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Special Feature

Mercury Biogeochemical Cycling and Bioaccumulation in Aquatic Environments: A Review

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Abstract: Over the last century the mercury (Hg) concentration in the environment has been increased by human activities with inputs from sources such as atmospheric deposition, urban runoff, and industrial effluents. Mercury can be transformed to methylmercury (MeHg) in anaerobic conditions by sulfate reducing bacteria (SRB) and sediments are the principal location for MeHg production in aquatic environments. Interest in bioaccumulation of Hg and MeHg into lower trophic levels of benthic and pelagic organisms stems from public health concerns as these organisms provide essential links for higher trophic levels of food chains such as fish and larger invertebrates. Fish consumption is the major exposure route of MeHg to humans. Recently, it was reported that blood samples in Korea showed much higher Hg levels (5-8 times) than those in USA and Germany. Although this brings much attention to Hg research in Korea, there are very few studies on Hg biogeochemical cycling and bioaccumulation in aquatic environments. Given the importance of Hg methylation and MeHg transfer through food chains in aquatic environments, it is imperative that studies should be done in much detail looking at the fate, transport, and bioaccumulation of Hg and MeHg in the environment. Moreover, there should be long-term monitoring plans in Korea to evaluate the environmental and health effects of Hg and MeHg.

Keywords: mercury, methylmercury, bioaccumulation, mercury methylation

Rationale

Specific fish consumption advisories for seafood have been issued by public health agencies such as the US FDA and EPA, Health Canada and the UK Food Standards Agency.[1)] These advisories have been arisen from public health concerns as fish consumption is the principal exposure route of MeHg to human.[2)] Concentrations of MeHg in fish have reached levels of concern in aquatic environments, such as lakes, river, estuaries, and ocean.[2-6)]

Although the US and many other industrialized countries have reduced Hg use and release in recent years, these reductions are not reflected yet in the environment and no fish consumption advisory has ever been removed from any water body. In fact, in the US, lake acres and river miles under advisories for Hg have increased far more than those for other bioaccumulative pollutants such as PCBs and dioxins.[7)] Additionally, it has received much attention that Hg is a global pollutant and persistent in environments. In line with this, UNEP (United Nations Environment Programme) published a report, "Global Mercury Assessment", in 2002, reflecting internationally growing concerns of Hg in the environment.[8,9)]

Recently, Korean Ministry of Environment (MOE) reported that the average Hg level in human blood (4.34 μg/*l*) was much higher than that in the US and Germany (0.82 and 0.58 μg/*l*, respectively).[10)] However, there is a lack of explanation for this high level of Hg in blood, raising the immediate necessity of Hg research in Korea much in depth. Extensive monitoring, as a first step, should be conducted to examine Hg distribution in water, sediment, and biota as well as to locate hot spots that urgently need our attention. Better understanding in Hg transport and behavior in our environment will certainly help achieve reliable assessment of Hg and MeHg environmental and health effects.

Mercury Sources

A variety of anthropogenic activities (e.g. mining, smelting, burning of fossil fuel, waste incineration, and the production of steel, cement, and phosphate) contribute to the increase of Hg levels in the environment.[9,10)] Atmospheric deposition and riverine

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inputs are typically the primary sources of Hg to aquatic systems.[11-15] Anthropogenic emissions have significantly changed the input of Hg into the global atmosphere and most of the Hg accumulating in the ocean, and most remote ecosystems, comes from atmospheric deposition.[16]

At present, emissions in the Western World appear to be decreasing while inputs in other locations are increasing, with Asia being the largest contributor of anthropogenic Hg emissions.[10,17-19] However, there is a paucity of reliable information regarding Hg emissions, distribution, and biogeochemical behavior in Asia.[20] Moreover, it is likely that fast growing economy in China will accordingly increase energy demand (e.g., coal combustion), leading to increased Hg emissions. Given the geographical location of Korea and westerlies typically blowing from China, the increased Hg inputs can be easily transported to Korean peninsula. Thus, accurate assessment to which extent Hg emissions from China contribute to Hg budget in Korea and their impacts are greatly in need. In addition, it is imperative to evaluate anthropogenic Hg inputs from Korea on a local basis.

Biogeochemical Cycling of Mercury in Aquatic Environments

Once Hg enters aquatic environments, it undergoes various chemical and biological processes. Within oxic waters, Hg binds with inorganic ligands (e.g. Cl^-, OH^-) or dissolved organic carbon (DOC), or sorbs to particulate matter. Hg can also be reduced microbially or abiotically to elemental Hg and it is volatilized to the atmosphere as most waters are supersaturated with respect to the solubility of atmospheric elemental Hg.[16] Within anoxic environments, Hg forms strong aqueous complexes with sulfide and precipitates as HgS or is incorporated with sulfide phases such as acid volatile sulfide (AVS).[21-23] Hg can be converted to MeHg in anaerobic conditions by SRB, the important mediators of Hg methylation.[24] A major organic form of Hg, MeHg, bioaccumulates through aquatic food chains more efficiently than inorganic Hg.

While sediment is considered to be an important sink for Hg, Hg contamination in the sediment is of concern because there are many potential pathways for the Hg to be transported to aquatic food chains. In other words, sediment can be a significant source of Hg into the overlying water via various processes including diffusion, resuspension, and bioturbation.[12,13,25-27] The mobility and bioavailability of Hg and MeHg depend upon the nature and concentration of the binding phases in the sediment, which apparently are controlled by sediment redox status. The methylation of Hg depends upon environmental factors that control the overall metabolic activity of the methylating organisms (e.g. SRB) and the bioavailability of Hg in the matrix where methylation occurs. As the supply of organic carbon enhances Hg methylation rate,[28] the distribution of methylation activity depends upon the distribution of biodegradable organic matter. In addition, it appears that recycling of Hg in the sediment can play a large role in balancing between methylation and demethylation that ultimately determines MeHg concentration.[29]

Furthermore, recent studies suggest that shelf sediments could be important sources of MeHg to ocean fish.[30,31] However, for this to be true, it must be relatively stable in ocean waters to be transported to regions where MeHg may be bioaccumulated into the food chain. As suggested by Whalin *et al.*,[32] the stability of MeHg in coastal waters is important in transporting any MeHg released from estuarine and coastal sediment to the ocean waters, where MeHg accumulation into the food chain can occur.

In order to obtain reliable data on Hg and MeHg biogeochemical cycles, Hg clean techniques should be strictly applied to sample collection and analysis. Especially for water, MeHg concentrations are typically very low in ppt (parts per trillion) levels 16, 34-36 and, thus, extra care must be taken in sample collection, handling, storage, preparation, and analysis. To avoid contamination issues, sampling devices and storage bottles must be acid cleaned before use. Dust free clean room condition is typically required for acid cleaning procedure and sample preparation. For example, it is strongly recommended that water filtration for Hg analysis is conducted under laminar hood or in clean room condition. In addition, Quality Assurance (QA) program should be included in order to ensure that all data generated are scientifically valid. Quality

Control (QC) procedures must be followed to estimate the quality of analytical data, for instance, the precision and bias of the data.

Summary

Mercury is continuously mobilized, deposited and re-mobilized in the environment. If Hg release to the environment is reduced, resultant decreases in Hg levels in the environment would occur slowly, most likely over many decades or centuries. Given the likely increased Hg inputs due to anthropogenic emissions in Korean Peninsula, it is likely that Hg burden in fish in regions impacted by local and regional deposition will be higher. However, there is a lack of studies relating Hg inputs from various sources (including point sources and atmospheric deposition) to Hg levels in fish and its impact on human health in Korea. Thus, it is imperative that studies must be conducted to evaluate the environmental and health effects of anthropogenic Hg inputs. There should be long-term studies in order to obtain reliable data for accurate assessment. Additionally, other factors besides increased Hg input may also be contributing to higher levels of Hg in fish and this needs further investigation. For assurance of data quality, QA/QC program must be accompanied in both field and laboratory activities.

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