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Are the existing guideline values adequate to protect soil health from inorganic mercury contamination?

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ABSTRACT

Currently, data that guide safe concentration ranges for inorganic mercury in the soil are lacking and subsequently, threaten soil health. In the present study, a species sensitivity distribution (SSD) approach was applied to estimate critical mercury concentration that has little (HC_5) or no effect (PNEC) on soil biota. Recently published terrestrial toxicity data were incorporated in the approach. Considering total mercury content in soils, the estimated HC_5 was 0.6 mg/kg, and the PNEC was 0.12–0.6 mg/kg. Whereas, when only water-soluble mercury fractions were considered, these values were 0.04 mg/kg and 0.008–0.04 mg/kg, respectively.

1. Introduction

Mercury (Hg) is a heavy metal that is widespread in the biosphere but has no known biological functions, rather it exerts toxicity on living organisms. Soil is one of the most important environments where Hg undergoes numerous chemical and biological reactions, and at certain concentrations disrupts soil health by altering soil biota such as microbes, plants, and animals (Ha et al., 2017; Rice et al., 2014). These bio-geo-chemical changes determine the degree of toxicity that different forms of Hg have toward organisms in different trophic levels (Schaefer, 2016). The metallic form of mercury (Hg^0) is the least toxic form because it is not water soluble, and does not bind to animal tissues and are not readily taken up by lower animals or microbes. Hg^0 can be oxidised in the atmosphere to inorganic mercury (Hg^{2+}) which is found in different salt forms such as chloride, nitrate or sulfide. Hg^{2+} is a reactive form that has high affinity to animal/plant tissues and can be taken up by micro- and macro-organisms resulting in many physical and biochemical adversities in the affected biota. Moreover, Hg^{2+} can serve as a substrate for bacterial methylation under anaerobic conditions, such as in sediments and water-logged soils (Mahbub et al., 2017a). The bioaccumulated Hg (after methylation) can enter into the food chain through intoxicated plants or animals, leading to severe acute and chronic disease in humans. Abnormalities in nervous, renal, cardiovascular and reproductive systems were found linked to Hg exposure (Kim et al., 2016; Yassa, 2014).

As the divalent and methylated forms of Hg are highly toxic, many industrial countries have developed regulatory limits or guideline values to control the use of Hg in agricultural and industrial practices. The estimation of a critical concentration of Hg in soil above which biological activity may be affected is important, as it constitutes a safe concentration or regulatory limit. Because of the severity of health problems from Hg pollution in waters, most of these regulatory limits are developed for aquatic environments. As such, a large number of studies have been carried out to estimate Hg toxicity in different water environments (Lavoie et al., 2013; Rodrigues et al., 2013). However, soils have not received much attention even though large portions of emitted Hg undergoes various changes in terrestrial environments.

The average contents of mercury in soils range from 0.001–1.5 mg/kg, which is related to the soil's property and proximity to an emission site (Kabata-Pendias and Szteke, 2015). However, high levels of soil-bound Hg in areas adjacent to the contamination sources have been identified in several studies. In China, 15–119 mg/kg Hg^{2+} was estimated close to a smelting area (Søvik, 2008). In different countries in Europe, contaminated soils were reported to contain 5–778 mg/kg inorganic Hg (Moreno-Jiménez et al., 2006). In agricultural soils, Hg concentrations have been reported from background level to approximately 180 mg/kg (Li et al., 2013; Meng et al., 2014; Şenilă et al., 2012). Soil-bound inorganic Hg can linearly accumulate and magnify in important plants such as rice (Li et al., 2013; Meng et al., 2014) which is a staple food in many countries. To protect soils as well as human health from soil bound Hg, industrial countries like Canada, America, UK, Netherland, Germany and Australia have developed guidelines for

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Hg use in residential, agricultural and recreational soils (Mahbub et al., 2017a; Tipping et al., 2010). However, the suggested safe soil Hg limits from different countries lack robustness because of inadequate toxicity data from soil environments; most of the studies being done on observing merely toxic effects, rather than estimating critical doses causing the effects from proper dose-response analyses (Mahbub et al., 2017a).

From our several recent investigations, it has been observed that the degree of toxicity of Hg depends on the biological species inhabited in soils and the soil's physicochemical properties. For instance, soil-bound Hg is highly toxic to soil microorganisms (Mahbub et al., 2016a; Mahbub et al., 2016b) but less toxic to soil invertebrates (Mahbub et al., 2017c) and plants (Mahbub et al., 2017b). Toxic doses also varied depending on varying end points. For instance, a dose required to observe negative effect on earthworm's reproduction rate is different from the toxic dose on their mortality or weight loss (Lock and Janssen, 2001). In addition, soil properties such as organic carbon content, pH, and cation exchange capacity play significant roles in bioavailability of Hg in the soil which is directly related to the degree of toxicity (Kim et al., 2016). As significant variation in the toxic doses of Hg in soil has been previously observed, this study was undertaken to consolidate recent toxicity data in the literature with a view to estimating a safe concentration that can be used to protect the majority of biota in the terrestrial habitat.

In the present study, a species sensitivity distribution (SSD) approach was applied to obtain critical Hg concentrations in soil that when exceeded, leads to toxicity. SSD is the recommended approach for ecological risk assessment and is used to predict hazardous concentrations (HC) that may affect a certain percentage of species in a biota, using extrapolation of ecotoxicity data from published literature or databases (Posthuma et al., 2001; US-EPA, 2005). This approach has recently been used by others to estimate critical Hg concentrations in water (Rodrigues et al., 2013). Generally, the SSD approach utilized to determine the HC_5 value, which denotes the concentration that affects 5% of the species in an environment. Alternatively, this concentration protects 95% of species. In this study, both total and water-soluble Hg concentrations were considered for the estimation of HC_5. Moreover, the predicted no-effect concentration (PNEC) had been estimated from the same approach. The HC_5 and PNEC values generated in the present study will advance the knowledge of Hg toxicity in terrestrial environments.

2. Materials and methods

2.1. Data collection

Toxicity data were collected from the existing published papers by a literature search using Scopus and Web of Science. Papers from last 20 years (1997–2017) were selected, based on data generated from experiments carried out in soil under laboratory conditions. Organisms from three trophic levels – microbes, invertebrates, and plants were chosen which have direct contact with soil. Statistically determined EC_{50} values were considered only when a proper dose-response relation was evident. In contrast, any data failing to demonstrate regression relation (i.e., merely a concentration that has a negative effect on any endpoint) were excluded from this study. As such for soil microbes, data were available for a range of soil enzymatic activities and soil microbial alpha diversity; for soil invertebrates, mortality rate, reproduction inhibition rate, and avoidance rate were available; for plants, only root elongation data were obtained. Based on the literature search, information from the twelve papers that met the above-mentioned criteria were selected for the present study (Table 1). EC_{50} values were either reported in the selected papers or generated from the available data using four parametric logistic model applying IBM SPSS version 17.

2.2. Estimation of critical Hg concentration

The toxicity data were subjected to SSD analysis using the SSD generator downloaded from https://www3.epa.gov/caddis/da_software_ssdmacro.html and HC_5 was determined. The predicted no-effect concentration (PNEC) was estimated by dividing the estimated HC_5 by a factor 1–5 (Rodrigues et al., 2013).

3. Results and discussion

Different species of plants, animals, and microbes have been used as indicator organisms in long term and short term exposure experiments to estimate the toxicity of Hg in soil environments, but not as extensively as the toxicological assessments in water environments. Plants are higher organisms, and their uptake rate of Hg through their root system is very low because of the presence of barriers in the root tips (Patra and Sharma, 2000). Plants also accumulate elemental Hg from the atmosphere through the leaves which is then translocated to other organs. At certain concentrations, Hg^{2+} is reported to exert oxidative stress (Israr et al., 2006; Tamás and Zelinová, 2017), disrupt membrane structure (Ma, 1998), damage DNA (Dogan-Topal et al., 2018), reduce the uptake of minerals and nutrients (Tangahu et al., 2011), interfere cell division (Azevedo et al., 2018) and disrupt chlorophyl synthesis (Liu et al., 2010a), photosynthesis and transpiration rates (Rai et al., 2016). Although a lot is known about toxic effects of Hg on plants, there is a scarcity of data where a proper dose-response relationship was reported for terrestrial plants to predict a safe Hg limit. Only one study is available where three Australian native plants namely *Iseilema membranaceum* (Barcoo), *Dichanthium sericeum* (Qld blue) and *Sporobolus africanus* (Tussock) were used in a 28 d laboratory experiment in three soils of different physicochemical properties (Mahbub et al., 2017b). The other studies report only Hg uptake and toxicity related syndromes in different plant parts harvested in contaminated fields (Azevedo and Rodriguez, 2012; Mahbub et al., 2017b; Nagajyoti et al., 2010).

Unlike plants, invertebrate animals in soils have been used more elaborately as indicator organisms to estimate safe Hg limits in the soil. At toxic concentrations, Hg can cause death, weight loss, lead to behavioural abnormalities, and interfere with reproduction rates in different species of terrestrial invertebrates. There are few studies (Table 1) where a proper dose-response relationship was established to estimate a Hg concentration that affects any of the endpoints. Most of these studies used different species of earthworms as they are considered a reliable bioindicator of soil pollution. The issue here is, the estimated toxic concentrations of Hg can vary depending on the species used and the endpoints observed (Buch et al., 2017b). Therefore there is a need to combine data obtained from different species of organisms where several endpoints are observed. To include soil invertebrates in the present study, data were obtained from studies where different species of *Eisenia*, *Pontoscolex*, *Enchytraeus*, and *Folsomia* were used to monitor the effect of Hg on their behaviour, mortality, weight loss and reproduction rate (Table 1).

Many studies have demonstrated that microbes are the most affected organisms in a contaminated area (Harris-Hellal et al., 2009; Liu et al., 2014; Mahbub et al., 2017a). Therefore, to predict a safe Hg concentration that protects organisms from all trophic levels, microbes can be used as the most reliable indicators. Changes in microbial community structure, diversity and functions are common in contaminated environments (Müller et al., 2001; Zappelini et al., 2015). Therefore, establishing a proper dose-response curve and subsequent estimation of HC values from microbial endpoints can provide reliable secondary data for establishing guideline values. Hence, we obtained a wider range of data that covers various soil microbial functions which included dehydrogenase enzyme activity (DHA), soil nitrification rate, urease activity, arylsulphatase activity, alkaline phosphatase activity (AP), Fe(III) reduction, microbial biomass carbon content (MBC) and