



Elemental mercury: Its unique properties affect its behavior and fate in the environment[☆]



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ABSTRACT

Elemental mercury (Hg^0) has different behavior in the environment compared to other pollutants due to its unique properties. It can remain in the atmosphere for long periods of time and so can travel long distances. Through air-surface (e.g., vegetation or ocean) exchange (dry deposition), Hg^0 can enter terrestrial and aquatic systems where it can be converted into other Hg species. Despite being ubiquitous and playing a key role in Hg biogeochemical cycling, Hg^0 behavior in the environment is not well understood. The objective of this review is to provide a better understanding of how the unique physico-chemical properties of Hg^0 affects its cycling and chemical transformations in different environmental compartments. The first part focuses on the fundamental chemistry of Hg^0 , addressing why Hg^0 is liquid at room temperature and the formation of amalgam, Hg halide, and Hg chalcogenides. The following sections discuss the long-range transport of Hg^0 as well as its redistribution in the atmosphere, aquatic and terrestrial systems, in particular, on the sorption/desorption processes that occur in each environmental compartment as well as the involvement of Hg^0 in chemical transformation processes driven by photochemical, abiotic, and biotic reactions.

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1. Mercury: a unique element

Mercury (Hg) is a naturally occurring element with a concentration of approximately $80 \mu\text{g kg}^{-1}$ in the earth crust and 0.3 ng L^{-1} in seawater (Fergusson, 1990; Jonasson, 1970; Gworek et al., 2016). In bedrock geology, it is mainly found in the mineral form of cinnabar (HgS), but it is also present in minor quantities in minerals such as livingstonite (HgSb_4S_8) and corderoite ($\text{Hg}_3\text{S}_2\text{Cl}_2$). The richest geologic deposits where mercury can be found are in areas called mercuriferous belts, which refer to geological regions associated with volcanic activity. One of the richest deposits found is in Almadén (Spain) which has been producing mercury for the past

2000 years (García Gómez et al., 2007). Since ancient times, mercury has fascinated humankind because it has a silver color, is liquid at room temperature, and forms an amalgam with gold. Due to its fascinating and unique properties, mercury has been used throughout history for different applications such as barometers, thermometers, electrical switches, fluorescent light bulbs, and ballast for submarines (Bank, 2012). Unfortunately, mercury is highly toxic to humans. The toxic effects of mercury were already known in the 19th century, where it was related to occupational exposure of mercury in Mad Hatter Disease (Wedeen, 1989; Buckell et al., 1993). One of the most toxic species of mercury is its methylated form, i.e. methylmercury, which can be bioaccumulated and biomagnified through the food chain, and in elevated concentrations, is highly toxic to humans. The first case of severe methylmercury poisoning was discovered in Minamata City, in 1956. During that time, people consumed large amounts of fish and shellfish contaminated with methylmercury that was from the wastewater discharge by the chemical factory Chisso Corporation

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to Minamata Bay and from methylation of wastewater inorganic mercury in the bay (Ekino et al., 2007; Eto et al., 2010). Local authorities initially thought that Minamata disease was caused by an infection, but further investigations led to the conclusion that methylmercury was the cause of Minamata disease. The symptoms that people from Minamata manifested due to consumption of contaminated fish and shellfish include sensory disorders, visual field constriction, hearing and speech impairment, ataxia, tremors, and disequilibrium, among others. The Minamata disaster and other instances of mercury poisoning led to the negotiation of the Minamata Convention Treaty in 2013 whose objective is to protect the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds (Selin, 2014).

Mercury is the only metal that is considered as a “global” pollutant because mercury in its elemental form (Hg^0) has an atmospheric residence time of 0.8 months to 1.7 years, allowing it to travel for long distances (Ariya et al., 2015). Also, mercury is considered a special element because its chemistry is different compared to other elements. For example, mercury is the only metal that is liquid at room temperature, and it can form amalgams with other metals. Since mercury is monomeric in the gas phase, it tends to form covalent bonds instead of ionic bonds such as $\text{Hg}^+ - \text{Hg}^+$ and $\text{Hg} - \text{C}$, and it has dramatically different properties than its neighbor gold (Au). In addition, its crystal structure is rhombohedrally distorted and so is different from the crystal structure of the other members of its group, e.g., zinc (Zn) and cadmium (Cd) which has a slightly distorted hexagonal close-packed crystal structure (Norrby, 1991).

Previous reviews on Hg in the environment have focused on the sorption of Hg^{2+} onto inorganic and organic colloids in aquatic systems (Liu et al., 2011a; Gerbig et al., 2011), chemical transformations of Hg^{2+} species occurring in aquatic systems (Vost et al., 2011), and Hg^{2+} fate in terrestrial environments (Gabriel and Williamson, 2004). To this point no review papers have focused on addressing the behavior of Hg^0 in the environment based on the fundamental properties of Hg^0 . Furthermore, there is a lack of understanding of the main processes governing Hg^0 behavior in the environment (Mason and Pirrone, 2009). Therefore, the principal objective of this review is to provide a better understanding of how the unique physicochemical properties of Hg^0 affect its cycling and chemical processes involved in different environmental compartments. This review is important because Hg^0 plays an important role in the air-water and air-soil exchange of Hg. Also, Hg^0 participates in chemical transformations driven by photochemical, abiotic, and biotic reactions.

1.1. Sources of elemental mercury

Elemental mercury can be introduced into the environment by both natural sources and anthropogenic activities (Fig. 1). Natural sources include volcanoes, forest fires, oceanic emission, and natural degassing of the earth's crust. Volcanic eruptions emit Hg^0 into the atmosphere due to tectonic movements and magmatic activity that can bring Hg^0 from geologically enriched deposits of mercury (mercuriferous belts) close to the plate tectonic boundaries to the atmosphere (Selin, 2009). From forest fires, Hg^0 that has been accumulated in the foliage through wet and dry atmospheric deposition as well as litterfall can be released back to the atmosphere with an annual emission estimate range from 300 to 675 Mg year⁻¹ (Amos et al., 2013). From oceans, Hg^0 can be re-emitted into the atmosphere by the reduction of Hg^{2+} in the water column through photochemical and biotic reactions (O'Driscoll et al., 2006; Amyot et al., 1997, 2000; Mason et al., 1995). From the earth's crust, Hg^0 evasion occurs due to geothermal activity.

Apart from natural sources, elemental mercury can also be released into the environment by anthropogenic activities such as mining, mineral processing, chlor-alkali production, and combustion of fossil fuels (Renzone et al., 1998). In gold mining, liquid mercury is used to separate gold from its ore by forming an amalgam. When heating the amalgam, Hg^0 is evaporated and released into the atmosphere while gold remains behind (Jain et al., 2016). Artisanal and small-scale gold mining are the major source of anthropogenic mercury emission to the atmosphere with an average worldwide emission of 727 tons per year (AMAP/UNEP, 2013). From mining operations, the accumulation of waste rock piles, tailings, and open pits containing mercury are important sources of Hg^0 emission (Eckley et al., 2011). From smelting process, Hg^0 can be released via flue gas to the atmosphere due to its presence in trace amounts in copper, zinc, nickel, and lead ores (Pirrone et al., 2010a). In chlor-alkali production, Hg^0 is used as an auxiliary material for the production of chlorine, hydrogen, and sodium hydroxide by electrolysis of a brine solution. Chlorine gas is formed at the anode of the mercury electrolytic cell and sodium amalgam is formed at the cathode. The amalgam is drawn out of the cell and decomposed into sodium hydroxide and mercury by reacting with water. Subsequently, mercury is recycled in the electrolytic cell. However, mercury cells have been discontinued because the chlor-alkali process releases mercury to the environment through air emissions, water emissions, and generated waste deposited on landfills (Kinsey et al., 2004; Hylander and Meili, 2003; NMR, 2002). From the combustion of fossil fuels, mercury is released as Hg^0 in the flue gas from coal combustion during the burning process for the production of energy (Presto and Granite, 2006). Combustion of fossil fuels also represents another major source of mercury emission into the atmosphere with an average worldwide emission of 475 tons per year (AMAP/UNEP, 2013; Pirrone et al., 2010a).

1.2. Chemistry of elemental mercury

Mercury has seven naturally occurring isotopes. The most common one is mercury-202. The properties and behavior of mercury depend on its oxidation states which mainly include elemental mercury Hg^0 (0), mercurous Hg^+ (+I), and mercuric Hg^{2+} (+II). Hg^0 has a water solubility of 60 $\mu\text{g L}^{-1}$ and a vapor pressure of 0.246 Pa at 25 °C (Mason and Sheu, 2002; Sanemasa, 1975; Schroeder et al., 1991). In nature, it can exist in the gas and liquid state, but it is more prevalent in the atmosphere in the gas state. Hg^+ can form a metal-metal bond with itself, producing Hg_2^+ , but Hg_2^{2+} is unstable and rapidly disproportionates into Hg^{2+} and Hg^0 . Hg^{2+} can exist in the gaseous, dissolved, and solid states and is more prevalent in aquatic systems (Boszke et al., 2002).

1.2.1. Why is mercury in liquid form at room temperature?

Elemental mercury is a special element in that it is the only metal that is liquid at room temperature (melting temperature $T_m = -38.83$ °C). The reason for this low melting temperature has contributions from the electronic configuration, relativistic effects, and lanthanide contraction. Molecular orbital theory, which is a good predictive tool for describing bonding behavior, can partially explain why Hg^0 is liquid at room temperature. The electronic configuration of elemental mercury is $[\text{Xe}] 4f^{14}5d^{10}6s^2$, with two electrons in the 6s orbital. If two atoms of Hg^0 combine to form a Hg-Hg dimer, two electrons are accommodated in the bonding molecular orbital (σ) and the other two electrons are accommodated in the antibonding molecular orbital (σ^*), as shown in Fig. 2.

The stabilizing effect that is provided by electrons in the bonding orbital is nullified by the destabilizing effect of electrons in the antibonding orbital. Therefore, the bond order is zero, and the

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