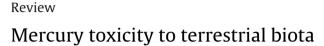
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### **Ecological Indicators**

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#### ABSTRACT

The heavy metal mercury is a non-essential hazardous element which concentrates up the food chain. It is necessary to assess the ecological risk of mercury to establish proper regulatory guideline levels. Most of the toxicological assessment of mercury has been focused on aquatic organisms, however in terrestrial bodies the information is limited. Hence this review critically discusses the toxicity of inorganic mercury to key terrestrial biota from recent literature and evaluate whether these information are adequate to establish safe regulatory limits or precautionary values which is invaluable for risk assessment of mercury in soil. Till date soil microorganisms, plants and invertebrates have been utilized for assessing mercury toxicity; among them, microorganisms have been observed to be the most sensitive indicators to mercury stress. Large inconsistency among the measured toxic concentrations indicates that measuring mercury toxicity in soil may be influenced by soil characteristics and ageing period of contamination. This review warrants more studies to obtain widely acceptable safe limit of soil mercury.

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#### 1. Introduction

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Mercury (Hg) has been considered as one of the most important metals since the beginning of human civilization. Ancient Chinese, Egyptian and Hindu civilizations used Hg as a pigment, to anoint their sculptures and to preserve dead bodies (Shephard, 2015). Furthermore, it was believed that Hg had healing properties, therefore it was used as an ingredient in many traditional medicines (Pal et al., 2014). There have been various reports of the toxicity of Hg to humans including the death of many people as a result of consumption of methyl-mercury (MeHg) contaminated fish in Japan (Yorifuji



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et al., 2013) and wheat in Iraq (Martinez-Finley and Aschner, 2014) in recent years.

The toxicity of Hg resulting from acute exposure to Hg can be associated with one or more of the following pathologies: brain damage, malfunction of the central nervous system (CNS), loss of memory, cardiac disease, liver damage, blindness and loss of sensation (Houston, 2014; Hsi et al., 2014; Newman and Leung, 2011; Rice et al., 2014). Alternatively, chronic exposure to Hg, especially its vapours, which can cross the alveolar membrane into the blood and subsequently the CNS can cause respiratory disease, erythrism, gingivitis, tremor and other CNS effects including Alzheimer's and Parkinson's disease (Nabi, 2014). Prolonged consumption of Hg contaminated fish has had deleterious effects on foetal development leading to neurological damage, behavioural problems, autism and reproductive damage (Bose-O'Reilly et al., 2010; Counter and Buchanan, 2004; Myers and Davidson, 2000).

Today Hg is considered a key global pollutant because of its persistence, bioaccumulation and toxicity in the environment. Elemental Hg<sup>0</sup> (also called "metallic Hg" which is a shiny liquid) is the most recognized form. Inorganic Hg, either Hg<sup>+</sup> (mercurous) or Hg<sup>2+</sup> (mercuric) is frequently found in the salts HgS, HgCl, Hg(OH) which may be bound to organic matter or particulates (Wang et al., 2004). As a result of the formation of covalent bonds, organomercurics such as methyl-mercury ion (HgCH<sub>3</sub><sup>+</sup>) and its compounds methyl-mercuric chloride (CH<sub>3</sub>HgCl), methyl-mercuric hydroxide (CH<sub>3</sub>HgOH), dimethyl mercury and phenyl mercury have been shown to be the most toxic forms of Hg. Of these forms, MeHg is the most frequently found, which binds to protein in various organisms, and is then concentrated up the food chain, leading to bioaccumulation, where the rate of intake of Hg exceeds the rate at which it can be excreted (Fleming et al., 2006; Wiener et al., 1990).

The fate, distribution and toxicology of Hg in aquatic systems have been thoroughly reviewed (Du et al., 2015; Rodrigues et al., 2013; Wu and Wang, 2014). However, the toxicity and biogeochemistry of Hg in soil habitats have been explored less because the baseline concentration and bio-concentration of Hg in terrestrial system is lower. To develop and manage bioremediation process, it is essential to know the maximum concentration of Hg in soil that can be tolerated without detrimental effects on any of the terrestrial system. Hence this review focuses on recent studies (a total of 715 articles recovered using Scopus search between the years 2000–2016) on potential Hg toxicity to soil inhabitants, particularly microorganisms, plants, and invertebrates.

#### 2. Source of mercury in terrestrial environment

Hg is present in the earth's crust in low concentrations (~0.5 mg/kg) (Canil et al., 2015) where it can occur naturally in rocks, plants, animals, aquatic environments and in the air. Within these natural environments, Hg concentrations can be high in certain compartments such as the earth's crust ("hot spots"). Hg is released from "hot spots" through natural processes such as hot springs or volcanic explosions. However in polluted areas the concentrations can be much higher than the background levels (Krabbenhoft and Sunderland, 2013; Randall et al., 2004).

In 2008, it was reported that the major sources of Hg (5000 Mg/year) were natural processes, especially oceanic emissions and biomass burning. A significant amount of 2320 Mg/year was released from anthropogenic sources including fossil fuel power plants, gold mining and metal manufacturing (Fig. 1) (Pirrone et al., 2010). In Australia a higher proportion of Hg in the environment has been attributed to natural and re-emitted sources compared to anthropogenic activities (95–297 Mg compared to 10–20 Mg) which reflects favourably on control over human generated wastes in this country (Nelson et al., 2012).

Primary anthropogenic sources of Hg are incidental emissions from Hg deposited source because of human activity such as mining and burning of fossil fuel (Pacyna et al., 2010). Mining activities such as gold, silver, mercury and lead mines release a huge amount of Hg into the environment during processing. For example, in South America, silver mines have been reported to release about 400 Mg of Hg annually over an extended period (Aula et al., 1995). Even a 100 years old disused mine has been a significant source of Hg contamination (Wang et al., 2004). In small gold mines throughout Brazil, where gold is recovered by the amalgamation method, significant amounts of Hg vapours have been released into the environment and contaminated process waters (Wang et al., 2004). Furthermore, sediments from inactive gold mines may also contain high Hg levels which can leach continuously into the surrounding environment (Hygelund et al., 2001). In the USA about 97% of the total anthropogenic Hg emission occurs from industrial combustion of fossil fuel, municipal waste and oil; whereas in Asia this is about 50%, predominately from coal combustion in energy plants (Wang et al., 2004; Pacyna and Pacyna, 2002). Hg released in these ways enters the atmosphere and subsequently settles in both aquatic and terrestrial systems.

The secondary sources of anthropogenic Hg result from the use of Hg in electrical switches, vehicle switches, thermostats, dental amalgam, thermometers, sphygmomanometers and chlor-alkali plants. The widespread use of Hg in dental amalgams has contributed significantly to environmental contamination by way of preparation and disposal of dental fillings (Oliveira et al., 2014). Chemical plants can be a major source of Hg pollution, for example, a heavily industrialized area in Siberia using Hg cathodes led to wastewater discharges containing 0.05 mg/L Hg even after purification (Koval et al., 1999). Furthermore, chlor-alkali plants have contributed significant quantities of Hg into the environment (Pacyna and Münch, 1991). A recent study reported that legacy anthropogenic Hg re-emission from historically contaminated surface reservoirs contributes significantly to the environment indicating that future emission of Hg will continue even if primary anthropogenic sources are controlled (Amos et al., 2013).

#### 3. Biogeochemistry of mercury in soil

Soil becomes contaminated with Hg mainly from wet and dry depositions of Hg<sup>2+</sup> and Hg<sup>00</sup>, and settling of particulate Hg (Biester et al., 2002; Yu et al., 2014). Leaf uptake of atmospheric Hg and its subsequent accumulation in soil by litter fall is also significant (Smith-Downey et al., 2010). Almost 60% of atmospheric Hg ends up in terrestrial surface in the oxidized form and 40% into the aquatic systems (Douglas et al., 2012; Mason et al., 1994). Contaminated lands adjacent to chlor-alkali plants have been reported to contain large amount of Hg. A recent estimation in Canada revealed 295-11,500 mg/kg Hg in soils adjacent to a chlor-alkali plant, which is 1475–57,000 times higher than the background concentration, although the soluble concentrations were very low (Zagury et al., 2006). Soils from another abandoned chlor-alkali plant in Botany Bay, NSW, Australia contain almost 300 times higher level of Hg than recommended Australian safe limit (Mahbub et al., 2017). After deposition to soil, Hg undergoes various chemical reactions which largely depends on soil properties, notably soil organic matter (SOM), soil pH, chloride concentrations and sulphide anions (Reis et al., 2014; Smith-Downey et al., 2010). Due to its strong affinity to SOM, sulphide anions and minerals, Hg rarely occurs in soil as free Hg<sup>2+</sup> (Skyllberg 2012; Tazisong et al., 2012). The majority is bound to soil minerals or absorbed to organic or inorganic solid surfaces, mainly organic materials in top soils (0-10 cm) (Grangeon et al., 2012; Obrist et al., 2011). In acidic soils Hg<sup>2+</sup> is mainly complexed to the SOM, whereas in neutral to alkaline soils mineral Download English Version:

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