

Mercury Dynamics in Aquatic Systems: A Critical Review of Methylation, Bioaccumulation, and Global Health Risks

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Abstract- Mercury is highly toxic environmental pollutant of serious concern to human and fish populations in this world we live in. The function of microbial methylation to convert inorganic mercury to the highly toxic and bioaccumulative form of methyl mercury (MeHg) in aquatic ecosystems is explored in this review. The bioaccumulation and cumulative nature of the methylmercury significantly impair nervous and developmental systems. It is also in high amounts in the tissue of animals higher on the food chain like fish consumed by humans. Here, we discuss the possible impacts of DOM, SO₄²⁻, and microbial consortia on the methylation and bioavailability of Hg. The review also focuses on how toxic levels of mercury impact the wellbeing of the wild life and food chains among other ecological impacts. We assess the effectiveness of community-based mercury level monitoring programs and the current methods of managing mercury containing products like the Minamata convention. Perceived research gaps present the need for further research and development of remediative technologies to closure. Some of these gaps are about identifying not merely the disposal of mercury in sediment and the behaviour of mercury under global warming and climatic alteration. The findings bear witness on how imperative it is for countries to come together in order to reduce the extent of the mercury's impacts on environment and people.

Keywords- Environmental toxicology, Microbial processes, Food web contamination, Mercury exposure, Ecosystem health, Climate change impacts, Pollution control strategies, Public health risks

I. INTRODUCTION

Overview of Mercury In Aquatic Systems

Mercury (Hg) is a globally recognised environmental contaminant that originates from both natural and anthropogenic sources. Natural processes, such as volcanic activity, weathering of mercury-containing rocks, and geothermal events, contribute significantly to mercury emissions (Bravo & Cosio, 2019; Luo et al., 2020). However, human activities, including coal combustion, mining, artisanal gold mining, cement production, and the

release of Hg from industrial processes, have dramatically increased global Hg levels in the biosphere over the last century (Bravo & Cosio, 2013; Bravo & Cosio, 2019). Mercury is unique among trace metals because of its volatility. It is released into the atmosphere as elemental Hg (Hg(0)), which has a long atmospheric residence time and can be transported globally before being deposited into aquatic systems (Bravo & Cosio, 2019). Once deposited, mercury undergoes complex transformations, with its most toxic form being methylmercury (MeHg), which is of significant concern because of its ability to bioaccumulate and

biomagnify in aquatic food webs (Hsu-Kim et al., 2013; Johnson et al., 2015).

Microbes are known to play role in the process of conversion of mercury into methylmercury in aquatic settings; the most significant converters are sulfate reducing bacteria (SRB) other converters include methanogens and iron reducing bacteria (Fleming et al; Hsu-Kim et al., 2013).

This methylation process occur in anoxic conditions, for example in sediments and wetlands where these bacteria are known to live. It is methylmercury which, unfortunately, is highly toxic because once it enters the water cycle it is easily absorbed by the vital tissues of plants and animals that live in water and is, therefore, concentrated through the food chain upwards to fish which are, in turn, consumed by humans (Avramescu et al., 2011; Driscoll et al., 2013). In the food web, methylmercury may stay for a long duration since its rate of demethylation is lower than its rate of production (Hsu-Kim et al., 2013; Drott et al., 2007). Mercury toxicity most of the time can also affect the nervous system especially the developmental stages of foetal and early childhood and the major route is through consumption of contaminated fish (Johnson et al., 2015; Eagles-Smith et al., 2016).

The formation of methylmercury varies by many factors that concern the biogeochemical characteristics of the aquatic environment such as DOM, sulfate, available iron and other electron acceptors (Chiasson-Gould et al., 2014; Avramescu et al., 2011). DOM also has two ways through which it affect Hg bioavailability; by increasing Hg methylation through transport of Hg to microbial cells or decreasing its methylation through binding with Hg thereby decreasing its accessibility (Chiasson-Gould et al., 2014; Luo et al., 2020).

One to one relationship between Hg and these environmental factors results in its complicated and dynamic response which varies from one ecosystem to another (Bravo & Cosio, 2013; Bravo & Cosio, 2019).

Significance of Studying Mercury in Aquatic Ecosystems

An understanding of the concentration of Hg particularly in aquatic systems is important because of the toxicity it poses in the environment to both animals and human beings. The next direct source of human exposure to mercury as a toxiant is through the consumption of fish most especially in societies that depend on fish as part of their meals (Johnson et al., 2015). High concentrations of methylmercury in fish is worrisome because methylmercury is neurotoxic and after passing through the blood-brain barrier, can cause developmental impairment among fetuses and young children (Hsu-Kim et al., 2013; Eagles-Smith et al., 2016). Methylmercury neurotoxicity is also well established, and previous exposure of fetuses and children results in a reduced IQ and developmental abnormalities (Bravo & Cosio, 2019; Fleming et al., 2006).

Furthermore, methylmercury impacts wildlife primarily fish consuming bird and mammals that experiences reproductive and neurobehavioral impacts resulting from mercury bioaccumulation (Eagles-Smith et al., 2016; Bravo & Cosio, 2019). Another environmental threat of Mercury is that it is seriously endangering aquatic life. Methylmercury builds up as one moves up the food chain particularly among fishes, birds and mammals feeding on these contaminated aquatic systems (Eagles-Smith et al., 2016). Such a biomagnification impact causes higher levels of mercury in the predators even if the environment concentration is small (Johnson et al., 2015; Luo et al., 2020). It is stated that, the ecological impacts of mercury are not only limited to given species but that can expanded to whole food chains and ecosystem (Hsu-Kim et al., 2013).

Purpose and Scope of the Review

This review will present a comprehensive synthesis of the advances in understanding of mercury in aquatic environments with emphasis on the transformation processes, such as methylation of mercury by microorganisms, the accumulation of the metal in the food web and its ramifications on

ecosystem health and human populations. Therefore, based on the aspects of controlling or inhibiting mercury methylation and bioavailability of mercury, this present review seeks to contribute to the knowledge on how mercury pollutes water and influences the ecosystems as well as humans. It will also discuss the implications of these processes in the management and the abatement of sources of mercury pollution in aquatic environments (Driscoll et al., 2013; Hsu-Kim et al., 2013). In particular, this review concentrates on ways in which characteristic abiotic variables like DOM, sulphate and iron in food web determine methylmercury and the ways to optimise these factors in order to reduce dangers that are associated with mercury pollution (Chiasson-Gould et al., 2014; Luo et al., 2020).

II. SOURCES OF MERCURY IN AQUATIC SYSTEMS

Anthropogenic Contributions

Human increased activities are the largest source of mercury release into the aquatic system and hence polluting it. Those parties that mine for gold, burn coal, manufacture cement, dispose industrial wastes as well as operate coal fired electricity producing facilities are among the greatest emissives of mercury in the world today according to Pirrone et al., (2010). He also attributed the combustion of fossil fuel particularly coal as the leading industrial emission contributing about 810 Mg of mercury per year. Second biggest emitter of mercury is artisanal and small scale gold mining (ASGM) which emits about 400 Mg/year (Pirrone et al., 2010). Non-ferrous metals manufacture and cement production emanate an extra 310 Mg and 236 Mg annually (Pirrone et al., 2010). Hospital waste disposal, including the treatment and disposal of waste mercury-containing products introduce a further 187 mg of mercury for annual discharge (Pirrone et al., 2010).

These anthropogenic sources release mercury in two primary forms: metallurgic mercury – elemental or free state mercury Hg(0) and chemical mercury – divalent mercury, Hg(II). Hg(0) is more lipophilic, has a higher volatility and a longer atmospheric

lifetime compared to Hg(II) so it travels long distances before it undergoes oxidation and returns to the ground (Corbitt et al., 2011). After entering water bodies, mercury is subjected to several biomethylation steps, which convert it to potentially neurotoxic methyl mercury (MeHg) and that is bio accumulated in food chains of water bodies (Pirrone et al., 2010; Mason et al., 2012).

Other sources of mercury pollution in water include; urbanisation and agricultural discharge into water systems. Urbanization optimally results in enhanced industrialization and release of mercury from products used in the urban areas such as batteries and fluorescent lamps into the water through discharge pipes. Agricultural Discojanery brings mercury into water bodies through fertilisers and pesticide which have mercury ions incorporated in them (Kocman et al., 2017). Erosion of soil and racing in urban and agricultural regions also releases mercury into water bodies importing the pollution in the case of severe rainfall (Kocman et al., 2017).

Natural Background Levels

The natural sources of this metal include volcanic emissions, the geological breakdown of rocks with mercury, fire in the forests and the re-release from different and other natural and anthropogenic sources (Pirrone et al., 2010). Natural sources estimate to release about 5,207 Mg of mercury per year into the atmosphere including those released from geological sites in addition to those that are remobilized from terrestrial and aquatic surfaces (Pirrone et al, 2010). Another natural source of mercury input is volcanic, which emits large quantities of elemental mercury directly into the tropical atmosphere (Driscoll et al., 2013). Other natural processes that cause the release of mercury include weathering of mercury rich rocks, geothermal activity and volcanic activity although these sources are more localised (Mason et al., 2012).

Natural mercury there are also transported by atmosphere and deposited together with anthropogenic mercury and often in more remote or preserved areas (Amos et al., 2013). Hg(0) with a

long atmospheric lifetime of up to one year can also be transported long distances and deposited through wet or dry deposition as seen by Song et al., (2015). This deposited mercury is frequently redeposited back onto the environment so that cycling of these Hg continues within the environment and it does not easy to differentiate between these two sources in some part of the world (Pirrone et al., 2010). Even though dynamism from natural sources, anthropogenic shows that the emissions have tripled since preindustrial levels (Mason et al., 2012). It is established that about ninety-five per cent of the total mercury in today's atmosphere is in some way linked to human activities, including even those areas that are completely devoid of local anthropogenic emissions (Streets et al., 2011).

III. METHYLATION OF MERCURY IN AQUATIC SYSTEMS

Microbial Methylation Processes

Mercury methylation in aquatic system occurs under anaerobic condition when microbes methylate inorganic mercury (Hg(II)) and produce methylmercury (MeHg) that is highly toxic and accumulates in food chain. The primary environmental microniches harboring the microorganisms capable of transforming Hg(II) to MMHg are SRB, IRB, and methanogens (Parks et al., 2013; Villar et al., 2020). The identification of the *hgcAB* gene cluster has given important data on the molecular processes, as it is present in many microorganisms that can undergo mercury methylation (Parks et al., 2013; Bravo & Cosio, 2019).

Methylation aims at the uptake of inorganic mercury [Hg (II)] by bacteria and the conversion of this metal into methylmercury [MeHg] enzymatically. Previous work has indicated that, in sulfate-reducing sediments and other environments, the process is closely associated with the reductive acetyl-CoA pathway, a versatile metabolic pathway in various anaerobic bacteria whose detailed biochemistry is still not fully elucidated (Parks et al., 2013). It has been demonstrated that mercury can be adsorbed at the

cell surface and then transported and thiomethylated intracellularly, depending on a number of factors, such as the availability of electron acceptors, such as sulfate and iron, as well as the DOM and sulfides that either enhance or inhibit mercury bioavailability Hsu-Kim et al.

Temperature, organic matter content and the microbial community are of special importance as they affect the rate and possibility of mercury methylation. Higher temperature increases microbial activity which in turn increase methylation rates especially in regions where methylation of mercury is slow due to colder temperatures (Bravo & Cosio, 2019). Among these factors, the amount and nature of organic material influence mercury biologic accessibility; organic matter can either inhibit mercury toxicity or promote methylation depending on the ability of vibrios to accumulate enough organic material to produce complexes that increase the rate of methylation, which requires specific electron donors (Hsu-Kim et al., 2013; Villar et al., 2020).

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Methylmercury Dynamics

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Bioaccumulation of Methylmercury in Aquatic Organisms

Mechanisms of Bioaccumulation

Methylmercury also known as MeHg biomagnifies through the water food chain beginning with phytoplanktons and other micro organisms. Dairy – Methylmercury taken by the phytoplankton from the water through metabolic processes. It is worthy to state that once it is taken into the body system, methylmercury partitions itself into the food chain and starts accumulating within food chains. Phytoplanktons contain lower concentrations of MeHg, but zooplankton, having a trophic level higher than phytoplankton, have higher concentrations of MeHg; small fish and large predatory fish which feed on contaminated zooplankton and small fish also contain higher concentration of MeHg (Wu et al., 2018).

The mobility of MeHg from water to other components of the base of the food chain is facilitated by BCFs, which are measures of the bioaccumulation of mercury by organisms in their environment. MeHg associated with seston consisting of microorganisms such as algae and bacteria is the dominant form of mercury found in higher trophic level organisms in many aquatic ecosystems. It has been established that the BCF for MeHg in seston is a better predictor of MeHg accumulation in fish than water column MeHg concentration only (Wu et al., 2019). Wu and co-authors presented a flowchart (Figure 2 in Wu et al. 2019) that describes the scheme of MeHg trophic transfer in the pelagic section of the water column starting with seston and ending with zooplankton and fish. lankton absorb methylmercury from the surrounding water during their regular metabolic activities. Once absorbed, methylmercury begins to bioaccumulate as it moves up the food chain. Zooplankton, which feed on phytoplankton, accumulate higher concentrations of MeHg, and this biomagnification continues as small fish and larger predatory fish consume contaminated zooplankton and smaller fish (Wu et al., 2019). The transfer of MeHg from the water into the base of the food web is driven by bioconcentration factors (BCF), which quantify the uptake of mercury by organisms from their surrounding environment. In many aquatic ecosystems, MeHg in seston (suspended organic particles like algae and bacteria) is the primary source of mercury for higher trophic organisms. Studies show that the MeHg bioconcentration factor for seston predicts MeHg concentrations in fish more reliably than water-column MeHg levels alone (Wu et al., 2019). Figure 2 from Wu et al. (2019) illustrates how MeHg bioaccumulates within the pelagic food web, starting from seston to zooplankton and fish.

The concentrations of MeHg vary depending on water characteristics, DOM, pH, and trophic status of the body of water. High acidic conditions improve the ability of MeHg to dissolve and accumulate in plankton and fish (Mergler et al., 2007). In the same line, oligotrophic water favour methylated Hg accumulation, while biodilution occurs when the water body offers high carry

capacity or eutrophy that supports the increased biomass of species (Karagas et al., 2012).

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Source category	Hg emission (Mg yr ⁻¹)	Reference
Coal and oil combustion	818	(Pirrone et al., 2010)
Non-ferrous metal prod.	310	(USGS, 2004)
Ally iron and steel prod.	43	(Pirrone et al., 2010); (Pacyna et al., 2006)
Cement production	238	(Pirrone et al., 2010)
Caustic soda production	163	(Pirrone et al., 2010)
Mercury production	50	(Pirrone et al., 2010)
Artisanal gold mining prod.	400	(Elkhrer and Vega, 2008)
Waste disposal	187	(Pirrone et al., 2010)
Coal bed fire	52	(Pirrone et al., 2010)
VCM production	28	(Pirrone et al., 2010)
Other	65	(Pirrone et al., 2010)
TOTAL	2320	

Figure 1: provides an overview of global mercury emissions, showing the relative contributions from anthropogenic and natural sources, with anthropogenic emissions dominating in recent decades.

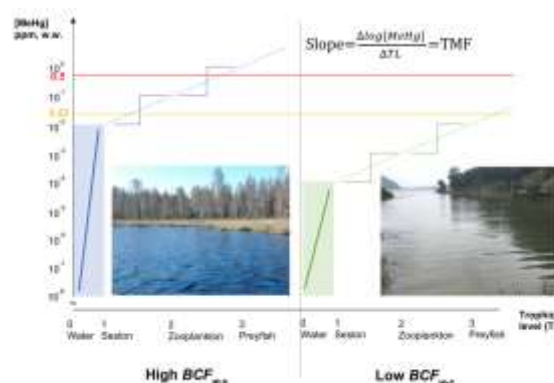


Figure 2: from Wu et al. (2019) shows the transfer and accumulation of methylmercury across different trophic levels in the pelagic food web, highlighting the role of seston as the primary entry point for MeHg into aquatic ecosystems.

IV. ECOLOGICAL AND HUMAN HEALTH IMPLICATIONS

When methylmercury is fed to aquatic organisms and moves up the food chain from one organism to the next, fish-eating animals such as large fish and piscivorous birds show the highest levels of toxicity. High levels of methylmercury in fish are also a concern ecologically because fish are the principal

dietary source of mercury for animals and people (Mergler et al., 2007). The eating of fish containing mercury is dangerous to the health of man mainly affecting the nervous system. The impact of methylmercury on human health is most devastating if a foetus is exposed prior to birth as it can cause deficits in the brains of developing foetal neurons, leading to developmental disorders and ineffective central nervous system function (Karagas et al., 2012).

Research focused on peoples of areas that heavily rely on fish, including Arctic and the Amazonian population, shows that prolonged methylmercury exposure affects people's health. Influenced by their diet of marine products such as mammals and fish, indigenous people from Arctic have higher mercury levels, increasing prevalence of neurological and developmental diseases (Mergler et al., 2007). Likewise, one study can census groups living along the river banks of Amazon which recorded high levels of mercury in their bodies due to consumption of fish which is their major source of protein and the effects are the same including tremors, poor coordination and cognitive difficulties (Kenji et al., 2020).

V. MITIGATION STRATEGIES AND FUTURE RESEARCH DIRECTIONS

Current Approaches to Mitigating Mercury Pollution

The most comprehensive global effort addressing mercury pollution is the Minamata Convention, which seeks to mitigate mercury emissions, especially from high-emission sources such as coal-fired power plants, cement production, and artisanal small-scale gold mining (ASGM). The convention emphasises both emission reduction and the development of cleaner technologies. It also focusses remediation efforts in areas already contaminated by mercury, with a particular focus on preventing the bioaccumulation of methylmercury in aquatic systems (Selin et al., 2018). This treaty has facilitated the implementation of regulatory frameworks targeting key sources of mercury emissions and promoting mercury-free alternatives, particularly in ASGM practices (Pacyna

et al., 2010). Technological interventions, such as the implementation of activated carbon injection systems and flue-gas desulfurization in industrial facilities, have significantly reduced mercury emissions. These technologies capture mercury before it can be released into the atmosphere, especially from coal-fired power plants and metal processing plants (Pacyna et al., 2016). Such advancements have led to a measurable decrease in atmospheric mercury deposition in many regions (Pacyna et al., 2010).

At the community level, mercury mitigation efforts focus on monitoring mercury levels in local water bodies, soil, and food sources. These efforts often involve public education and outreach, particularly in regions where subsistence fishing is common and where mercury-contaminated fish pose a significant health risk (Hsu-Kim et al., 2018). Fish consumption advisories and mercury monitoring programs are examples of community-based interventions that have proven effective in mitigating human exposure to methylmercury (Rice et al., 2014).

Research Gaps and Future Directions

However, the following gaps have been identified, which prevent efficient regulation and remediation of mercury pollution:

There is, however, one major omission: little is understood about how mercury behaves in sediments over the long term and whether it tends to be remobilised when environmental conditions change. Sediments act as sink for mercury but various conditions like increasing temperatures, change in land use and use physical means or natural disturbances to transport mercury and especially methylmercury to aquatic systems. To this end, research has to be conducted for estimating those variables and for creating models that will predict further risks arising from climate change and changes in land use (Obrist et al., 2018). However, the relationships between climate change and mercury cycling should be explored to understand how higher temperatures can boost microbial methylation of mercury to bioavailability in water bodies (Selin et al., 2018).

Another research gap that can be identified is the applicability of current remediation strategies on the highly contaminated site such as ASGM and industrial areas. Current practices applied to contaminated sediments include removal through excavation and covering with a 'cap', but their sustainability is uncertain. For in situ remediation measures, there is a dire lack of effective techniques, like using stabilisers or bioremediation agents which will help to counterbalance the impact of mercury without necessarily disturbing the environment in the process (Pacyna et al., 2016).

Another difficulty is the absence of information concerning the concentration of mercury and its ability to accumulate with the members of specific species of a particular habitat. Although a great deal is understood about the bio magnification of mercury in temperate environments, little is known about the processes in tropical, Polar and arid zones. It is important to fully understand these dynamics so that one could anticipate how mercury would respond in future, the change in conditions ago environmental (Pacyna et al., 2010). More importantly, researchers should concentrate on performing extensive and sustained ecological research which examines variation in bio magnification of mercury across and amongst species and ecosystems.

Furthermore, interdisciplinary approaches that integrate geochemistry, ecology, toxicology, and public health are crucial for addressing the broader impacts of mercury pollution. Collaboration between scientists, policymakers, and communities will be essential to ensure that new research findings are translated into effective policies and local action (Selin et al., 2018). For example, combining local knowledge with cutting-edge scientific research could greatly enhance community-based monitoring programs and lead to more tailored and effective interventions.

Perspective on Future Directions

Looking forward, I see two key areas where research could have the most significant impact:

Mercury Fate in Changing Climate Scenarios: As the global climate warms, new research must focus on how changes in precipitation patterns, melting permafrost, and shifting ecosystems may affect mercury cycling. It is vital to predict how these changes could influence mercury methylation rates and how newly mobilised mercury could interact with natural and human systems.

Integrating Technology and Policy: Technological advances, such as the development of cost-effective, scalable remediation methods, should be closely aligned with international policy frameworks. Emerging technologies, such as nanotechnology-based adsorbents, could offer new solutions for in situ mercury remediation. Aligning these innovations with policy enforcement and community engagement would help drive global mercury mitigation efforts more efficiently.

VI. CONCLUSION

It is very important to examine dynamics of mercury in water environment and in sediments to protect water environment and human health. Mercury is a conservative chemical species and has a long biogeochemical cycle dominated by human and natural inputs. Mercury is not existent in its original form in the environment but transforms, especially into methylmercury (MeHg), a potent neurotoxin that biomagnifies in food chains. This is hazardous as humans who consume fish – the top predators – are contaminated with toxic mercury (Mergler et al., 2007; Karagas et al., 2012). The major conclusion of this review is that microbial methylation processes, especially where the methylation and demethylation of mercury occur totalling the methylmercury formation, are mainly in anoxic environments such as sediments. It beats that other environmental parameters such as dissolved organic carbon, sulphate concentrations and temperature greatly affect the rates of methylation (Hsu-Kim et al., 2018; Villar et al., 2020). Sediments serve as a sink and as an active local source of methylmercury and mercury-enriched sediments may be again mobilised (Gascon Díez et al., 2016).

This is particularly evidenced by the fact that methylmercury biomagnifies to reach top predators and accumulates in almost all type and sizes of fish and marine mammals, providing evidence of the severe impact of mercury pollution on the ecological balance of the world's water bodies. Human health is especially affected with such population groups as pregnant women and populations consuming fish products throughout their diets suffering from a range of adverse health effects including neurodevelopmental and cognitive deficits (Mergler et al., 2007).

Even though concrete advancements have been achieved in the reduction of mercury emissions still more efforts are needed for the adequate elimination of the effects of mercury on the environment and public health. While measures like the Minamata Convention have really helped to curb the emission of mercury emissions, there is still need to continually enforce these standards and call on technology to cut emissions even further.

Continuing studies are necessary to determine the further behavior of mercury in sediment environments, to clarify the influence of global warming on the mercury cycle, as well as to assess the efficiency of existing technologies for elimination of hazardous Hg forms. However, some of the future research directions that are likely to fill the gaps include; employing statistical models to explain the fluctuations in mercury behaviour (2007); and investigating the effects of methylmercury accumulation in non-temperate zones where information is limited (Obrist et al., 2018; Pacyna et al., 2016). Mercury might be amenable to new forms of treatment, such as in situ bioremediation, which could be effective for the management and removal of mercury at cheaper and without causing destruction to the environment (Pacyna et al., 2016).

Last but not the least, the scientific cooperation between different disciplines, with political decision-makers, and with those population groups most at risk are important precursors to the implementation of the mercury mitigation

measures. Remediation efforts will rely strongly on grassroots surveillance and participation to map mercury pollution hotspots, especially where ASGM and industrial operations will be relevant. Thus, the development of this partnership approach to mercury management policies will be most coherent and provide sustainable ecosystems for the people's health in the future.

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