MERCURY CYCLING IN FRESHWATER SYSTEMS - AN UPDATED CONCEPTUAL MODEL

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Abstract

The widely accepted conceptual model of mercury (Hg) cycling in freshwater lakes (atmospheric deposition and runoff of inorganic Hg, methylation in bottom sediments and subsequent bioaccumulation and biomagnification in biota) is practically accepted as common knowledge. There is mounting evidence that the dominant processes that regulate inputs, transformations, and bioavailability of Hg in many lakes may be missing from this picture, and the fixation on the temperate stratified lake archetype is impeding our exploration of understudied, but potentially important sources of methylmercury to freshwater lakes. In this review, the importance of understudied biogeochemical processes and sites of methylmercury production are highlighted, including the complexity of redox transformations of Hg within the lake system itself , the complex assemblage of microbes found in biofilms and periphyton (two vastly understudied important sources of methylmercury in many freshwater ecosystems), and the critical role of autochthonous and allochthonous dissolved organic matter which mediates the net supply of methylmercury from the cellular to catchment scale. A conceptual model of lake Hg in contrasting lakes and catchments is presented, highlighting the importance of the autochthonous and allochthonous supply of dissolved organic matter, bioavailable inorganic mercury and methylmercury and providing a framework for future convergent research at the lab and field scales to establish more mechanistic process-based relationships within and among critical compartments that regulate methylmercury concentrations in freshwater ecosystems.

1. Current view of the mercury cycling in freshwater lakes and the motivation for this review

The textbook representation of the environmental mercury (Hg) cycle in lakes is practically accepted as common knowledge. Indeed the most commonly seen version is taken from an edited volume (Hudson et al., 1994), is widely distributed online (and frequently unattributed), used in government websites and fact sheets on Hg (e.g. Survey United States Geological, 1998) and

reproduced in other syntheses and reviews. This general representation has effectively remained largely unchanged for decades and it, or a version is almost guaranteed to be included in the introductory slides of almost any conference presentation or lecture about Hg. The model is that gaseous elemental mercury (GEM) is emitted to the atmosphere from both anthropogenic and natural sources, oxidized to ionic forms of Hg in the atmosphere which falls in wet and dry deposition, is transported to lakes in runoff, delivered to anoxic sediments via often unspecified mechanisms, methylated in sediments, and then bioaccumulated and biomagnified up the food web from primary producers to top predators. Significant additions that are sometimes incorporated into more detailed versions are abiotic photodemethylation in the epilimnion and GEM evasion (Sellers et al., 1996), which created a mass balance deficit of MeHg in the water column that is (at least in part) compensated for by the addition of net methylation in anoxic hypolimnetic waters (Eckley and Hintelmann, 2006; Watras et al., 1995). This model is effective in generically conveying the relative complexity of the Hg cycle in freshwater lakes compared to other non-speciating or multi-phase pollutants, however there is mounting evidence that the dominant controls on the biogeochemical cycling of Hg in freshwater systems may at best be dramatically oversimplified in this depiction, and at worst factually incorrect in many landscapes. Although the research community is cognizant of the many additional factors that regulate Hg biogeochemistry in freshwaters, we believe that the ubiquity and persistence of this model continues to lead us to not fully consider the context-specific controls on Hg bioavailability and net MeHg production, which ultimately will regulate the amount of MeHg available for bioaccumulation and its potential biomagnification.

The focus of research on the compartments and fluxes in this long-standing conceptual model may be resulting in a failure to focus research attention on critical zones of MeHg production/degradation that have come to light in recent years, and make targeted measurements of the most important biotic and abiotic factors regulating Hg methylation that would allow for more a direct mechanistic link between MeHg production and MeHg in biota. A redirection of attention

towards factors that truly regulate the supply of MeHg to the base of the food web will improve our ability to mechanistically model biotic exposure to MeHg in freshwater systems under current conditions (Wu et al., 2019), but will even more importantly provide a roadmap for understanding Hg cycling in a future non-stationary climate. In this review we posit that the persistence of this conceptual model is in large part, a function of the geographic scope of research on freshwater Hg biogeochemical cycling. The preponderance of published work on temperate and boreal stratified, oligo-to-mesotrophic lakes has resulted in it becoming the epitome of freshwater Hg research. Indeed, there are many examples of lakes that have been shown to elegantly conform to this model of the aquatic cycle of Hg (e.g. Todorova et al., 2009). However it is also becoming increasingly clear that this model does not apply as well to lakes in higher and lower latitudes, shallower wind-mixed/unstratified lakes, and/or more nutrient-rich ecosystems (Bravo et al., 2017).

The scope of this freshwater lake-centered review is bounded at one end by inputs of inorganic divalent Hg (HgII), elemental Hg (Hg0), MeHg, and organic matter from the catchment, and at the other, the formation of a bioavailable MeHg-ligand. Although this in some respects appears to succumb to the very limitations that we have identified above, the processes in the catchment that are the very controls on some of the issues highlighted in this review, along with the critical role of the aquatic food web in regulating MeHg bioaccumulation and biomagnification, cannot be adequately addressed in a single paper. Recent advances in the understanding of within-catchment processes regulating Hg supply and speciation are reviewed in this special issue (Bishop et al., 2020). Lake trophic structure, species assemblage (from benthic meso-macro invertebrates to top piscivorous fishes), primary productivity, and other factors affecting bioaccumulation and biomagnification like fish growth rates and age structure, are at least equally as important as the supply of MeHg in predicting the MeHg concentrations of aquatic organisms, and are also reviewed in this special issue (Chételat et al., 2020). (Bravo and Cosio, 2019; Paranjape and Hall, 2017; Regnell and Watras, 2019)These controls are not independent, and there is a complex interplay of

biophysical factors that influence within-lake processes regulating the supply of bioavailable MeHg supply to biota. In this context, it has become increasingly clear in the recent years that anoxic hypolimnetic waters and profundal sediments are not necessarily the dominant sources of MeHg in many freshwater lakes (or possibly most, in a global context), yet we frequently continue to focus on these compartments in whole-ecosystem Hg studies. The objective of this paper is thus to focus attention on what we consider under-recognized or emerging places and processes regulating the net supply of MeHg in freshwater lakes:

- Reduction-oxidation (redox) chemistry as a control on Hg cycling.
- The overwhelming importance of dissolved organic matter (DOM) in freshwater systems as both a vector of delivery of MeHg to lakes as well as a control on Hg speciation but also methylation at the cellular level.
- The under-recognized but critical role of biofilms and periphyton as sources of MeHg to freshwater food webs.
- The importance of the catchment in regulating lake Hg biogeochemistry.

We will include them in a revised conceptual model allows us to explore the major effects of a changing climate on these key processes that regulate MeHg supply to biota. We also encourage the reader to consider this model as a component of a multi-part synthesis of this special issue that, taken as a whole, provides an updated perspective on the range of factors that ultimately regulate the amount of MeHg in the aquatic food web. This paper is not intended to serve as a comprehensive review of the Hg cycle in general, nor an exhaustive check-list of the controls on MeHg production freshwater systems. We refer the reader to other works in this special issue, as well as foundational, and more recently published reviews on the Hg cycle (Bravo and Cosio, 2019; Paranjape and Hall, 2017; Regnell and Watras, 2019).

2. Understanding the complexity of methylmercury formation

2.1 Redox chemistry controls mercury cycling, but not always in the way that we think.

Redox reactions are traditionally seen as important in controlling Hg speciation and therefore its chemical properties, but beyond the formation of MeHg, they are often ignored in the context of within-lake changes in Hg bioavailability. The redox reactions regulate the exchange of $Hg0_g$ between lakes and the atmosphere, but the discovery that methylators can also use Hg0 as a substrate for methylation (Colombo et al., 2013; Hu et al., 2013) suggests that anoxic redox reactions can regulate the amount of HgII or Hg0 available for methylation in ways that are unaccounted for in current models. In our commonly held conceptual cycle, Hg settles to the anoxic zones of lakes as less bioavailable Hg-DOM or Hg-particle complexes after deposition from the atmosphere as more bioavailable HgII (Chiasson-Gould et al., 2014). In a revised model (Figure 1), redox reactions can "reset" Hg speciation far from the air/water interface results in the incorporation of an additional source of fresh bioavailable Hg (Hg0, or its oxidation products) for methylation (Chiasson-Gould et al., 2014; Grégoire and Poulain, 2018). Under anoxic conditions, HgII reduction can occur through abiotic reactions with DOM (Gu et al., 2011) and iron-bearing minerals (Bone et al., 2014; Wiatrowski et al., 2009), but anaerobic microbes can also participate directly (Lin et al., 2014; Liu and Wiatrowski, 2018; Lu et al., 2016; Schaefer et al., 2002; Wiatrowski et al., 2006; Zhao et al., 2017). The well-known mer operon (genes encoding for Hg detoxification via reduction) is generally absent in obligate anaerobes (Barkay et al., 2010) and phototrophs (Grégoire and Poulain, 2018) suggesting that alternate yet unknown pathways exist to explain their ability to produce Hg0. Recent work found no evidence of $Hg0_{aq}$ abundance *directly* limiting Hg methylation (Poulin et al., 2019) , and although at face value the findings could be seen as contradicting prior work, it is equally likely that Hg undergoes active redox cycles under anoxic conditions which may not necessarily result in the net accumulation of detectable levels of $Hg0_{aq}$. Most importantly, very few data exist on Hg0 levels in anoxic environments in lakes (sediment porewaters, biofilms) where

143 they may be relevant to the fate of Hg in the context of biotic uptake. The contribution of anaerobes
144 to HgII reduction in anoxic habitats remains largely overlooked and the mechanisms, for the most
145 part, are unknown. The relevance of cryptic redox cycles (i.e., without net accumulation of Hg0) on
146 HgII bioavailability and subsequent methylation remains unexplored and warrants deeper
147 investigation.

148 ***2.2 The critical role of organic matter biogeochemistry in freshwater mercury cycling***

149 In natural waters, DOM is one of the most important HgII complexing agents (Hsu-Kim
150 et al., 2013; Mangal et al., 2019a; Poulin et al., 2019). DOM is composed of a spectrum of
151 molecules of varying size (e.g., from 200 to >2000 Da) (Remucal et al., 2012) and in most cases,
152 interacts with Hg via thiol (Adediran et al., 2019; Liem-Nguyen et al., 2017; Schaefer et al., 2011;
153 Schaefer and Morel, 2009; Thomas et al., 2018; Thomas and Gaillard, 2017), sulfide (Graham et al.,
154 2017; Pham et al., 2014), and amine groups (Mangal et al., 2019b). Its role is complex; DOM can i)
155 inhibit HgII uptake by forming large complexes, ii) facilitate dissolved or nanoparticle Hg delivery
156 to membrane transport sites (Graham et al., 2012b; Graham et al., 2013), or iii) possibly act as a
157 shuttle allowing Hg inside the cell when components of DOM are used as a carbon or energy source
158 (Chiasson-Gould et al., 2014; Schaefer et al., 2011). Although microbial Hg uptake most often limits
159 MeHg production in laboratory experiments (Graham et al., 2012a; Schaefer et al., 2011), the nature
160 and sources of the Hg-OM complexes available for anaerobic microbial methylation in the
161 environment are challenging to define because both active transport and passive diffusion of Hg
162 species across the cell wall are likely involved (An et al., 2019; Hsu-Kim et al., 2013; Regnell and
163 Watras, 2019). Furthermore, Hg typically does not comply to theoretical frameworks for bio-uptake
164 of metals such as the Free Ion Activity, Biotic Ligand or Surface Complexation Models (Fein, 2017;
165 Morel, 1983; Paquin et al., 2002) although a recent study investigating the role of microbial
166 biogenic synthesis of thiols is challenging this view (Adediran et al., 2019). Moreover, the complex
167 physicochemical mosaic that areHg-DOM complexes is subject to change under varying pH, ionic

strength, redox or surface interactions (Chen et al., 2019). It is therefore important that field studies complement laboratory approaches in investigating its role in affecting HgII bioavailability for methylation (Schaefer et al., 2011; Schaefer and Morel, 2009; Schwartz et al., 2019). (Andrew M Graham et al., 2012; Schaefer et al., 2011)(An et al., 2019; Hsu-Kim et al., 2013; Regnell and Watras, 2019)(Fein, 2017; Morel, 1983; Paquin et al., 2002)(Adediran et al., 2019)

In stratified lakes it is now known that HgII methylation can occur in *both* water column and sediments of oxic and anoxic water columns (Eckley and Hintelmann, 2006; Gascón Díez et al., 2016) with the highest rates of net methylation occurring primarily at the oxic/anoxic interface (oxycline) whether that be in the water column or in sediments (Bravo et al., 2014; Ullrich et al., 2001). The relative contributions of water column versus sediment produced MeHg depends on the strength and duration of stratification, the volume of the anoxic hypolimnion and OM concentrations in both sediment and water (Obrist et al., 2018). DOM attenuates incoming solar radiation, and DOM concentration thus strongly influences the depth and stability of the thermocline through heat transfer (Fee et al., 1996; Read and Rose, 2013). Combined with DOM that supports higher rates of heterotrophic respiration, higher thermal stability can result in stronger hypolimnetic oxygen depletion (Jankowski et al., 2006) promoting higher rates of methylation in the water column in particular. In two boreal lakes from southeast Norway, contrasting DOM concentrations drove (in part) differences in the position of the oxyline, which in turn regulated not only the net amount of MeHg production but also where MeHg was formed (sediment *versus* water column) (Isidorova et al., 2016). These observations stress the importance of the need to understand the interplay between geochemical and physical environmental parameters which independently, and together, regulate net MeHg production.

Besides the unequivocal importance of the molecular composition of DOM on Hg cycling (Bravo et al., 2018a, 2017; Herrero Ortega et al., 2018; Jiang et al., 2018; Lescord et al., 2018), the amount of OM itself is a very important parameter. DOM enhances the dissolution and inhibits the

precipitation of highly insoluble HgS (Graham et al., 2012; Graham et al., 2013; Ravichandran, 2004), contributing to higher concentrations of Hg_{aq} in high DOM lakes than those with clear waters. While DOM promotes and maintains dissolved forms of Hg in freshwaters and by many measures would appear to be associated with conditions that would promote greater net MeHg production in lakes, high(er) DOM (measured as dissolved organic carbon, DOC) concentrations have also been implicated in decreased HgII availability and lower methylation rates (Chiasson-Gould et al., 2014; French et al., 2014). Upon closer examination, it is clear that the threshold of DOC is not in its concentration, but in DOM composition. Thus it is likely not a *threshold* in concentration, but a *shift* in chemical properties toward more complex moieties (e.g. aromatic) that are regulating Hg bioavailability (and likely microbial metabolism). In many respects, the continuum of freshwater systems that have been used to define these concentration-based thresholds are difficult to synthesize into a single dataset as they represent catchments that are delivering very different qualities of DOM to the water column due to differences in landcover type, slope and surficial geology. The presence of a concentration threshold is somewhat circumstantial; lakes with a greater terrestrial subsidy of OM will tend to have both higher concentrations of DOM, and more high molecular weight, recalcitrant compounds that may be an effective HgII transporter, but do not encourage in-lake methylation to the same degree as autochthonous OM (Bravo et al., 2017). The balance between DOM composition and concentration regulates the amount of HgII available for methylation (Chiasson-Gould et al., 2014; Zhao et al., 2017) *and* the activity of the microorganisms involved in MeHg formation (Bravo et al., 2017; Shao et al., 2012).

Further complicating this relationship is a significant non-stationarity in the supply of allochthonous DOM to lakes from catchments. Anthropogenic atmospheric Hg (HgII and Hg0) deposition peaked around 1970, concurrent with maximum deposition of anthropogenic sulphate (Moldan et al., 2013), and then declined to current levels (Enrico et al., 2017). With this decreased loading of anthropogenic sulphate, increased water color (browning) has been observed in many

boreal lakes (Monteith et al., 2007) caused by increased terrestrial runoff of colored dissolved organic matter (CDOM) which is dominated by more aromatic, high molecular weight DOM compounds (see overview by Creed et al., 2018). Increased delivery of CDOM to lakes has been attributed to both a change in acidity, and to increasing precipitation and runoff and vegetation cover (Finstad et al., 2016; Kritzberg, 2017). Hydrological processes play a major role in the transport of OM through the landscape, with OM being more colored during high flow periods (Hongve et al., 2004), and a selective loss of the colored portion of soil-derived OM during its transport through freshwater ecosystems (Weyhenmeyer et al., 2012). The selective loss is water residence time dependent, suggesting that changes in runoff will change both the supply, and within-lake biogeochemical cycling of DOM and subsequently Hg. These factors are all acting across a range of time scales, suggesting a critical temporal dimension to environmental processes regulating MeHg supply in lakes that is rarely, if ever, captured in field studies but must be if we are to ultimately understand the dynamics of bioaccumulation.

Moving forward, the measurement of DOC concentrations alone, or even the application of slightly more refined fractionation techniques are insufficient to aid us in understanding DOM-Hg interactions in freshwater systems and make process-based connections among DOM, inorganic HgII speciation, HgII bioavailability, microbial metabolism and ultimately MeHg production. Despite their frequent citation and inclusion in geochemical modeling software, the qualitative and operationally measured fulvic and humic fractions of DOC are not chemically defined beyond the fact that one is soluble at pH 2, and the other is not. The direct characterization of OM composition in freshwater systems using modern techniques such as pyrolysis/GC-MS (Bravo et al., 2017) or Orbitrap MS and FT-ICR-MS (Simon et al., 2018), or even the use of proven proxies for OM chemistry such as absorbance and fluorescence measures (e.g. Lescord et al., 2018) is essential if we are to develop a mechanistic understanding of the relationship between OM, Hg biogeochemistry, and ultimately biotic uptake.

2.3 Microbial diversity, activity and mercury methylation: Linking biology and environmental geochemistry

The discovery of the *hgcAB* gene cluster necessary for HgII methylation (Parks et al., 2013) has prompted (meta)genomic surveys that have identified a wide range of microbes, many in novel environments, involved in Hg methylation (Podar et al., 2015). While sulfate reducers have traditionally been seen as key methylators, recent work has identified methanogens, fermenters and iron reducers as potentially equally important (Bravo et al., 2018b; Christensen et al., 2019; Gilmour et al., 2018; Liu et al., 2018). Using competitive experiments with CdII, ZnII and MnII, Stenzler et al., (2017) and others (Schaefer et al., 2014, 2011; Szczuka et al., 2015) suggested that one common active uptake mechanism in phylogenetically distant proteobacteria involves the accidental transport of HgII through non-Hg metal importers. That being said, the wealth of critical information that we have gained so far from studying HgII bio-uptake in Proteobacteria is unlikely to be directly applicable to all microbial guilds involved in Hg methylation. Indeed, microbial cell wall biophysical properties and overall cell physiology differs among *Proteobacteria*, *Firmicutes* and methanogenic *Archaea*.

Acknowledging the wealth of information generated from studies such as these, very recent work demonstrates that environmental geochemistry (notably DOM) plays at least as important a role as genetics in regulating Hg methylation at the cellular level. The role of functional groups in the cell membrane (Fein et al., 2019) was recently highlighted in a study comparing HgII methylation in *Desulfovibrio desulfuricans* ND132 and *Geobacter sulfurreducens* in the presence of two sources of DOM (one of aquatic origin with low aromaticity and the other of terrestrial origin with relatively higher aromaticity) (Zhao et al., 2017). In this study, MeHg production by *D. desulfuricans* increased with DOM concentration whereas MeHg production in *G. sulfurreducens* decreased (Zhao et al., 2017). Another study examining Hg stable isotope fraction during HgII methylation in *D. desulfuricans* and *G. sulfurreducens* demonstrated that the same strains accessed

different intracellular and extracellular pools of HgII during methylation (Janssen et al., 2016). These studies highlight that strain specific characteristics, even within the larger *Deltaproteobacterial Class*, can have a considerable impact on HgII uptake and subsequent methylation.

Recent advances in shotgun (meta)genome sequencing and genetic engineering - namely with the advent of the CRISPR-based genome editing tools (Luo et al., 2016)- allow for the combined used of genomic and genetic approaches to be applied to anaerobic microbes that were traditionally deemed intractable. Combining these tools with more classical approaches traditionally used to evaluate HgII bioavailability such as quantifying methylation as an outcome of uptake, washed cell assays plus mass balance, or biosensors (Graham et al., 2012a; Graham et al., 2012b; Stenzler et al., 2017, 2018; Szczuka et al., 2015; Zhang et al., 2012), with the screening of a greater number of phylogenetically diverse strains to identify mechanisms involved in HgII transport representing diverse microbial cell walls and physiologies. The continued refinement of our understanding of the genetic basis of Hg methylation is required in order to mechanistically understand the process at the cellular level, however at the ecosystem level it is likely that environmental controls on HgII bioavailability will play an equal role in developing predictive models of Hg sensitivity of freshwater lakes. The convergence of these areas conceptually and practically is the next major frontier in environmental Hg biogeochemistry.

3. Overlooked sources of methylmercury to freshwater systems

3.1 Primary producers: an important niche for Hg methylators

Despite the fixation on anoxic waters and sediments being the dominant sources of MeHg in freshwater lakes, microenvironments such as periphyton, roots of macrophytes (Achá et al., 2011; Bouchet et al., 2018; Cleckner et al., 1999; Guimarães et al., 2006; Hamelin et al., 2011; Mauro et al., 2002) and settling particles in oxic water columns (Cossa et al., 2009; Gascón Díez et al., 2016; Lehnherr et al., 2011; Monperrus et al., 2007; Sunderland et al., 2009) have all been identified as

important sources of MeHg in freshwater systems. These sources have likely been discounted in favour of sediments and anoxic bottom waters in large part due to an oversimplified notion of the environmental requirements of obligate anaerobes (anoxic sediments and bottom waters) reinforced by the dominant conceptual model of the lake Hg cycle. However, 20 years ago, pioneering studies in the Amazon revealed that roots of floating aquatic vegetation were important Hg methylating sites, showing a 30x higher production of MeHg versus surface sediments (Guimarães et al., 2000a, 2000b). Similarly, another study reported high MeHg concentrations and production in Sphagnum *spp*. mats typical of wetlands in northern forest freshwater lakes (Yu et al., 2010), acting as an important sink for the accumulation of HgII but also environments conducive for the production of MeHg and therefore a source of MeHg to these environments (Liu et al., 2012). Other studies in lakes and reservoir in France and Romania, pointed to the roots of floating aquatic plants and plant-colonized sediments as the principal location for MeHg production and as important sources for the MeHg contamination of freshwater biota (Gentès et al., 2013; Regier et al., 2012).

Submerged aquatic vegetation are often ideal hotpots for HgII methylation due to moderately anoxic conditions, availability of carbonaceous plant exudates serving as substrates for microbial growth (Zhao et al., 2018), and a high surface area for biofilm formation. Indeed, macrophyte-associated periphyton and microbes found in anoxic micro-environments therein have been unequivocally shown to be responsible of HgII methylation (Mauro et al., 2002). In floodplain lakes of the Bolivian Amazon, a diverse community of HgII methylators was found associated to the roots of different floating macrophytes (Achá et al., 2011, 2005). Subsequent studies in periphyton supported HgII methylation in both dry season and wet season in the Amazon (Lázaro et al., 2018). A wide occurrence of HgII methylating *Deltaproteobacteria* and *Firmicutes* was observed in periphyton collected in the Everglades (Bae et al., 2019). Because of the high abundance of macrophytes in shallow freshwater environments in tropical, subtropical and northern climates wetlands, macrophyte-associated periphyton were identified as contributors of MeHg production in

these ecosystems (Hall et al., 2008) although their relative role in the lake Hg cycle remains largely unquantified.

The importance of periphyton-associated biofilm living on rocky substrates in boreal shield lakes (Desrosiers et al., 2006) and in streams (Olsen et al., 2016) as a source of MeHg to biota has been virtually ignored in favour of the continued focus on unproductive, depauperate profundal sediments, despite their direct connection to the littoral food web. This misdirection is particularly problematic for Hg studies in shallower, wind-mixed or unstratified lakes; sources of MeHg are unquantified in systems such as these when only sediments and the water column are considered.

Periphyton is a highly dynamic microhabitat formed by a community of algae, archaea, bacteria, fungi, micro-invertebrates, organic and mineral matter more or less isolated from the surrounding water by a self-produced matrix of extracellular polymeric substance (EPS). Their contribution to total annual productivity of shallow lakes is high (42 to 97%). Periphyton shows strong vertical spatial and temporal (day-night) redox gradients resulting in reducing micro-environments ideal for microorganisms capable of Hg methylation. Periphytic algae produce photosynthetic byproducts (e.g., reductants) and excrete organic substrates that promote redox reactions and fuel bacterial activity and growth. Indeed net HgII methylation was higher for *Desulfovibrio desulfuricans* when growing on periphyton than on planktonic algae (Lin and Jay, 2007).

Not surprisingly, there are strong abiotic-biotic interactions that regulate biofilm-associated MeHg production in freshwaters. In tropical systems, periphyton community composition, HgII accumulation, and net MeHg production in biofilms have been shown to be influenced by flooding

cycles (Lázaro et al., 2018). In a temperate shallow lake environment in Canada, MeHg production on periphyton varied across plant growing season and with environmental variables such as water depth, light, oxygen, temperature, plant community structure, and total productivity (Hamelin et al., 2015). In the Amazon, hydrological connectivity of wetlands with the main river channel, total phosphorus and DOC concentrations in water correlated with MeHg concentration (Lázaro et al., 2016). In Lake Titicaca, higher Hg methylation yields were found in benthic biofilms and *Characeae's* periphyton during the rainy season correlated with the abundance of extracellular low-molecular-weight (LMW) thiols, while Hg methylation remained low in sediments and aquatic plant-associated periphyton during dry season (Bouchet et al., 2018). As periphyton attached to macrophyte supports are hotspots for MeHg production in freshwater lakes (Correia et al., 2012; Hamelin et al., 2011), deeper investigation into their structure, function and net contribution to MeHg that enters the aquatic food web is highly warranted. As the microbial community composition, and the biofilm structure that provides the anoxic micro-niches for various microbes are critical controls on net Hg methylation, care to preserve the integrity of biofilms and their natural growing surfaces is highly desirable in future experimental work.

Environmental conditions favouring the abundance of cyanobacteria in the periphytic community have also been associated with higher rates of HgII methylation (Lázaro et al., 2019, 2013). There is currently no evidence that Cyanobacteria can methylate Hg (at least for strains tested until now). However, Cyanobacteria can shape the physical (via biofilm formation) and chemical (by controlling nutrient cycling) environments supporting methylation. Their role must be considered at temperate and higher latitudes as a warmer climate leads to a higher frequency of cyanobacterial blooms (Chapra et al., 2017).

Finally, there is also evidence that plankton in the water column play a role in the overall supply of MeHg to freshwaters. A study conducted in the Petit-Saut Reservoir in French Guiana showed MeHg production to be 1–2 orders of magnitude higher in 90 day-long incubations with

unfiltered water than from biofilms, both collected at the same depth in the anoxic hypolimnion of the reservoir (Huguet et al., 2010), suggesting that plankton communities in the water column play a major role in HgII methylation in this reservoir. Similarly, a study conducted in Lake Geneva (Switzerland) higher Hg methylation yields in settling particles sinking through the oxygenated water column than in surface sediments (Gascón Díez et al., 2016). These studies point to primary producers as sites of important HgII methylation (Figure 2), though there is little evidences of free or attached primary producers participating directly in HgII methylation (Grégoire and Poulain, 2018). The current hypothesis is that primary producers provide substrates that affect the activity of attached HgII methylating microbes, and/or release ligands that modify the uptake of HgII (Bouchet et al., 2018; Grégoire and Poulain, 2018). Quantifying the role of periphyton, biofilms and primary producers in the freshwater lake Hg cycle will require both more mechanistic information at finer spatial and temporal scales about rates of net MeHg production, exchange with the water column, and direct grazing by biota, as well as better estimates of biomass at much larger scales. Estimates at the lake scale is possible (Kahlert et al., 2002), but the added complexity of the role of light, nutrient availability and physical disturbance in the spatial and temporal patterns of periphyton biomass present an exciting opportunity for the convergence of freshwater ecology and Hg biogeochemistry.

3.2 The catchment as a source of methylmercury to freshwater systems

The catchment as a source of MeHg to freshwater food webs is another area of long-standing general conceptual agreement in the scientific community (Meili, 1997; Rudd, 1995) but has actually only been circumstantially demonstrated. It has been established for decades that catchments that contain sites that support high rates of methylation (e.g. wetlands) export more MeHg to receiving waters than those without (e.g. Louis et al., 1996; St. Louis et al., 1994; Tjerngren et al., 2012). However concomitant with that export of more MeHg is the export of more DOM and HgII that in principle, support methylation within the lake system itself. We have known for even longer that DOM is an important transport vector of THg from watershed soils to lake

water (Mierle and Ingram, 1991), and both HgII and MeHg correlate with DOM in a range of higher latitude lakes lakes under natural (Braaten et al., 2014) and disturbed (Garcia et al., 2007) conditions. Increases in Hg in some lake sediments over time have been associated with increasing terrestrial OM inputs because of the strong associations between DOM, HgII and MeHg (Isidorova et al., 2017). Recent work has shown that lake sediments dominated by catchment-derived OM have higher MeHg concentrations but lower rates of in situ methylation, while sediments dominated by autochthonous organic matter had higher rates of in situ methylation but lower MeHg concentrations (Bravo et al., 2017). This finding convincingly implicates the catchment as a source of OM-associated MeHg to the aquatic ecosystem, however we still lack the information required about the relative bioavailability of catchment versus lake-derived MeHg to mechanistically link it to biological uptake and ultimately to MeHg in higher trophic level organisms. It is increasingly demonstrated that the terrestrial subsidy of energy via OM to freshwater lake food webs is not only important, but also geographically widespread (Guillemette et al., 2017; Tanentzap et al., 2017). The use of stable isotopes ratios of O and H on OM have been essential in revealing this subsidy; the application of natural stable isotopes of Hg to the question of the catchment subsidies of HgII and MeHg will likely be equally revealing. A mechanistic disentangling of the supply of HgII, DOM and MeHg from the catchment to lakes is required before we can fully understand the relative role of the autochthonous production and allochthonous supply of MeHg to aquatic food webs.

Atmospheric deposition of HgII and MeHg to catchments and lakes are well-documented and important aspects of the Hg mass balance in many lakes (Munthe et al., 2007; Schroeder and Munthe, 1998), yet it has largely fallen out of favour in our current conceptualization of the freshwater mercury cycle. Indeed, there are some instances in which the delivery of MeHg (in snow in particular) represents a compelling fraction of MeHg inputs to lakes, suggesting that it should not be discounted. Snowmelt runoff was found to be the most important source of MeHg for a high Arctic aquatic ecosystem on Ellesmere Island, despite the presence of wetlands where elevated

MeHg would have been expected (Loseto et al., 2004b, 2004a). Other work has shown that MeHg in snow was up to 7.5% of the total Hg (Constant et al., 2007; Ferrari et al., 2004; Lahoutifard et al., 2005; St. Louis et al., 2005). Another high arctic study in Kuujjuarapik found a significant increase in MMHg concentration over the snowmelt period, with concentrations reaching as high as 700 pg/L (Constant et al., 2007). Correlation between MeHg snow concentrations and culturable bacteria or snow particles, as well as an increasing fraction of MeHg as THg during the snowmelt period suggested active methylation in the snow pack (Constant et al., 2007). Further exploration of the biotic and/or abiotic mechanisms of MeHg production associated with the snowpack is warranted.

Taken together we suggest that a more integrated understanding of the lake biological, physical and chemical environment is required in order to formulate better estimates and predictions of the amount of MeHg produced in lake sediments and waters, sinking particles and/or associated with primary producers. This information must be coupled to a detailed characterization of the catchment including slope, wetland area, land-use and hydrological connectivity in order to better quantify autochthonous MeHg, HgII and DOM leading to a more complete picture of in-lake Hg cycling. Finally, the net concentration of MeHg will be controlled not only by the internal and external MeHg production but also but its degradation, that is photochemically (Sellers et al., 1996; Zhang and Hsu-kim, 2010) or biologically (Lu et al., 2016; Schaefer et al., 2004) mediated. While photolysis of MeHg is expected to occur in open lake waters, biological MeHg degradation can occur in both soils, wetlands, water column and sediments. Unfortunately, there is an important gap in knowledge and lack of understanding on MeHg degradation processes at the lake and catchment scale. Ultimately, an accurate quantification of MeHg degradation is required to predict lake MeHg concentrations, but these processes remain grossly understudied relative to the biotic and abiotic controls on Hg methylation.

4. A different conceptual model and the way forward

Despite decades of focused research, there still remain many uncertainties in our understanding of freshwater Hg biogeochemistry that impair our ability to develop fully mechanistic predictions of sensitivity of freshwater ecosystems to Hg pollution. These uncertainties are complicated by variation in many of the key processes regulating the supply of OM, bioavailable HgII and MeHg to the water column and ultimately, to biota. These variations are driven by changes in the terrestrial and aquatic compartments in the catchment operating over a wide range of temporal scales. Catchment hydrology, through its regulation of inputs of nutrients, minerals and DOM, controls lake chemistry and is ultimately the dominant control of key factors regulating MeHg delivery to, and production in, freshwater lakes. In particular, characterizing the dynamics of DOM quality and quantity is the cornerstone for understanding Hg biogeochemical processes from the cellular to ecosystem level. The complex geochemistry of lakes regulates interactions in an intricate network of microorganisms that collectively create the environment conducive to HgII methylation. Net MeHg production is not a process governed by the activity of specific groups but by the interactions among them and the chemical characteristics of their (micro)environment (Bravo et al., 2018a). These relationships play out most profoundly in periphyton and biofilms, where MeHg production is regulated by aquatic geochemistry, extracellular substances, and photosynthetic exudates in what may be one of the most under-recognized sources of MeHg to freshwater ecosystems.

Our model (Figure 3) takes a different perspective and considers the relative roles of the lake, catchment and atmosphere in two very different physiographic contexts. The stratified, oligotrophic lake that physically dominates its catchment perhaps not surprisingly also dominates the processes that ultimately regulate net MeHg supply to the aquatic foodweb (Figure 3A). For lakes such as these, the atmosphere contributes effectively no DOM, but may be an important source of bioavailable HgII directly to the lake surface (rain or snow), and a small but not trivial amount of MeHg may also be delivered this way. Despite a small lake to catchment ratio, runoff from the catchment is a source of terrestrial DOM-associated HgII but in an upland-dominated catchment, is

not a large source of MeHg to the lake. The lake itself is an important source of labile autochthonous DOM derived from primary production, which fuels methylation in the anoxic hypolimnetic waters and deep sediments. The water column and sediments serve as an indirect source of bioavailable inorganic Hg through the redox cycling processes described earlier in this paper. Critical compartments and measurements in systems such as this include hypolimnetic water (volume, oxygen concentration/redox) methylating bottom sediments (surface area, OM content, redox). Finally, the more transparent water column facilitates proportionally greater light penetration and photolyic transformations of Hg.

The unstratified lake situated in a large catchment is dominated by a very different set of controls that regulate net MeHg supply (Figure 3B). In terms of the dominant biogeochemical factors, the atmosphere plays virtually no role in regulation of the the lake MeHg cycle, although the delivery of water from the atmosphere regulates catchment hydrological processes. The supply of bioavailable HgII and MeHg associated with terrestrial DOM may be overwhelmingly important, as depicted in our model, however processes within the lake may be important to the supply of MeHg, and are the most poorly constrained with respect to their relative importance. Here, critical compartments that support methylation are more cryptic than anoxic waters and bottom sediments – littoral wetlands, and macrophyte and sediment-associated biofilms and periphyton are zones of MeHg production. Labile aquatic DOM derived from primary producers are important sources of energy for these much more discrete but potentially critical sources of MeHg to the aquatic food web. A more coloured water column that due to higher DOM concentrations would result in relatively lower rates of photolyic transformation of Hg and a longer residence time for MeHg in the water column. Critical compartments/measurements in a case such as this include littoral sediments and wetlands (surface area, biofilm and periphyton areas, total productivity), and the catchment (area, DOM and Hg supply).

Although this conceptual model presents two cases, there are many combinations of catchment and lake characteristics that we hope may be readily conceptualized from it. For example, a stratifying lake

with a larger catchment containing significant sites of methylation or with extensive productive littoral zones may share characteristics of both examples and be even more sensitive to MeHg contamination (and the effects of climate change); in many respects this is the intention of our model – to consider lake and catchment characteristics on a case by case basis and consider the wide range of potential controls on net MeHg supply.

The model presented here is only one side of the equation governing MeHg bioaccumulation in biota, and these considerations must be coupled with aquatic food web structure and bioenergetic data in order to fully resolve the sensitivity of a freshwater ecosystem to MeHg contamination. Very recent work has clearly shown that both food web ecology and catchment connectivity must be considered together in order to unravel MeHg supply to aquatic food webs. Burke et al., (2020) demonstrated that the dominant primary production (littoral macrophyte/biofilm vs. pelagic phytoplankton) and benthic food web structure (benthic vs. grazing) were regulated by the degree of catchment connectivity to thermokarst lakes on the Arctic Coastal Plan of Alaska, ultimately exerting a significant control on the amount of MeHg in a ubiquitous small fish, the ninespine stickleback (*Pungitius pungitius*). Although fish growth rates were the strongest control on tissue MeHg, even fish growth may ultimately be linked to primary production and nutrient availability which are both catchment regulated. This work unequivocally illustrated the influence of the catchment on the lake Hg cycle in both direct and indirect ways, and demonstrates the need to fully integrate biotic/abiotic, and catchment/lake processes if we hope to understand the impacts of climate change on the lake Hg cycle, particularly in higher latitude catchments. By focusing our collective scientific attention on the link among catchment compartments and the processes within each compartment, we will make more robust mechanistic connections between the abiotic and biotic processes that regulate the supply of MeHg to the biota in freshwater lakes now, and in the future.

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Figure 1. Conceptual summary for the role of the redox wheel in the context of the diversity of HgII and Hg^0 species available for microbial transformations (modified from Grégoire and Poulain 2018). The pink disks highlight sites where Hg speciation can be reset via biotic or abiotic redox processes that directly affect Hg (see text) or the ligands to which Hg is bound (e.g., via heterotrophy or DOM photo-transformation). These processes can occur in oxic or anoxic conditions and be catalyzed by light, microbes, or both. Hg methylators are represented in brown, dissolved organic matter has been abbreviated as DOM, labile organic matter available to microbes is abbreviated as LOM, and particulate matter is denoted by small grey circle. Hg-DOM represents poorly bioavailable Hg complexes formed with organic matter ligands of a large size. Hg-LOM represents highly bioavailable Hg complexes formed with labile organic matter ligands; these labile organic matter ligands can act as shuttles for Hg inside the cell. The Lightning bolt highlights the role of light energy (hν) required for photobiological or photochemical processes controlling the redox wheel. HS^- (sulfide), CH_4 (methane), and $Fe^{II/III}$ (iron oxides) are meant to represent some of the anaerobic metabolisms known to be involved in HgII methylation: sulphate-reduction, methanogenesis, and iron-reduction, respectively.

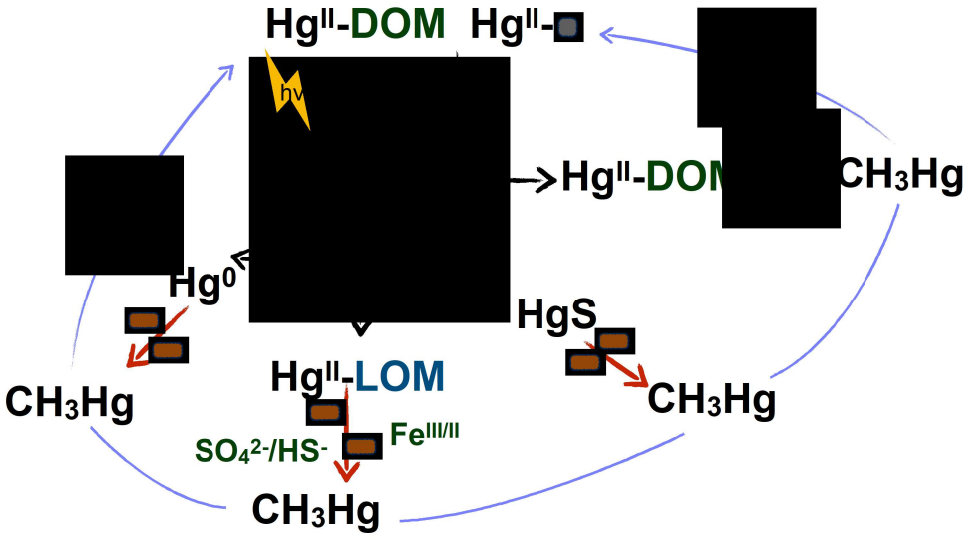

Figure 2. Conceptual summary highlighting the role of primary producers as important sites for MeHg formation. The pink disks highlight sites where Hg speciation can be reset via biotic or abiotic redox processes that directly affect Hg (HgII and Hg0) availability for methylation.

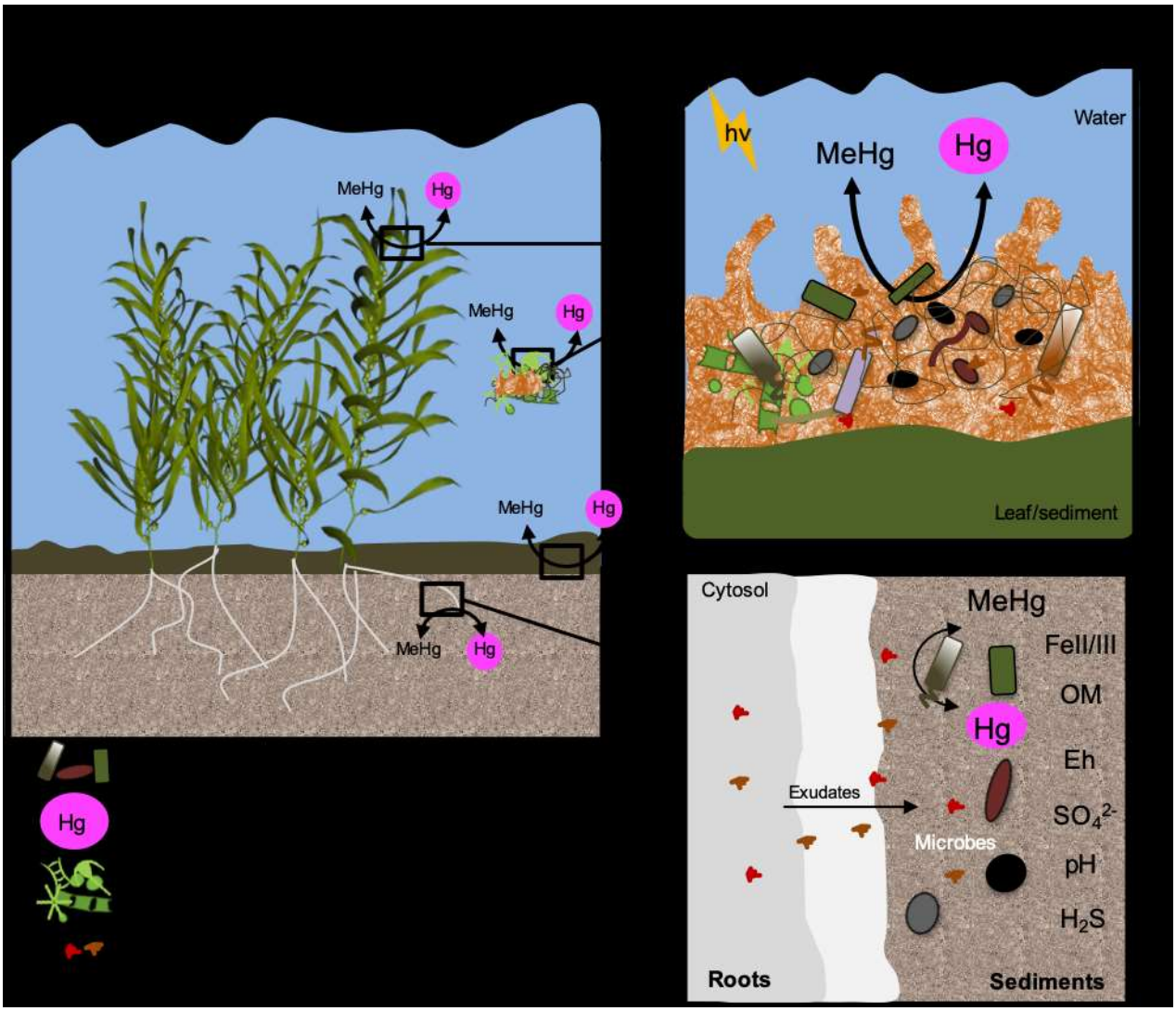

Figure 3: The relative role of sources of dissolved organic matter (DOM) bioavailable divalent mercury species (HgII), and methylmercury (MeHg) to aquatic food web in two distinct catchment-lake systems with theoretically equal levels of methylmercury in biota. The left pane of each panel is a schematic representation of each lake type (A) deeper/stratified, B) shallower/unstratified) and its catchment characteristics (large (A) to small (B) lake to catchment area ratio, respectively). The pie charts in the right pane of each panel show the relative importance of the atmosphere, catchment, and in-lake processes in supplying bioavailable HgII, DOM, and MeHg to the water column. In example (A) the stratified oligotrophic lake is the dominant source of MeHg to the water column, formed in seasonally anoxic bottom waters and profundal sediments fuelled by autochthonous DOM derived from in-lake primary production. The catchment and atmospheric serve primarily as sources of bioavailable HgII. In the shallower more well-mixed lake with a larger catchment (B), the catchment serves as the dominant source of methylmercury, formed in hydrologically-connected sites of methylation like wetlands which also supply allochthonous DOM and bioavailable HgII. The lake is also a potentially important source of MeHg to biota, but methylation is not in the water column or profundal sediments, but in littoral sediments, biofilms and periphyton which are directly coupled to the littoral food web. See article text for a complete discussion of the continuum of lake MeHg vulnerability.