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Review Article

HAZARDS OF MERCURY POISONING & PREVENTION STRATEGIES

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In the long history of water pollution, the Minamata incident was unique. The mystery of the existence of methylmercury in sea fish was baffling at first since the source was inorganic mercury compound discharged into the Bay by the Minamata chemical company (Japan). The missing link between inorganic mercury in Bay water and methyl mercury in sea fish was bridged only after extensive research since the 1950s. This is the first known case where the natural *bioaccumulation* (in fish) of toxic material (methyl mercury) killed about hundred people and genetically damaged a large population. Genetic defects were observed in babies whose mother had consumed the contaminated fish from the Bay. The Minamata incident was followed by a more tragic report of Hg-poisoning from Iraq in 1972 where 450 villagers died after eating wheat, which had been dusted with mercury-containing pesticides. These two tragic events boosted the awareness of Hg as a pollutant so that was studied more extensively than any other toxic element [1].

India is becoming the dumping ground for mercury as industrialized nations phase it out of their systems. India still imports over 250tonnes of Hg every year and more than 220tonnes find its way out in emissions from sources such as coal-fired thermal power plants and the chlor-alkali industry which uses it in the production of caustic soda.In nature, Hg occurs as a trace component of many minerals, continental rocks containing an average of about 80 ppb of Hg. The principal ore of Hg is cinnabar (HgS). Fossil fuels, coal and lignite contain about 100 ppb of Hg. The natural abundance of Hg in soil is 10 ppb. Hg finds a wide variety of applications. The largest consumer is the chlor-alkali industry, which manufactures Cl_2 and NaOH by an electrolytic process using Hg-electrodes. The second largest consumption of Hg is in the production of electrical apparatuses e.g. Hg vapour lamp, electrical switches, Hg batteries. The third largest consumer is the agricultural industry using a large number of fungicides (viz. methyl mercury nitrite, methyl mercury acetate and ethyl mercury chloride) for seed dressings. The impact of seed dressing is enormous since it is applied to a large volume of seed, which is subsequently sowed over millions of acres, thereby causing widespread dispersal of Hg compounds. Furthermore, Hg undergoes translocation in plants and animals and then finds its way into the human food chain.

Natural water contains 0.1 to 0.01 ppb of Hg. Once Hg is absorbed on sediments of water bodies and streams, it is slowly released into water and constitutes a reservoir which is likely to cause chronic pollution long after the original source of Hg is removed. Natural addition of Hg to oceans is about 5000tonnes per annum and a further 5000tonnes is added via human activities [2]. Elemental Hg is fairly inert and nontoxic. If swallowed, it is excreted without serious damage. It has a fairly higher vapour pressure and so the vapour, if inhaled enters the brain through blood stream, leading to severe damage to the central nervous system (CNS). Hence Hg should be handled only in well-ventilated areas and spills should be cleaned up as quickly as possible. Hg^+ (mercurous ion) is not toxic as it combines with chloride ions present in stomach and forms insoluble salt, however Hg^{2+}(mercuric ion), is fairly toxic. Because of its high affinity for sulphur atoms, it easily attaches itself to the sulphur-containing amino acids of proteins. It also forms bonds with haemoglobin and serum albumins containing sulphydryl groups [3].

The most toxic species are the organomercurials, particularly CH_3Hg^+ which are soluble in fat, the lipid fractions of membranes and brain tissues. The most dangerous aspect is the ability of RHg^+ to move through the placental barrier and enter foetus tissues. Attachment of Hg to cell membrane is likely to inhibit active transport of sugars across the membrane and allow the passage of potassium to the membrane. In case of brain cells, this results in energy deficiency in the cell and disorders in the transmission of the nerve impulses. This explains why babies born to mother subjected to methyl mercury poisoning suffer from irreversible damage to the central nervous system (CNS), including cerebral palsy, mental retardation and convulsions. Methyl mercury poisoning also leads to segregation of chromosomes, chromosome breakage in the cell and inhibits cell division [4].

All the symptoms of mercury poisoning set in at blood levels of 0.5 ppm of methyl mercury ion. It is methyl mercury ion, which enters the food chain, through plankton, and is biologically magnified (*biomagnification-* in fish), by a factor of 10^3 or more as it passes through the food chain. The Hg concentration builds up at each level of the food chain. This is valid even in uncontaminated waters. Hg has always been a part of our environment and Hg cycles existed long before any industry developed. Large fish of ancient ages preserved in some museums, have been found to contain significant levels of mercury. However, mercury pollution considerably enhances the Hg concentration in each level of the food chain [5, 6]. Mercury- and compounds such as methyl mercury are neurotoxins which leave children in particular, very vulnerable. Hg poisoning can lead to memory loss, impaired co-ordination, vision disturbances, irritability, depression, suicidal tendencies, bleeding gums and Alzheimer's effect on heart, kidney & immune system. It can cause frequent abortions and lead to the birth of mentally retarded babies. There is also a suggested link to cardiovascular problems and effects on digestive system, liver & skin. "Levels of mercury currently regarded as safe for adults could impair brain function. Low levels of mercury are already thought to damage the nerves systems of foetuses and babies," in accordance with a report published in esteemed journal- *New Scientist*.

According to a report of Toxics link - chlor-alkali industry is responsible for about 100-150tonnes of Hg-emissions. Power plants using coal, which contain Hg, release about 60tonnes-unshackled by any emission standards. Other sources-thermometers, blood pressure instruments and more all adding up to about 20 tonnes a year. Once released, Hg persists in the atmosphere, first impacting locally and then travelling thousands of miles. While it is also released naturally, human activities have boosted atmospheric levels three fold since pre-industrial times. The problem spots in the report are Singrauli, Bhopal, Delhi, Gujarat and industrial areas such as Alkeshwar and Panipat. A 2002 CPCB estimate is that 17 per cent of power plant Hg emissions are from the Singrauli region.

Karnataka's Kali river peters out to a slow, toxic end. There are six dams on Kali to facilitate hydro-electric projects. Virtually Karnataka's powerhouse producing 1200 MW power, it supports the Kaiga nuclear power plant which produces an additional 440 MW of power. For a river which is so giving, the Kali has, for decades, suffered the injection of toxic effluents from a paper factory, West Coast Paper Mills Limited, one of the India's oldest paper mills and the biggest industrial unit located on Kali's bank. Besides the paper mill, there is a ferro alloys factory, a plywood factory and other small industries along its path that spew effluents into the river. According to an estimate, the mill releases nearly 64,800 Kilolitres of effluents into the river daily.

The Peoples' Science Institute (PSI) at Dehradun, which studied Kali's physicochemical and microbiological characteristics in 2004 to analyze the effluents' impact, made some startling revelations. It said the daily influx of Hg from the effluents into the river was "around 345gms/day". Downstream, they found various percentages of Hg concentration in the river and it was highest at the Bomana Halli dam site. "The concentration of toxic metal recorded here was 12μg/L..... This is a perilous situation.... considering the fact that the fishes reared here are sold in Dandeli and other towns", the report warned. In the agricultural fields around Kariampalli, the dilemma faced by farmers becomes clear [7]. River waters of Ganga, Gandak and Gomti too, have shown the poison with high Hg levels having been found in fish in two major metros Kolkata and Mumbai.

While India has had brushes with Hg waste dumping - the most publicized case being Hg used in the production of NaOH escapes into the air. In feb-2003, the UN environment programme's first global study on this hazardous heavy metal revealed that Asia accounts for the bulk or 860tonnes of quantified new man made emissions into the atmosphere. Overall coal fired power station and waste incinerators are responsible for about 1500tonnes or 70 per cent of new emissions to the atmosphere annually.

Mitigation strategies: Removal of Hg from polluted sites includes incineration at high Hg concentrations, and safe storage in landfills or in underground storage at low concentrations. Bioremediation is one of the potent methods that can be used for Hg-reduction. The method relies on the potential of the meroperon-based resistance mechanism in bacteria, which functions by enzymatic breakdown of organomercurials and reduction of mercury ions (Hg^+, Hg^{2+}) to water-insoluble metallic Hg. The enzymes involved in this process are organomercurial lyase and mercuric reductage. The former converts an organomercury compound to mercuric ions and later reduces Hg^{2+} to metallic mercury with the help of NADPH. Hg thus produced diffuses out of cells and accumulates in pure form in the medium. The high vapour pressure of Hg ultimately results in its volatilization from media.

A Hg-resistant bacterial strain, *Pseudomonas putida* Spi^3, isolated from river sediment for treatment of chloralkali wastes, was used. Biofilms of *P. Putida* Spi^3 were grown on porous carrier material in laboratory column bioreactors and fed with chloralkali waste water with 7-9mg/l Hg. The bacteria carried out Hg reduction with 90-98 per cent efficiency. Two actinomycete strains, CHR3 and CHR28, from metal contaminated sediments from Baltimore Inner Harbour which were found to be resistant to $HgCl_2$ and phenylmercuric acetate (PMA), were isolated. Hybridization experiments indicated that genes homologous to mercuric reductase and organomercurial lyase of *Streptomyces lividans were* present in the strains. Broad spectrum Hg- resistant *Bacillus pasteurii* strain DR2 from industrial effluent of Durgapur Steel Plant was isolated the strain grew in presence of PMA as the sole carbon source and could tolerate phenyl mercuric acetate (PMA) up to a concentration of 40µM. the enzyme PMA lyase synthesized by the bacteria was found to degrade not only PMA but also other organomercurials like methylmercuric chloride and methoxyethylmercuric chloride [8]. Mercury resistant bacteria isolated from guts and gills of fishes collected from East Kolkata wetland could tolerate high level of Hg. Narrow spectrum Hg-resistant bacteria could reduce $HgCl_2$ from liquid medium in the range of 64-89 per cent. The broad-spectrum Hg-resistant bacteria volatalised $HgCl_2$ at the level of 80-94 per cent and PMA 72-84 per cent [9].

Lemna minor (duckweed) is another prospective tool for absorbing Hg from polluted water. High concentrations of Hg has been found in the plant samples collected from Tiljala wetlands of the eastern fringes of Kolkata that serves as a sink for deposition of urban and industrial wasrtes. Natural unexposed population of duckweed, when cultivated in laboratory, was also found to accumulate Hg^{+2}. A model plant *Arabidopsis thaliana* with a bacterial gene merB, the product of which converts organomercurials to inorganic Hg, was also engineered. Transgenic plants expressing the gene could tolerate a wide range of concentrations of monomethyl $HgCl_2$ and PMA [10].

The usual process for removal of Hg is the safe storage in landfills or in underground sites at low concentrations. In European countries, the process effluent from chloralkali factories is currently cleaned by hydrogen sulphide (H_2S) precipitation, hydrazine ($H_2N\text{-}NH_2$) precipitation or ion exchange columns [11]. The processes ultimately lead to confined dumping of Hg instead of its removal. The technologies related to chemical engineering for Hg removal are expensive and disruptive. Excavation and roasting of soil in the Hg-contaminated sites is considered as the best demonstrated treatment technology, but it's impractical for very large sites and requires a high amount of energy. Vitrification and concrete capping which aims to stabilize Hg, render the site uninhabitable for plants, insects and other organisms. Bioremediation seems to be an ideal treatment that would degrade organomercurials, sequester other Hg forms and convert Hg to the least toxic chemical species without disturbing biological productivity.

Prevention measures: Hg-pollution can be prevented by adopting the following measures, as recommended by the Environmental Protection Agencies of USA and Sweden:

- All chloralkali plants must stop using Hg-electrode and switch to new greener technology.
- All alkyl Hg pesticides must be banned.
- All other mercurial pesticides must be restricted to some selected areas.

The Central Pollution Control Board (CPCB) has been trying to implement a Hg phase out programme for the caustic soda industry. Scientist have strongly recommended that fish consumption advisories be issued as is done in many other countries after a Delhi based NGO (Center for Science and Environment) used government data to show a six fold rise in imports of Hg in seven years.

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