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Review Article

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Interactions between Mercury and Biogeochemical Features of Aquatic Ecosystems: A Critical Review

Abstract

Background: Mercury (Hg) is a pollutant known to affect the nervous system. The most threatening form of Hg is methylmercury (MeHg), which can biomagnify in aquatic biota. This critique summarizes our current understanding of the major relationships between mercury speciation in aquatic environments and various environmental factors to determine the most suitable indicators of MeHg pollution.

Methods: Searches were performed using Web of Science. Ultimately, 33 studies were chosen and reviewed. Priority was given to recent studies as this review focused on the current state of our knowledge.

Summary: The total amount of Hg (THg) alone cannot be used as an indicator of MeHg since the relationship between THg and MeHg is poorly correlated. Microbial DNA is often used in research to give insight into the mercury cycle and fate in aquatic systems, but further studies are needed to accurately assess MeHg concentration using DNA. Based on an early study, it was thought that water colour could indicate the amount of Hg in aquatic biota. However, subsequent work has shown this to not be the case since dissolved organic matter (DOM) can help or hinder Hg bioavailability and bioaccumulation. There is a nonlinear relationship between dissolved organic carbon (DOC) and MeHg bioaccumulation where there is a threshold concentration (~8.5 mg C L^{-1} DOC) above which mercury bioaccumulation is hindered. A recent study found that the methylation rate of an aquatic system was correlated to the type of organic matter present in the sediments, although it could not predict the amount of MeHg present in the water since runoff brings Hg from the catchment to the downstream aquatic system. Recent advancements have been made to understand components of the mercury cycle (e.g. land-water interactions, microbial methylation, water-sediment interactions), but a model encompassing all components has yet to be constructed.

Introduction

The Minamata Bay disaster that occurred in Japan in the 1950s raised awareness about the level of mercury (Hg) in aquatic environments.(1) Minamata Bay was contaminated with methylmercury (MeHg) discharged through the wastewater of a nearby chemical plant.(2) Many forms of Hg are hazardous neurotoxins to humans, but MeHg is the most concerning one since it can biomagnifiy throughout food webs.(2-4) By unknowingly ingesting contaminated fish and shellfish from the Minamata bay, many citizens suffered from methylmercury poisoning, also called "Minamata Disease".(2) Since Hg affects the nervous system, common symptoms of the Minamata Disease are visual, sensory and auditory disturbances as well as uncontrolled muscles movements.(2) A global interest to extensively study the Hg cycle was stimulated by this ecological disaster. This article presents an overview of our current knowledge on the Hg cycle in the aquatic ecosystem.

Global emission and deposition of Hg have increased significantly since the industrial revolution.(5,6) Anthropogenic sources of mercury emission include fuel combustion and industrial manufacturing.(4,7,8) As a global pollutant, the elemental form of mercury (Hg_0) can travel for tens of thousands of kilometers within the atmosphere before being deposited in an aquatic environment or before being retained within the soil or the vegetation.(8-10) Moreover, once deposited, Hg is not necessarily trapped. In fact, secondary Hg re-emission from its aquatic and terrestrial substrates is not negligible since it can contribute to 56-65% of the total Hg emitted. (10)

The Hg cycle is influenced by many biogeochemical factors that can make it difficult to predict its behaviour in different natural settings.(10,11) For example, in the atmosphere, Hg_0 is the main form of mercury, but within the aquatic and terrestrial systems, inorganic Hg (Hg(II)) is predominant. (12) In the aquatic systems, a small amount of Hg(II) is transformed into MeHg primarily through a biotic pathway, but an abiotic methylation process does exist.(7,11) Even if minute concentrations of MeHg are present within the water column, the concentration of Hg in the apex predators can be up to 10^7 times greater than that of the water.(1)

The present review outlines the current understanding of the major relationships between mercury speciation in aquatic environments and various environmental factors to find the best indicators of MeHg pollution. The relationship between the total amount of mercury (THg) and MeHg was considered with regards to the physical setting of the aquatic systems. The possibility of using microbial DNA in the sediments to detect Hg pollution was also examined, since the principal producers of MeHg are anaerobic microbes.(4) Moreover, the interactions between mercury species and organic matter (OM) were studied with a particular interest to lake browning, which is an increase in water colour caused by the increased export of coloured OM.(13)

Methylmercury

Relationship between THg and MeHg

Understanding the speciation of mercury is essential when assessing the impact of mercury on ecosystems or on human health. Since Hg(II) is the prevalent form of mercury in aquatic systems, the total amount of mercury (THg) within the water or in the sediments can be used as a proxy for the level of Hg(II) within these systems.(14,15) MeHg is produced from Hg(II), thus many studies have tried to examine the relationship between THg and MeHg.(1,16) Some studies found a positive relationship between THg and MeHg.(12,16) However, several other studies have found no consistent relationships between the concentration of THg and MeHg in both water and sediments, which suggests that THg concentration is not always reflective of MeHg concentration in various aquatic ecosystems.

(10,12,14,17,18)

The ratio of MeHg to THg was found to be inconsistent (10) and could only explain 25% of MeHg variations in model used by Fleck et al..(12) However, THg can be used to find some relationships. For example, Drott et al.(16) showed a significant relationship between the potential methylation rate constant (K_m) and the concentration of MeHg normalized to the total concentration of Hg. This relationship was not significant when only the bulk concentration of MeHg was used. Also, the ratio of MeHg to THg can be used to indicate the relative methylation efficiency of an ecosystem. (12) Thus, THg is a factor that contributes to the production of MeHg but, since the relationship is inconsistent, it should not be used alone as an indicator of MeHg concentration.(15,16)

MeHg and THg are also found in sediments.(14) However, Eagle-Smith et al.(10) found no relationship between the sediment THg and the fish THg and only a weak positive correlation was found between the concentration of MeHg in the sediments and the THg concentration in fish tissue. Overall, the results to date suggest that the amount of MeHg present in the sediment alone is not a good indicator of the MeHg cycling in the food web. Even though the relationship between THg and MeHg is not always reflective of the bioaccumulation of Hg in the food web, several pollution assessment methods use the THg concentration in sediments to determine the mercury pollution of aquatic systems.(10,12,19) Various sediment quality guidelines (SQG) were developed, which all have their own limitations and advantages.(20) In an effort to obtain values applicable to different aquatic systems, Macdonald et al.(20) gathered many SQG to evaluate them and obtained a consensus whereby the threshold effect concentration of Hg in a freshwater ecosystem was 0.18 mg/kg DW and the probable effect concentration was 1.06 mg/kg DW. However, this consensus was shown to be limited.

Gao et al.(19) determined that those SQG was not representative of China's aquatic ecosystems, since the results obtained with SQG did not match the results obtained by three other mercury pollution assessment methods: contamination factor, geoaccumulation index, and potential ecological risk. Furthermore, SQG are not universal since they ignore the bioavailability and the methylation rate of Hg in an aquatic system.(21) Conder et al.(21) suggest that SQG could be used only as an initial screening method.

Influence of landscape and environmental settings

In their study, Fleck et al.(12) demonstrated that MeHg concentration is more influenced by environmental conditions and by landscape features than by THg, since those characteristics accounted for 51% of the MeHg variation independently of the THg. The authors evaluated the THg and MeHg concentrations of various aquatic feature types (canals, estuaries, lakes and streams) and environmental settings (agriculture, forested, open-water, rangeland, wetland, urban) of western North America by using the data sets of several sources. Lakes and streams generally had the highest THg and MeHg concentrations. However, Fleck et al. (2016) also noticed that THg concentrations were highest in open-water, whereas MeHg concentrations were not. The methylation efficiency tends to be lower in estuaries, open-water, and urban settings (Fig. 1; 12).

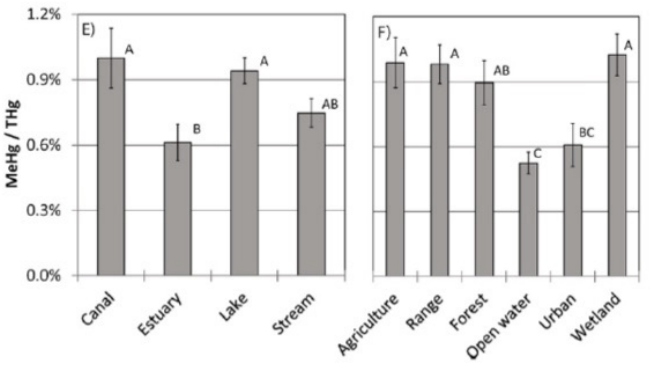

Fig. 1. Ratio of methylmercury (MeHg) to the total amount of mercury (THg). A) MeHg to THg ratio for the studied aquatic feature types, B) MeHg to THg ratio for the studied environmental settings. (Modified from Fleck et al., 2016)

Research on the Canadian Arctic freshwater systems showed that while rivers and streams tend to have higher concentrations of THg, it is in the ponds where MeHg concentration tends to be the highest.(22) In the Arctic, there is a tendency for ponds and wetlands to have a high MeHg concentration.(1,22) This might be due to the warm, shallow water that enhances bacterial activity.(22)

Furthermore, in recent years, Hg emissions in North America have decreased,(23) yet point sources still discharge Hg in the water systems, preventing these systems from responding to the decreased Hg emissions. (6) Drevnick et al.(6) found that for lakes not directly polluted by point sources, the time to respond to decreased emissions was inversely correlated with watershed size. Since the soil can sequester Hg and is a great Hg sink, the runoff water from the watershed carries Hg into the aquatic systems.(24) Larger watersheds will be slow to respond to the decreased Hg emission as the Hg moves slowly from the catchment to the aquatic environment.

Mercury methylation

Poor correlation between MeHg and THg suggests that the methylation of mercury does not depend solely on the quantity of inorganic mercury present within systems.(4,18) Since Hg(II) methylation is primarily microbial, the bioavailability of Hg(II) and the microbial productivity greatly influence the Hg methylation rate.(4,25) The main methylators are sulphate reducers, iron reducers and methanogens, which are present in surficial sediments, anoxic bottom waters and wetlands.(10,25) The ability to produce MeHg depends on the bacteria strain, not the genus. (4,26)

The capacity to methylate Hg is often found in the microbes possessing the gene cluster *hgc*A/*hgc*B.(27) Du et al.(26) studied the relationship between the abundance of certain genes in soils and sediments and the concentration of MeHg in those. *Dsr*B, a gene found in sulphate reducers, and *hgc*A, a gene for Hg methylation, were positively correlated with the concentration of MeHg, which suggests that bacteria with these genes contribute to the methylation of Hg.(26) In another study done by Poulain et al.(5), the mercuric reductase gene (*mer*A) was used to observe the bacterial response to the increase in Hg emissions. They concluded that *mer*A could be a potential tool to study the delivery of mercury to the aquatic systems, since the evolutionary response of microbes to changes in mercury deposition is fast and seems correlated to the changes in anthropogenic emissions.

Relationship Between Dissolved Organic Matter and Hg

Water Colour and Hg

Wescott and Kalff (28) established that water colour and pH could be used as indicators of zooplankton MeHg concentration, which can be used as a proxy for fish tissue MeHg concentration. However, the 24 lakes studied by Wescott and Kalff (28) did not allow for a large variation, which limited the applicability of their findings. Not all lakes respond to Hg additions in the same manner. Isidorova et al.(13) noted that lake browning increased the transport of Hg to the sediments, where the methylation of Hg would be pronounced.

Lake browning is often caused by an increase in dissolved organic matter (DOM) in the aquatic systems.(13,29) DOM is known to interact strongly with Hg and affect its cycling and fate in the aquatic systems.(30) There is often a correlation between the amount of organic matter (OM) and the THg present in the system,(30) as DOM is the main mediator of mercury into aquatic systems through catchment area.(31)

Kinetics of DOM and Hg interaction

French et al.(32) showed that dissolved organic carbon (DOC) influences the bioaccumulation of Hg in Arctic lakes. Their research identified the existence of a DOC threshold concentration at about 8.5 mg C L-1. Exceeding that, the DOC concentration starts to hinder the Hg bioaccumulation(Fig. 2; 32). In the study conducted by Isidorova et al.(13), the reference used to associate lake browning to the increase of Hg concentration in fish was research done by Hongve et al.(33)

Hongve et al.(33) studied the increase of total organic carbon (TOC) and the variation in fish tissue MeHg concentration in two lakes. The authors noticed an increase in fish Hg in the lake where the increase in TOC reached a concentration similar to the DOC threshold of 8.5 mg L^{-1} determined by French et al.(32), yet both studies do not agree perfectly. French et al.(32) observe a decrease in Hg bioaccumulation past the 8.5 mg L^{-1} threshold while Hongve et al.(33) observe and increase at 9 mg L^{-1}. However, Hongve et al.(33) measured the TOC, which is the combination of particulate organic carbon (POC) and DOC, in their studied lakes, while French et al.(32) only measured the DOC. The use of TOC instead of DOC might explain the subtle differences between the studies.

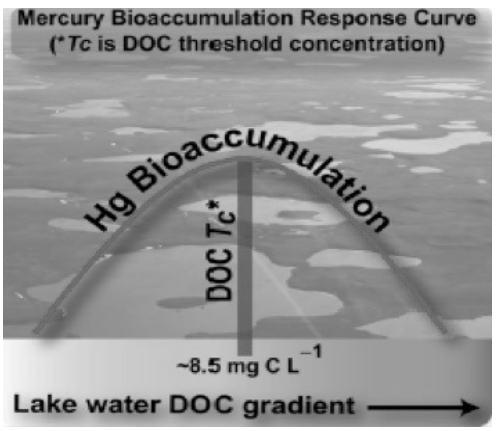

Fig. 2. Bell-shaped relationship between mercury (Hg) bioaccumulation and the concentration of dissolved organic carbon (DOC) present in the lake water. The DOC Tc represents the threshold after which DOC starts to hinder Hg bioaccumulation (Modified from French et al., 2014)

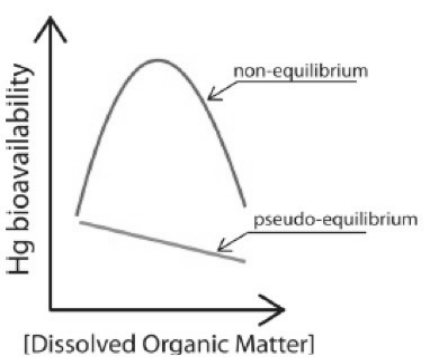

Fig. 3. Bell-shaped relationship between mercury (Hg) bioavailability and the concentration of dissolved organic matter (DOM) the water. The bell-shaped pattern is only present when Hg and DOM are in non-equilibrium condition. Hg bioavailability is lower and represented by a negative correlation in pseudo equilibrium conditions. (Modified from Chiasson-Gould et al., 2014)

Chiasson-Gould et al.(25) found that DOM was influenced by the bioavailability of Hg(II) to the bacteria and concluded that the presence of the same bell-shaped relationship between MeHg and the DOM suggests that the two variables are in non-equilibrium. During a short time period of less than 24 h, the freshly deposited Hg has more chance of being introduced in the food chain with the help of DOM (Fig. 3; 25).
Chiasson-Gould et al.(25) proposed a few hypotheses for this relationship. The first hypothesis is that when Hg first enters the aquatic system, it will bind to a small, kinetically accessible DOM. However, as time passes, Hg will bind to bigger, more stable DOM which will be too big to penetrate a bacterial cell wall.(25) The second hypothesis suggests that long exposure to DOM can change the bacterial cell wall properties.(25) The last hypothesis suggests the existence of a cycle of bioavailability and non-bioavailability.(25)

Collectively, these results suggest that browning may not be the best indicator of lake MeHg because the increase in water colour cannot always be associated with an increased of Hg in the aquatic biota since, after a certain threshold, DOM hinders Hg bioaccumulation. Recently, a study done by Bravo et al.(24) suggested that researchers should also focus on the type of DOM rather than only focusing on the concentration of DOM. Bravo et al.(24) found a relationship between the type of DOM and the methylation rate. The sediments containing more fresh algal, autochthonous organic matter tend to have a higher methylation rate than sediments dominated by terrigenous, allochthonous organic matter.(24) However, since the soil is a good sink for Hg and MeHg, there was a greater concentration of MeHg in the sediments of the terrigenous dominated lakes despite the lower methylation rate.(24) Further studies should be made on the relationships between the type of organic matter and the bioaccumulation of Hg.

Variables affecting MeHg	Relationships with MeHg	Suitability as a method to assess MeHg concentration
THg	• Poor correlation • THg/MeHg ratio varies for different physical setting • SQG are based on the THg concentration in the sediments	Suitable as a screening method only (SQG)
Microbial DNA	• Positive relationship between *dsr*B, *hgc*A and MeHg concentration • Consideration of *mer a* as a potential tool to study mercury delivery in the system	Potential method, but need further study
Water color	• Hg methylation hindered by DOC concentration above ~8.5 mg L^{-1}	Unsuitable
Types of DOM	• May influence the methylation rate of Hg • Can not predict the amount of MeHg in the water	Unsuitable at the moment, but very recent concept that need further study

Table 1. Summary of the relationships between methylmercury (MeHg) and various environmental parameters that are used to assess MeHg concentrations.

Conclusion

Mercury is a global pollutant that poses a threat to human health. Our understanding of the interactions between Hg and various biogeochemical factors is central to properly assess and control concentrations of MeHg. Although the relationship between THg and MeHg in the aquatic systems is inconsistent, THg is still a factor influencing MeHg concentration in the systems. The landscape and environmental settings also greatly influence the amount of MeHg present within a system. Furthermore, the relationship between DOM and Hg in the aquatic systems is complex since DOM can both hinder and facilitate Hg bioavailability and bioaccumulation. (25,32) Therefore, lake browning, which is caused by an increase of DOM in the water, is not reflective of the amount of Hg present in fish tissue. Recently, it was found that the type of OM is correlated with the methylation rate, although it does not indicate the amount of mercury present in the system.(24) Moreover, microbial DNA is becoming an important tool to understand Hg cycle and fate.

The Hg cycle is still not fully understood. Future research directions should focus on the relationship between the types of OM and the bioaccumulation of Hg. It would also be worthwhile to create a model that can integrate the multiple features studied in this review article (THg, land use, concentration and type of OM and the bacterial distribution) to assess

more efficiently mercury pollution in the aquatic systems.

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