THE IMPACT OF NATURALLY OCCURRING PHYTOPLANKTON ON MERCURY BIOGEOCHEMICAL CYCLING IN AQUATIC ECOSYSTEMS: IMPLICATIONS FOR GLOBAL MERCURY POLLUTION AND PUBLIC HEALTH

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The biogeochemical cycling of mercury in aquatic ecosystems is a multifaceted process influenced by various factors, including ambient temperature, seasonal fluctuations, the activity of methylating bacteria, dissolved oxygen levels, and the interaction of mercury with dissolved organic matter (DOM). Consequently, a significant portion of mercury contamination originating from human activities, which had previously settled in sediments, is reintroduced into the water column, primarily in the form of highly toxic organic mercury compounds like methylmercury and dimethylmercury. This phenomenon is particularly pronounced in the shallow coastal waters of industrialized regions across the globe. Naturally occurring phytoplankton serve as the primary entry point for these highly toxic mercury forms into the aquatic food web. The availability of mercury, its uptake by phytoplankton, its impact on population size, cell toxicity, subsequent biotransformation, and intracellular stability within phytoplankton are of paramount importance for human health. It is important to note that the mercury sequestered inside phytoplankton cells, owing to biomagnification effects, eventually finds its way into aquatic wildlife, fish, seafood, and ultimately, the human diet. This review aims to provide an overview of recent findings on the interaction between organic mercury forms and natural phytoplankton. Additionally, it offers fresh insights into this intricate relationship and suggests potential directions for future research, with a focus on preventing mercury biomagnification considering scenarios involving climate change and increasing global pollution.

Keywords: Biogeochemical Cycling; Biomagnification; Aquatic Food Web; Methylmercury; Climate Change.

I. INTRODUCTION

Mercury (Hg) is a naturally occurring trace metal found throughout the environment. Severe exposure to it can result in central nervous system damage, leading to symptoms such as tremors, speech distortion, kidney issues, respiratory failure, dizziness, blurred vision, hallucinations, and even fatality. Some studies have also reported developmental delays in children, as well as adverse cardiovascular and immunological effects. In recent research, mercury has been investigated as an immunotoxin, primarily in susceptible mouse models, demonstrating the immunotoxicity of inorganic mercury (IHg) in these models (Levin 2014).

Mercury can enter the environment through both natural geological processes and human activities. Once in the atmosphere, it can travel long distances before settling into soils or bodies of water, where it may undergo methylation. Methylmercury (MeHg), the organic methylated form of mercury, is highly toxic, primarily due to its strong binding to proteins, leading to its retention in tissues. This results in biomagnification throughout the food chain, from plankton to apex predators. The accumulation of mercury in fish is particularly concerning, especially in regions where the local population heavily relies on fish as their primary protein source (Li et al. 2020).

The bioconcentration of mercury in phytoplankton is a major entry point for this metal into the aquatic food web. The concentration of MeHg in phytoplankton cells can be up to 105 times higher than in the surrounding seawater. Phytoplankton, as primary producers, are essential for ecosystem biomass production and serve as a food source for higher trophic levels. Consequently, exposure of phytoplankton to low levels of inorganic mercury (IHg) or MeHg can jeopardize the functioning of entire aquatic systems and, ultimately, impact human health through seafood consumption (Wu et al. 2019).

Anthropogenic activities, such as mineral processing, have elevated atmospheric mercury levels by at least a factor of three over the past century. Due to widespread and continuous industrial use of mercury, its concentration in certain regions has reached alarming levels, with concentrations of up to 27 μg/L in coastal...
Cious metal mining contributed to mercury inputs into the atmosphere and, consequently, the thermal structure of elemental Hg0, occasionally as divalent HgII. HgII is the predominant form of mercury. Natural waters predominantly contain methylmercury (MeHg) and dimethylmercury (DMHg). The chemical characteristics of these different mercury forms play a pivotal role in the biogeochemical cycling of mercury (Liu et al. 2008).

While elemental mercury (Hg0) enables long-distance transportation, it constitutes only a fraction (10 to 30%) of the total dissolved mercury in oceans and freshwater environments. In aquatic systems and soils, divalent mercury (HgII) is the predominant form of mercury. Natural waters predominantly contain methyl- and dimethylmercury, with methylmercury (MeHg) being the most prevalent and highly toxic organomercury compound in freshwater and estuarine ecosystems, whereas dimethylmercury (DMHg) is generally not detected. MeHg is subject to bioconcentration and biomagnification in aquatic food webs, accounting for a significant portion, up to 80–100%, of the total mercury (THg) found in fish muscle. Toxic effects related to mercury contamination have been observed in freshwater fish species on a global scale (Meng et al. 2019).

III. BIOGEOCHEMICAL CYCLING OF MERCURY AND METHYLMERCURY

Human activities have significantly increased atmospheric mercury (Hg) concentrations by a factor of three over the past century. Mercury naturally resides in various minerals, where it remains relatively stable and poses minimal risks. However, the issue arises when these minerals are extracted for human purposes, as this process releases substantial amounts of mercury into the environment. Recent research indicates that anthropogenic sources of mercury emissions encompass fossil fuel combustion, non-ferrous metal production, iron and steel manufacturing, waste incineration, cement production, and various industrial processes. It has been suggested that 24% of anthropogenic mercury emissions originate from coal combustion and thermal conversion. Furthermore, evidence suggests that before the rapid industrialization of the last century, the use of mercury in precious metal mining contributed to mercury inputs into the atmosphere and, consequently, elevated inputs into the ocean. The total annual emissions of mercury into the atmosphere are estimated to range between 6000 and 9000 tons, primarily in the form of elemental Hg0, occasionally as divalent HgII. Recent studies indicate that approximately 800 tons of atmospheric mercury are generated by natural processes, constituting around 18% of the total atmospheric mercury pool (Zhang et al. 2019).

The primary sources of mercury input into open ocean areas include runoff from rivers and estuaries, groundwater, discharges from benthic sediments, hydrothermal vents, and direct atmospheric deposition. Models and measurements suggest that the predominant source of mercury deposition into oceans is direct
atmospheric deposition into surface waters, with global inputs ranging from 2800 to 5800 tons over the past decade. Another significant source of mercury for the marine ecosystem is of fluvial origin, stemming from industrial discharges that contaminate rivers with various pollutants. Additionally, mercury vapors in the atmosphere may come into contact with suspended particles, forming bonds and adhering to them, eventually leading to their deposition into seabed sediments. From there, mercury can enter the aquatic environment through the action of sea currents and microorganisms. These factors have caused current mercury levels to be five times higher in the atmosphere and twice as high in the oceans compared to natural levels (Mason et al. 2012).

In the environment, methylmercury (MeHg) formation is primarily facilitated by mercury-methylating bacteria, which convert inorganic divalent mercury (HgII) into MeHg under oxygen-deficient conditions (see Figure 1). Such mediators include specific sulfate-reducing bacteria, iron-reducing bacteria, methanogens, and fermenters. However, it’s worth noting that oxygenated surface waters in the ocean are also important, as some studies have shown that approximately 20-40% of the MeHg found below the surface mixed layer originates from the surface and then enters deeper ocean waters. This methylation process primarily occurs in sediments, water columns, and periphyton (Ma et al. 2019).

The emergence of oxygen-deficient conditions in seafloor sediments, often referred to as "dead zones," rich in dissolved sulfates, creates ideal conditions for methylating sulfate-reducing bacteria. The expansion of these dead zones is accelerating due to anthropogenic eutrophication of various water bodies and global warming. Several other environmental factors, such as temperature, pH, and medium composition, also influence the divalent mercury methylation process (Lalish 2015).

**Figure 1:** Biogeochemical cycling of mercury (Hg) in coastal regions is illustrated in the legend below: Hg(0) signifies elemental mercury, Hg(II) represents divalent mercury, Me2Hg denotes dimethylmercury, and MeHg stands for methylmercury. The index "p" indicates that any Hg form with this index is bound to particulate organic matter. Chemical processes are depicted by black arrows, while green arrows denote biologically mediated processes. Phytoplankton and sulfate-reducing bacteria are represented by green and black dots, respectively. Sulfate-reducing bacteria flourish in environmental conditions conducive to Hg methylation, typically within a pH range of 5 to 10. The redox potential spans from slightly negative (-0.4 mV) to zero, and dissolved oxygen levels are maintained at less than 0.2 mg/L.
IV. THE INFLUENCE OF HUMAN-INDUCED CLIMATE CHANGE ON THE BIOGEOCHEMICAL CYCLE OF MERCURY

Anthropogenic climate change can have significant impacts on the biogeochemical cycling of mercury (Hg), a toxic heavy metal that can cause harm to ecosystems and human health. The relationship between climate change and mercury cycling is complex and involves multiple interconnected processes (Sonke et al. 2023). Here are some key ways in which anthropogenic climate change can influence the biogeochemical cycling of mercury:

Temperature and Methylation: Warmer temperatures associated with climate change can enhance microbial activity in aquatic environments. Mercury undergoes a process called methylation, where microorganisms convert inorganic mercury (Hg^2+) into methylmercury (MeHg), a highly toxic and bioaccumulative form of mercury. Increased temperatures can stimulate microbial activity, potentially leading to higher rates of mercury methylation (Poff et al. 2002).

Changes in Precipitation Patterns: Climate change can alter precipitation patterns, leading to changes in hydrological cycles. This can influence the transport of mercury through watersheds and into aquatic ecosystems. Increased or decreased rainfall can affect the mobilization of mercury from soils and its transport to rivers and lakes (Allan et al. 2020).

Sea Level Rise: Rising sea levels, another consequence of climate change, can impact coastal ecosystems. Coastal areas often serve as sinks for mercury, and sea level rise can lead to the mobilization of mercury from sediments into the water column. This can increase the availability of mercury for methylation and uptake by aquatic organisms (Kirwan et al. 2010).

Changes in Vegetation and Land Use: Climate change can alter vegetation patterns and land use. Changes in vegetation can affect the uptake of mercury by plants, and alterations in land use can influence the release of mercury from soils. Deforestation, for example, can release stored mercury into the environment (Hansen et al. 2001).

Ecosystem Disturbances: Extreme weather events, such as floods and droughts, are expected to become more frequent and intense due to climate change. These events can disturb ecosystems and impact the cycling of mercury. Floods, for instance, can mobilize mercury from soils and transport it to aquatic systems (Huber et al. 2011).

Ocean Acidification: Increased levels of carbon dioxide (CO₂) in the atmosphere, leading to ocean acidification, can influence the behavior of mercury in marine environments. Changes in pH and other chemical conditions can affect the speciation and bioavailability of mercury in seawater (Zeng et al. 2015).

Feedback Loops: There can be feedback loops where the impacts of climate change on mercury cycling further exacerbate climate change effects. For example, the release of mercury from thawing permafrost in polar regions can contribute to the global mercury pool, potentially impacting ecosystems and human health.

Understanding and predicting the complex interactions between climate change and mercury cycling is crucial for effective environmental management and the development of strategies to mitigate mercury pollution. Additionally, it highlights the interconnected nature of environmental processes and the importance of addressing multiple environmental issues simultaneously. The transfer of methylmercury (MeHg) from the aquatic environment to the food chain is influenced by various environmental factors, with a critical role played by bioconcentration in foundational organisms like microalgae. The transition of MeHg from the liquid medium to phytoplankton is a pivotal step, shaping subsequent bioaccumulation in higher organisms and significantly determining their bioconcentration (see Figure 1) (Chen et al. 2018).

Understanding the mechanisms of intracellular accumulation becomes crucial for developing bioremediation techniques, enabling the targeted removal of accumulated contaminants from phytoplankton cells. Phytoplankton employs specific tolerance mechanisms, such as binding to intracellular ligands, primarily phytochelatins and sulphhydryl groups, forming cumulative metal complexes. Some microalgae species exhibit a notable capacity for intracellular accumulation of various heavy metals, potentially serving as a basis for innovative bioremediation techniques. While adsorption on activated carbon is selective for Hg ions, its high cost due to limited resources hinders widespread use (Mani et al. 2014).
Phytoplankton species with high bioaccumulation capacities could serve as reliable bioindicators of water quality, offering greater sensitivity and quicker responses to environmental changes than other organisms. In light of these findings, it is conceivable that anthropogenic Hg pollution and persistent biogeochemical cycling may elevate global Hg levels in the environment, leading to increased bioavailability, bioaccumulation, and consequently, heightened public health risks (Zhou et al. 2008). To mitigate pollution impacts, rapid diagnostic methods for environmental hazard assessment are fundamental. Ecotoxicology, studying biota responses to toxic substances, can provide insights into the current level of toxic pollution and function as an early warning tool. Modern ecotoxicology techniques, utilizing genome sequencing to differentiate toxicants based on gene expression profiles, enable the direct detection of the earliest stages of toxicological responses. Since mercury species enter the food chain through phytoplankton, these organisms can be key indicators for assessing Hg exposure in the environment (Wang et al. 2010).

Coastal areas are subject to the influence of various biological and nutrient factors, alongside changes driven by source water and circulation patterns. These factors collectively impact ocean dynamics, influencing ventilation and respiration processes, and subsequently affecting dissolved oxygen (DO) levels. A decline in oceanic DO levels contributes to a notable expansion of oxygen minimum zones in global water bodies. These zones are characterized by DO concentrations below 80 μM (2.9 mg/L), rendering them inhospitable for marine organisms dependent on continuous respiration (Zhang et al. 2010).

The role of sea ice extends to the freshwater and seawater budget of the global ocean. Global warming intensifies heat release from the ocean, leading to thinner sea ice and larger expanses of open water. This alteration diminishes the planet's capacity to maintain a global heat balance. As a result, a hypothesis emerges that the rising ocean temperatures associated with anthropogenically induced climate change, coupled with factors such as sea acidification due to elevated atmospheric CO₂ concentrations and the depletion of nutrients from surface waters, could trigger shifts in the composition of phytoplankton populations. These changes may contribute to the extinction of numerous species of primary producers (Reid et al. 2009).

## V. ACCUMULATION OF MERCURY IN AQUATIC FOOD WEBS

Once mercury infiltrates the water system, microorganisms convert it into organic forms such as methylmercury and dimethylmercury. These highly toxic organic mercury forms, possessing bioavailable properties, are consumed by various organisms, thus progressing through all trophic levels in the food chain. Ingested mercury persists in the organism and accumulates, with larger organisms accumulating higher amounts due to their diet relying on numerous smaller organisms that have previously ingested mercury. Consequently, the consumption of sizable marine species like tuna or swordfish may pose health risks to both humans and different animal species, as they tend to amass significant mercury levels. Human exposure to methylmercury primarily occurs through the consumption of marine organisms. The bioconcentration of methylmercury in phytoplankton and zooplankton can reach levels up to 105 and 106 times higher than concentrations in seawater, respectively. Intracellular methylmercury binds to proteins in phytoplankton cells and further accumulates in marine food webs. As a primary entry point for mercury into aquatic food webs, algae play a pivotal role in the absorption and transformation of mercury species in aquatic ecosystems (Naja et al. 2017).

Upon entering the human body, methylmercury becomes entangled in the enterohepatic cycle, making expulsion difficult and significantly increasing its half-life in the body. Methylmercury's hydrophobic nature allows it to breach the blood–brain barrier and even cross the placenta. Direct interaction with cellular and nuclear components induces neurotoxic effects in the brain and nervous system, inflicting damage on the kidneys and causing irreversible harm to fetuses. Legislation addressing mercury limits in the environment and food varies across states and the considered environmental matrix. The Minamata Convention on mercury doesn't stipulate specific environmental limits but mandates global control and reduction of mercury emissions and releases. The World Health Organization (WHO) raises awareness of mercury toxicity and exposure risks, citing documented central nervous system damage in subjects exposed to 20 μg/m³ of mercury in air for several years. The European Union's Directive 2008/105/EC establishes environmental quality standards, limiting mercury content to 20 ng/L in surface water to protect aquatic organisms and ecosystems. Additional
EU regulations include Directive 2023/915/EC, setting maximum mercury levels at 1 mg/kg for fish (Hong et al. 2012).

The methylmercury ion (CH$_3$Hg$^+$) exhibits a strong affinity for organic and inorganic sulfuric compounds, such as sulfides and thiols, influencing methylmercury speciation. This imparts hydrophobic properties and enhances its bioavailability. For instance, the methylmercury complex with cysteine acts as a mobile nutrient, actively transported to the endosperm of rice grains. The concentration of thiols can both promote and inhibit the methylation of inorganic mercury by anaerobic bacteria. Generally, the methylation rate may be influenced by specific bacterial strains and the chemical structure and concentration of organic ligands and thiol compounds (Dong et al. 2010).

**VI. IMPACT OF THE EXPOSURE OF MERCURY IN THE PHYTOPLANKTON**

Photosynthetic marine microorganisms, specifically phytoplankton, contribute significantly to global CO$_2$ sequestration, accounting for half of the process and concurrently producing 50% of the Earth's oxygen. This equates to approximately 1% of the global biomass of plants. The pivotal role played by phytoplankton extends to the regulation of biogeochemical cycles, particularly carbon cycles, and their impact on the global ecosystem and climate change. Given their remarkable ability to fix CO$_2$, there is a promising potential for designing CO$_2$ capture systems based on microalgae, as they require minimal space and resources, exhibiting an efficiency 10 to 50 times higher than other photosynthetic organisms. Additionally, the prospect of using microalgae as a food source gains traction due to their non-competition with terrestrial crops for agricultural land (Singh et al. 2014).

Phytoplankton comprises free-floating photosynthetic microorganisms found in the upper layer of natural waters, including eukaryotic algae and cyanobacteria. Through photosynthetic biomass production, microalgae significantly influence the composition and productivity of higher organism communities. Nutrients, including trace metals, are essential for microalgae to perform photosynthesis, thereby influencing the biogeochemical cycling of these elements as they are transferred to other microbial communities and grazers. Microalgae are susceptible to various pollutants present in aquatic ecosystems, with heavy metals, especially mercury, posing a significant threat due to their metabolic toxicity (Pal et al. 2014).

Mercury, distinct from other heavy metals, exhibits a propensity to bioaccumulate throughout aquatic food webs. Its interaction with sulfhydryl groups in enzymes, coupled with oxidative stress from exposure, leads to toxicity at all trophic levels. The toxicity mechanism involves blocking functional enzyme groups by either displacing ions or modifying conformation within algal cells. Hg-II, in particular, proves highly toxic to the photosynthetic system of microalgae, affecting the electron transport chain, altering photosystem II photochemistry, and ultimately reducing the quantum yield of photosynthesis (Kidd et al. 2012).

The intake of metals in phytoplankton cells involves passive (diffusion and adsorption) and active uptake mechanisms (complexation of dissolved metals) driven by metal bioavailability conditioned by speciation and abundance. Hg-II and Me-Hg exist in different forms in the environment, impacting their bioavailability and toxicity for microalgae. The influence of dissolved organic matter (DOM) on Hg uptake is challenging to predict, with studies showing both increased and decreased uptake depending on DOM concentration, composition, and microalgae species (Li et al. 2020).

Both plants and animals, including phytoplankton, have developed defense mechanisms against mercury exposure. Microalgae mitigate mercury toxicity through metal exclusion, cellular mercury vaporization, and the employment of intracellular sulfur-rich complexes. Metal exclusion involves reducing the metal-reactive cell surface to limit accumulation, while cellular mercury vaporization converts mercury to dissolved gaseous Hg0, a less bioavailable form. The third strategy employs intracellular sulfur-rich complexes to sequester present Hg, controlling intracellular speciation and allowing separation into vacuoles. This sequestration involves the production of metal-binding thiol peptides, primarily phytochelatins, which bind cytosolic Hg and minimize nonspecific binding to important biomolecules. Glutathione, the main precursor of phytochelatins, increases in concentration during mercury exposure, contributing to metal detoxification and mitigating oxidative damage in cells. The excretion of accumulated Hg poses challenges due to strong intracellular binding, and MeHg appears to be a poor inducer of phytochelatins (Winch 2020).
VII. CONCLUSION

Given the ongoing trends in anthropogenically induced climate change, including rising temperatures, sea acidification, and nutrient depletion in surface waters, it is conceivable that a significant number of phytoplankton species could face high endangerment, leading to the potential loss of primary producer biomass by the year 2050. The escalating adverse conditions such as seawater acidification, increasing ocean temperatures, reduced dissolved oxygen, and limited nutrients, particularly phosphorous, may contribute to the extinction of vulnerable phytoplankton species. This scenario could result in a substantial decline in the global phytoplankton population, consequently diminishing global oxygen production.

Simultaneously, the anticipated rise in global anthropogenic inputs of mercury species into oceans and the atmosphere poses additional concerns. With the persistent biogeochemical cycling of mercury, the bio-available levels are expected to increase. In future oceans, a reduced volume of phytoplankton may be subjected to even higher concentrations of dissolved organic mercury species, intensifying bioaccumulation. This heightened bioaccumulation, in turn, could lead to biomagnification across all trophic levels, presenting a significant risk to human health as a final consequence. To mitigate this potential worst-case scenario, gaining new insights into the cycling of mercury and methylmercury and their interactions with naturally occurring phytoplankton is crucial. Such knowledge can inform strategies to prevent or mitigate adverse impacts on marine ecosystems and human health in the foreseeable future.

VIII. REFERENCES


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