Chapter

Perspective Chapter: The Toxic Silver (Hg)

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Abstract

In the late 1950s, residents of a Japanese fishing village known as "Minamata" began falling ill and dying at an alarming rate. The Japanese authorities stated that methyl-mercury-rich seafood and shellfish caused the sickness. Burning fossil fuels represent ≈52.7% of Hg emissions. The majorities of mercury's compounds are volatile and thus travel hundreds of miles with wind before being deposited on the earth's surface. High acidity and dissolved organic carbon increase Hg-mobility in soil to enter the food chain. Additionally, Hg is taken up by areal plant parts via gas exchange. Mercury has no identified role in plants while exhibiting high affinity to form complexes with soft ligands such as sulfur and this consequently inactivates amino acids and sulfur-containing antioxidants. Long-term human exposure to Hg leads to neurotoxicity in children and adults, immunological, cardiac, and motor reproductive and genetic disorders. Accordingly, remediating contaminated soils has become an obligation. Mercury, like other potentially toxic elements, is not biodegradable, and therefore, its remediation should encompass either removal of Hg from soils or even its immobilization. This chapter discusses Hg's chemical behavior, sources, health dangers, and soil remediation methods to lower Hg levels.

Keywords: Hg sources, soil contamination, Hg poisoning, chemical behavior, remediation techniques

1. Introduction

In the late 1950s, people and animals of a Japanese fishing village, called Minamata fell ill one after another and suffered from the same symptoms then died [1, 2]. The Japanese government named this strange disease "Minamat" and announced officially that its cause was the consumption of fish and shellfish that contained high levels of methyl-mercury due to mixing the bay water therein with industrial wastes coming from a chemical factory [3]. Since then, the scientists and government administrators tried hard to avoid a repeat of such type of incidents [4]. Mercury (Hg) is one of the 10 leading worldwide chemicals of concern [5, 6]. This element is denoted by the symbol "Hg" with atomic number equal to 80. Its melting point is −38.83°C while the boiling point is 356.73°C. In the periodic table, only Hg is a metal found in a liquid state at standard temperature and pressure [6]. Generally, mercury level increases progressively in the environment due to anthropogenic activities [7]. All mercury forms that are released during mining and other industries will eventually wind up in soils or surface water representing a potential threat to human health, and the surrounding ecosystem. Every living organism, in the environment (humans, animals, and plants to the smaller ones such as bacteria), is vulnerable to the effects of mercury poisoning. As a result, countries stand to lose millions of dollars in earning potential every year due to mercury contamination.

2. Forms of mercury in the environment

Mercury (Hg) is recognized by its characteristic shiny silver appearance. In the environment, it occurs in different inorganic (mercurous ion (Hg^{+1}) and mercuric ion (Hg^{+2}), and organic forms (methyl mercury (CH_3Hg^+), ethyl mercury ($C_2H_5Hg^+$), and phenyl mercury ($C_6H_5Hg^+$). The elemental mercury is the purest form [8, 9] and, at the same time, exhibits the least toxicity [10]. Under anoxic and suboxic conditions, inorganic Hg can be transformed into CH_3Hg^+ through sulfate-reducing and iron-reducing bacteria [6].

2.1 Sources of mercury

Mercury is introduced into the environment *via* natural and anthropogenic pathways. The first route results from volcanoes, weathering of rocks, forest fires, and soils [11]. The second one represents one-third of its content in nature which is related to anthropogenic activities coming from industrial processes [12] such as the burning of fossil fuels which represent up to 52.7% of Hg emissions [13], gold mining, cement production [9] and combustion of fossil fuel and agricultural additives that increases Hg levels in soil, for example, municipal [6], sludge, fertilizers, lime, and manures [10].

Long-term mining and smelting activities could bring considerable amount of Hg to the surroundings [14]. The majority of mercury's compounds are very volatile and thus travel hundreds of miles with the wind before being deposited on the earth's surface, hence contaminating the surrounding areas [15]. Generally, mercury in air can be carried by rain and eroded soils and run off to the surface waters and no one becomes safe [13]. In a study by Rodríguez Martín [16], most emitted Hg results from power plants that burn coal to create electricity; they account for about 42% of all manmade mercury emissions.

The main countries, contributing to the majority of emitted mercury (kg year^{-1}) according to the United Nations Environment Program report in 2018, are: China (572,195), India (205862), Indonesia (156766), Brazil (71470), and Russia (60,949 tonnes), representing an average percentage of 25.73, 9.25, 7.05, 3.21, and 2.74% of total emitted mercury, respectively [17].

3. Mercury in medicine

Mercury is used in dental amalgam fillings to increase its strength and longevity; yet it plays a negative role in increasing human toxicity [18, 19]. Although this type of pollution is going down as the number of medical waste incinerators is reduced, the health community is concerned about patients and other vulnerable groups who are exposed to in healthcare products [20]. Thiomersal is an organic compound used as a preservative in vaccines, and Merbromin (Mercurochrome) is a topical antiseptic used for minor cuts and scrapes and is still in use in some countries [21]. Mercury compounds are found in some over-the-counter drugs, including topical antiseptics, stimulant laxatives, diaper-rash ointment, eye drops, and nasal sprays [22]. The skin-whitening cosmetic products can also be a source of Hg pollution [23]. Even some traditional medicines in China as Siddha and Ayurveda may contain mercury that causes chronic poisoning [24]. Overall, air, water, food, cosmetics, and even vaccines are potential sources of human pollution with Hg [25]. Mercury and most of its compounds are extremely toxic and must be handled with care.

4. Mercury in food chain

Mercury enters the food chain *via* various pathways. Chloralkali industry is one of the European users that pollute Europe's aquatic environments with tones of mercury [20]. In aquatic environments, inorganic mercury biotransforms into methyl mercury, which makes mercury biomagnify in food chains [13]. High acidity and high concentration of dissolved organic carbon in the water enhance the mobility of mercury that enters the food chain [26, 27]. People, who eat a lot of fresh or marine food, have the high risk of mercury intake [28].

On the other hand, this pollutant (Hg) is highly mobile in soils; and can be absorbed easily by plant roots [12]; yet, in the presence of organic additives, the mobility of inorganic and organic forms of Hg could be diminished considerably, forming low mobile complexes [29]. Also, Hg in the atmosphere is taken up in substantial amounts by areal plant parts *via* gas exchange [30], accumulates in edible plant parts [8], and hence enters the food chain [6, 18, 19]. Additionally, sewage irrigation practices account for further soil contamination with Hg [31]. Anyhow, this contaminant has no identified biological role in plants [8]; nevertheless, it exhibits high affinity to forms complexes with soft ligands such as sulfur in the form of insoluble and stable compounds [32]. This in turn inactivates numerous enzymatic reactions, amino acids, and sulfur-containing antioxidants [33].

5. Mercury in sewage effluents

Municipal sewage has been noted as a significant environmental mercury (Hg) source. Mercury in the effluents of waste water treatment plants and mercury-based fungicides increase the discharge of mercury to the aquatic environment [34, 35]. Consumption of Hg-containing foods [12, 36] and exposure to common items like batteries [29] would increase the risks of mercury being excreted and flushed away in the city's sewage system. The mercury released by hospitals, dentist clinics, and other service facilities is a major source of Hg in sewage [37]. A total of 30 tons of total Hg (organic and inorganic) was loaded into sludge in China in 2019, accounting for around 3.6% of the total anthropogenic Hg release (including direct and secondary anthropogenic releases). It is worth noting that sludge treatment methods such as incineration, carbonization, and sludge/brick/cement manufacture pose the greatest threat to atmospheric Hg pollution [27]. Therefore, attention should be paid regarding Hg pollution of sewage effluents and standard regulations should be formulated in order to prevent the environment and human health.

6. Health risks associated with mercury hazards

The excessive population growth, Industrial Revolution, and unmanaged development led to negative impacts on the surrounding environment [34, 35].

Consumption of food high in its content of mercury is the main route of Hg-mediated health risks [12, 36]. Long-term human exposure to Hg increases its level in blood, sometimes exceeding 150 ng mL^{-1} [37], and this results in negative health risks related to neurodevelopment and neurotoxicity in children and adults [8, 23, 38], immunological, cardiac, motor reproductive and genetic disorders [13], nephrotic syndrome, peripheral neuropathy complications, Alzheimer's, Parkinson's, autism, lupus and amyotrophic lateral sclerosis [39]. Other symptoms may be included such as poor muscle coordination, tingling, numbness in fingers and toes [40, 41], reduced oxidative defense, thrombosis, vascular smooth muscle dysfunction, endothelial dysfunction, and dyslipidemia [33].

7. How to reduce human exposure from mercury sources

- Using clean renewable energy sources rather than the coal;
- Eliminate the use of mercury in mining, gold extraction and other industrial processes;
- Phase out use of non-essential mercury-containing products and implement safe handling, and use and disposal of remaining mercury-containing products [42].

Selenium and fish containing omega-3 fatty acids are thought to diminish mercury toxicity [33] *via* "restoring seleno protein activity" protection against mitochondrial injury and DNA damage, demethylation of methyl mercury and sequestration in complexes, as well as redistribution in the blood away from brain [43].

8. Remediation of Hg-contaminated soils and water

Increasing Hg emissions due to anthropogenic activities caused severe soil pollution issues [44–46]. As a crucial link between the atmosphere and water, soil plays a central role in the global Hg cycle [47]. Soil is not only an Hg sink, receiving Hg input from the environment but also reemitting it to the atmosphere [48, 49], water [42, 50], or the plants grown thereon [39].

Mercury, like other potentially toxic elements, is not biodegradable, and therefore, its remediation should encompass either removal from soil or immobilization [32]. The main Hg removal technologies are physical and chemical remediation methods, as well as bioremediation technology. Adsorption of Hg^{2+} and Hg(0) from water on surfaces of high surface area and high porosity such as chitosan derivatives, synthesized thioether-functionalized covalent triazine nanospheres, pentasil zeolite (type ZSM-5), and utilized silica-coated magnetic nanoparticles are the most common physical approaches for remediating Hg-contaminated soil [51]. Other techniques could help such as soil replacement, physical separation, soil vapor extraction, fixed/stabilized soil, vitrification, thermal desorption, and electrokinetic remediation technology [6]. The latter technique (electrokinetic remediation) depends on passing a direct current between electrodes through the soil to make the Hg ions move through an ion exchange membrane from the soil to the electrodes. The addition of chelating agents to soil could effectively increase the solubility and removal efficiency of Hg [6]. Recently, He and his research group introduced a novel *in situ* immobilization technology by injecting stabilized iron sulfide nanoparticles into soil to immobilize Hg [32].

The *in situ* thermal desorption is a promising technique of Hg remediation that does not need to dig up the contaminated soil; instead, thermal conductive heating (TCH) elements are inserted into the soil in order to directly transfer heat to above 600°C to volatilize various species of mercury, such as HgO, HgS, $HgCl_2$, and mercury associated with organic matter and thus achieve an acceptable decontamination level [51].

Biological remediation/bioremediation depends on plant and microbial in remediation soils [6]. In particular, genetically engineered plants can change methylmercury complexes, and mercury ions into metallic forms of lower toxicity, and then extract, detoxify, and/or sequester this contaminant from soil and water [10]. Phytoremediation is an umbrella term, which refers to the different low cost and eco-friendly technologies that utilize plants in decontaminating areas [52]. This includes: phytostabilization, phytoextraction, and phytovolatilization. This *in situ* application of phytoremediation lessens the disturbance of the surrounding environment and also declines the spread of contamination *via* air and water [32]. There are many other technologies such as the use of nanoparticles to remove/absorb Hg from soil, water, and flue gas, owing to their high adsorption capacity, small dimension, and other unique electrical, mechanical, and chemical properties [53].

Continuous monitoring of Hg levels in air, soils, water, and foods is necessity to ensure their sustainable safe use in order to protect human health and the surrounding ecosystem. In addition, increasing the awareness of humans about the danger of Hg is a proactive step to prevent and reduce the danger of Hg pollution. Furthermore, remediation protocols should be followed in Hg-contaminated areas to lessen its toxicity.

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