
IMPACT OF MERCURY ON MARINE AND TERRESTRIAL ECOSYSTEM

A Project Report

CHY 1001 (Environmental Studies)

Submitted by

PRATHAPANI SATWIKHA

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VIT-AP UNIVERSITY
AMARAVATI
ANDHRA PRADESH, INDIA

ABSTRACT :

Mercury (Hg) is a global pollutant that affects humans health and ecosystem . We synthesize understanding of sources, atmosphere-land ocean Mercury dynamics and health effects, and consider the implications of Hg control policies . A key link between inorganic Hg inputs and exposure of humans and wildlife is the net production of methylmercury, which occurs mainly in reducing zones in freshwater, terrestrial, and coastal environments, and the subsurface ocean. Elevated human exposure to methylmercury primarily results from consumption of estuarine and marine fish. Developing the most at risk from this neurotoxin but health effects of highly exposed populations and wildlife are also a concern.

Mercury contamination in water has been an issue to the environment and human health. Mercury in marine and oceanic waters has been reviewed. In the aquatic environment, mercury occurs in many forms, which depend on the oxidation-reduction conditions. Mercury concentrations in marine waters in the different parts of the world have been presented .The mercury content in benthic sediments usually reflects is level in the water reservoir, particularly in reservoirs situated in contaminated areas .

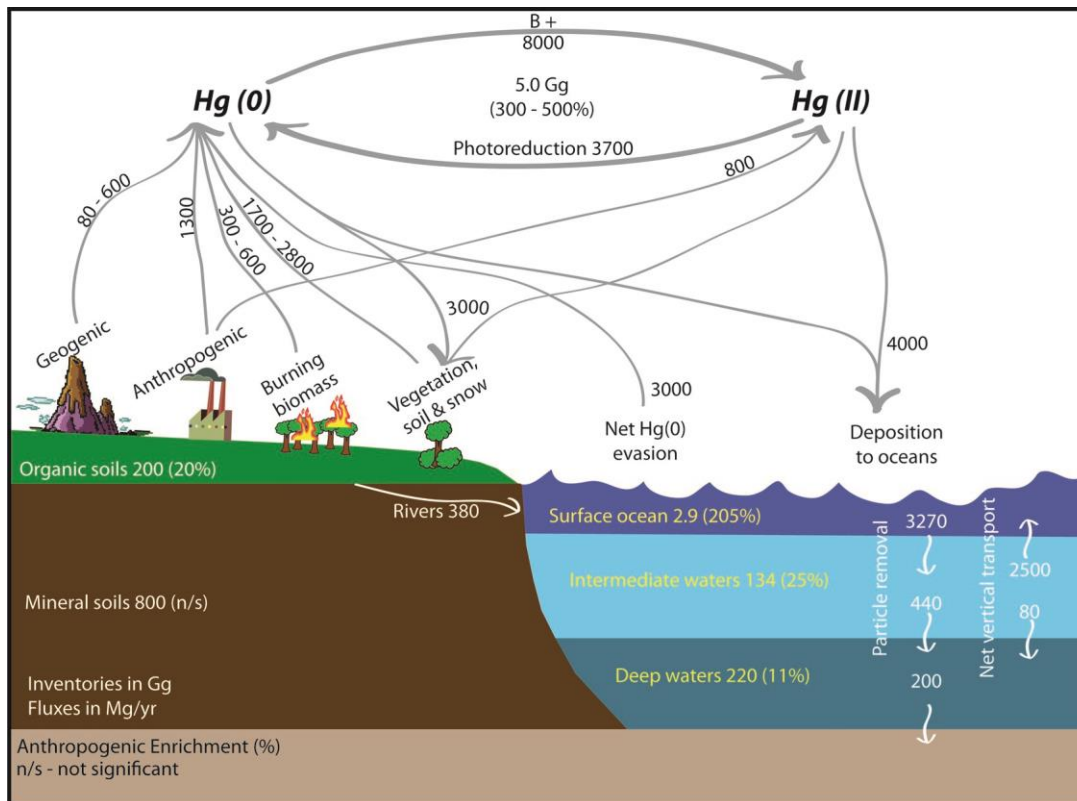
INTRODUCTION :

The socio-economic consequences of mercury (Hg) contamination and exposure of humans and wildlife to methyl Hg (CH₃Hg) have prompted policies and regulations to limit Hg releases from human activities and to control its transport within and among the atmosphere, freshwaters, the lithosphere, and the ocean at local, regional, and global scales. We synthesize the current understanding of Hg and CH₃Hg sources, transport and fate globally, and discuss the potential variation of CH₃Hg exposure to changes in Hg emissions and other environmental perturbations, and impacts on human health and environmental quality. We discuss the most current knowledge on

- (1) the scale of Hg emission impacts (local-regional-global);
- (2) the relative importance of geogenic vs anthropogenic emission sources;
- (3) the recovery response time for ecosystems after emission controls (years decades-centuries);

Mercury is a naturally occurring element, but has been directly mobilized by humans for thousands of years into aquatic and terrestrial ecosystems through mining, the use of Hg in precious metal extraction, its presence as a trace contaminant in many materials (e.g., coal, metal ores), and its use in products (e.g., paint, electronic devices) and by industry (chlor-alkali plants; as a catalyst).The atmosphere is the foremost transport pathway of Hg emissions, whereas land and ocean processes play an important role in the redistribution of Hg in terrestrial, freshwater, and marine ecosystems and the production of CH₃Hg that drives the major human exposure route, consumption of fish, particularly marine fish. The temporal and spatial scales of Hg transport in the atmosphere and its transfer to aquatic and terrestrial ecosystems depend primarily on its chemical and physical forms.

Mercury is a concern because it is absorbed easily into the food chain. In other words, tiny organisms can absorb mercury, and then tiny ocean fish eat those organisms, and then larger fish eat the smaller fish.



OBJECTIVES :

- **Atmospheric concentrations :** The three major Hg species in the atmosphere are elemental $Hg(0)$ in the vapor phase, gaseous inorganic $Hg(II)$ compounds (also termed reactive gaseous Hg; RGM), and particulate-phase Hg ($Hg(p)$).
- **Precipitation:** Although atmospheric Hg is dominated by $Hg(0)$, gaseous $Hg(II)$ is much more soluble and is the dominant form in precipitation. In a global pattern similar to that of atmospheric TGM concentrations, Hg concentration in precipitation over land generally increases from south to north .
- **Dry deposition :** Dry deposition, deposition to surfaces during precipitation-free periods, also contributes atmospheric Hg to terrestrial systems. Because of the large area of receptor surfaces, dry deposition of Hg is much more important in forests.
- **Litterfall :** If adsorption of gaseous $Hg(II)$ and capture and oxidation of $Hg(0)$ by the canopy are likely sources of Hg in throughfall and if Hg strongly binds to organic matter it is unlikely that all of the adsorbed Hg will be removed from the canopy during precipitation events.

- **Foliar uptake :** The source of foliar Hg appears to be almost exclusively the atmosphere. Several greenhouse and laboratory studies have indicated that Hg uptake from soil is limited, with roots acting as a significant adsorption site for Hg and hence a barrier for its further transport to foliage .
- **Flux :** Both the quantity of litterfall and its Hg concentration are important in affecting inputs to forested watersheds.. Forests in areas with longer growing seasons are likely to have both a greater quantity of litterfall and higher Hg litter concentrations as a consequence of a longer period of foliar uptake.

DISCUSSIONS :

Deposition of Hg by direct precipitation in the open in unpolluted North Temperate areas is the range of 5 to 15 $\mu\text{g m}^{-2} \text{a}^{-1}$ with an overall mean of 10 $\mu\text{g m}^{-2} \text{a}^{-1}$. Atmospheric deposition of Hg to forests is about four times open precipitation (38 $\mu\text{g m}^{-2} \text{a}^{-1}$) because of additions via throughfall, wash off of dry deposition, and litterfall, dropping of senescent leaves that have accumulated atmospheric Hg. Atmospheric deposition of Hg to lakes is only about one-fourth that to forests in the same geographic area because the lakes lack the forest canopy and hence surfaces for both dry deposition and foliar accumulation. Deposition of MeHg is only about 1% of HgT deposition, and variations in ratios of MeHg to HgT in deposition do not appear to be related to variations in ratios in streamflow from watersheds.

Loss of Hg from terrestrial ecosystems can be either as a gas or in solution. The first pathway has implications for Hg in the atmosphere, including concentrations and deposition to other systems, while the latter has implications for aquatic systems and human health. The strong binding of Hg to organic matter, including dissolved organic matter (DOM) (or dissolved organic carbon (DOC)) in waters and soil organic matter (SOM), is critically important to its behavior in the environment. Although ligands such as OH^- and Cl^- have some theoretical importance, in most cases “It is mainly the physical fractioning of soil organic matter (dissolved vs. adsorbed) that determines the behaviour and distribution of Hg in soils.” and “chloride complexation is not quantitatively important in most soil and fresh water systems”. It is generally acknowledged, then, that “Studies at the watershed level have shown that Hg^{2+} is the predominant form of Hg in soils and surface waters and that it is associated with organic substances” . The binding of Hg to organic matter appears to be exclusively associated with reduced S groups whose concentration in natural systems is high enough to bind all Hg(II).

Volatilization because of the relatively high vapor pressure of Hg(0) at ambient conditions, Hg can be lost from terrestrial watersheds by volatilization. Most research has emphasized loss from soils, where volatilization is presumed to require three steps, reduction of Hg(II) to Hg(0), diffusion or mass transport of Hg(0) to the soil surface, and

diffusion or mass transport of the Hg(0) across the soil–air boundary layer into the atmosphere. If Hg(0) is present in soil as a gas, in solution, or adsorbed, the first step is obviated. The reduction of Hg(II) can potentially be accomplished by both biotic and abiotic agents. In an adaptation to Hg toxicity, microbes can enzymatically reduce Hg(II) to Hg(0). This reduction is induced by toxic levels of Hg, and below the minimum Hg threshold concentration there is usually no induction and hence no reduction. Levels of Hg(II) found in uncontaminated environments are usually lower than that threshold (about 10 ng L⁻¹ in solution). Microbial Hg reduction is also unlikely in anaerobic environments; presence of organic sulphides in such environments may strongly bind Hg, reducing its toxicity so that the microbial enzyme systems are not induced.

Both early and more recent laboratory work have shown that when Hg(II) is applied as salts to soils, a rapid loss of 10 to 30% of the Hg occurs within 10 to 15 days. The pattern of loss is a rapid initial rate followed by a sharp decline to low rates, suggesting an abiotic reduction mechanism because of lack of a lag phase characteristic of enzyme induction. The Hg(II) reduction has been attributed to a reaction with DOM in soil solution, with the rate decline attributed to the decreasing availability of Hg for reduction because of binding with SOM. Because of the much greater concentration of DOM than Hg(II) in soil solution, it can be described as a pseudo-first-order reaction with the rate linearly related to the Hg(II) concentration. Another potential agent of reduction is sunlight, either by direct photolysis of Hg compounds or by photolysis of other reactants that then reduce Hg(II). Such reactions are unlikely in closed-canopy forests, but could be important in open agricultural areas. Because of the plethora of reactants and conditions in terrestrial environments, many other reduction reactions could also occur. In particular, wet areas in the landscape such as near stream channels or microtopographic depressions are usually strongly reducing environments and could provide conditions leading to significant Hg(II) reduction .

Many other factors can influence Hg volatilization. Both the vapor pressure of volatile Hg species and biotic or abiotic reaction rates are temperature dependent, and higher temperatures increase rates of Hg loss in the laboratory . Temperature dependence of volatilization in the field is more difficult to assess because of the interactions of temperature with other environmental factors. In general, however, highest rates of Hg volatilization have been reported in summer as compared to other seasons and during the day as compared to night. In a boreal forest in Sweden, Hg that was deposited to the soil surface during the winter was apparently emitted or re-emitted during the remainder of the year. Similarly, Hg concentrations in the organic-rich aspen forest floor in Alberta, Canada, declined from high levels in spring following snowmelt through the summer to a minimum in August, and then increased in autumn, a time of both leaf fall and cooler temperatures. These observations could be interpreted as volatilization by higher summer temperatures of labile forms of Hg that were deposited during the winter. Finally, in portions of a peat core from an ombrotrophic bog in Spain that were deposited during periods of globally cool climate, up to 50% of the Hg was represented by Hg(0); in other parts of the core nearly all (>80%) Hg(II) was bound to organic matter.

In the aquatic environment, mercury can be adsorbed on sediment particles, thus constituting a substantial mercury resource. In the sediments in water reservoirs, both as a result of chemical reactions and under the impact of biological factors, e.g., those related to the activity of microorganisms, methylmercury, CH_3Hg^+ , and dimethylmercury, $(\text{CH}_3)_2\text{Hg}$, emerge.

Biological mercury transformations, along with the processes of its chemical transformations, provide the basis for mercury cycling in the biosphere; furthermore, the role played by the biological transformations themselves is not fully known and probably depends on mercury concentrations and the conditions occurring in the environment.

The reduction of Hg^{2+} and the degradation of organic mercury compounds are processes constituting natural detoxification mechanisms, which unfold in bacteria and enable their growth and development in the presence of these toxic compounds. Bacteria that are resilient to the harmful impact of Hg^{2+} are capable of producing mercury, which catalyses the reaction with the involvement of nicotinamide adenine dinucleotide phosphate (NADPH). Due to its low water solubility and high vapor pressure, Hg^0 which emerges as a result quickly escapes into the atmosphere. Some bacteria which are resilient to Hg^{2+} due to the presence of organomercurial lyase (OL) also demonstrate resistance to the toxic impact of organic mercury compounds. The resistance to the harmful impact of organic forms of mercury is related to the action of both enzymes, lyase and reductase, while all the bacteria which are not vulnerable to the impact of organic mercury compounds are at the same time resilient to the toxic effect of Hg^{2+} (a wide range of resilience). However, a large part of bacteria do not show the capacity to produce organomercurial lyase; as a result, they are vulnerable to the presence of this form of mercury in the environment (a narrow range of resilience).

Mercury in Marine and Oceanic Waters :

In the biogeochemical mercury cycling, a substantial part of it reaches seas and oceans and its important source is its atmospheric deposition.

In oceanic waters, mercury mainly occurs in the forms of Hg^0 , Hg^{2+} , MeHg , and diMeHg and in colloidal form. In marine waters, mercury forms compounds with chlorine (HgCl_3^- and HgCl_4^{2-}) to a greater extent than oxides, as is the case in freshwaters. It has been demonstrated that in salt waters, Hg^{2+} forms complexes with halides, such as those of chlorine, and these complexes do not undergo the reduction and methylation processes as quickly as the other Hg^{2+} compounds do. Dissolved gaseous mercury (DGM) arises as a result of the transformations of both Hg^0 and Me_2Hg with the form Hg^0 dominating in the upper layer of the ocean.

CONCLUSION :

The Volatilization is an important Hg flux from terrestrial systems. Its measurement is highly uncertain with measured rates from soils having a central tendency near $10 \text{ ng m}^{-2} \text{ h}^{-1}$. Gas-phase exchange of $\text{Hg}(0)$ between the atmosphere and the forest canopy may be the

largest mechanism of loss of Hg from terrestrial systems, but data are limited and uncertain. Watershed factors that increase hydrologic export of DOC are likely to increase Hg export. Particulates are also important in Hg transport, especially in steep or erosive systems such as cultivated land, but their absolute significance is difficult to determine because their episodic nature makes measurement difficult. Transport of Hg in lower soil horizons and groundwater is minimal. Concentration and flux of HgT from watersheds are weakly and inversely related to watershed size.

The surveys on the mercury contents in oceanic and marine waters carried out in the second half of the twentieth century showed that its levels were comparable to those that now occur in the waters of the global ocean. This phenomenon relates to the fact that the mercury level in the global ocean has not yet reached the phase of a dynamic equilibrium with its level in the atmosphere.

REFERENCE :

1. Aastrup, M., Johnson, J., Bringmark, E., Bringmark, I., and Iverfeldt, Å. 1991. Occurrence and transport of mercury within a small catchment area. *Water Air Soil Pollut.* 56: 155–167.
2. Allan, C.J., and Heyes, A. 1998. A preliminary assessment of wet deposition and episodic transport of total and methyl mercury from low order Blue Ridge watersheds, S.E. U.S.A. *Water Air Soil Pollut.* 105: 573–592.
3. Pirrone, N.; Mahaffey, K. R. *Dynamics of Mercury Pollution on Regional and Global Scales*; Springer Publishers: New York, 2005; p 744.
4. Pirrone, N.; Mason, R. *Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models*; Springer: New York; p 637.
5. Elin, N. E.; Wu, S.; Nam, K. M.; Reilly, J. M.; Paltsev, S.; Prinn, R. G.; Webster, M. D. Global health and economic impacts of future ozone pollution. *Environ. Res. Lett.* 2009, 4, 9.
6. Aidin'yan N. Content of mercury in some natural waters. *Chemical Abstracts.* 1962;57:16336.
7. Bilandžić N, Dokić M, Sedak M. Metal content determination in four fish species from the Adriatic Sea. *Food Chemistry.* 2011;124:1005–1010. doi: 10.1016/j.foodchem.2010.07.060.