of MMHg production due to prolonged inundation. We note that these definitions of 'hot spots' and 'hot moments' differ from those used in prior research on biogeochemical transformation (McClain et al., 2003), where the focus was on accelerated rates of biogeochemical changes. However, we believe these adapted terms represent reasonable extensions which highlight the specific role of variable hydrology in affecting redox over a large area. We set out to answer these questions: 1) What are the spatial and temporal patterns of inundation in the river-floodplain corridor? 2) How does the history of inundation