

MERCURY CONTAMINATION IN AGRICULTURAL WETLAND ECOSYSTEMS-A CASE STUDY FROM KERALA

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ABSTRACT

Mercury is a potent neurotoxin which is released into the natural environment, through a wide range of natural and anthropogenic sources. It is easily dispersed and introduced into the aquatic systems through atmospheric deposition. Methyl mercury is the species of most concern for humans owing to its highly bioaccumulative nature. In the aquatic environment, inorganic mercury is converted into methylmercury, primarily by anaerobic bacteria. The mobility and toxicity of mercury is greatly attributed to its speciation in the environment. In the present study, fractionation as well as total mercury analysis of soil samples from agricultural wetland ecosystems was done using USEPA method 1631 and Bloom's five-step sequential extraction scheme. The maximum value obtained for total mercury was 0.216mg/kg and the minimum value obtained was 0.119 mg/kg. F1 (water soluble) and F3 (organochelated) were the major fractions among the samples.

Key words: Pollution; metals; sediment; accumulation

INTRODUCTION

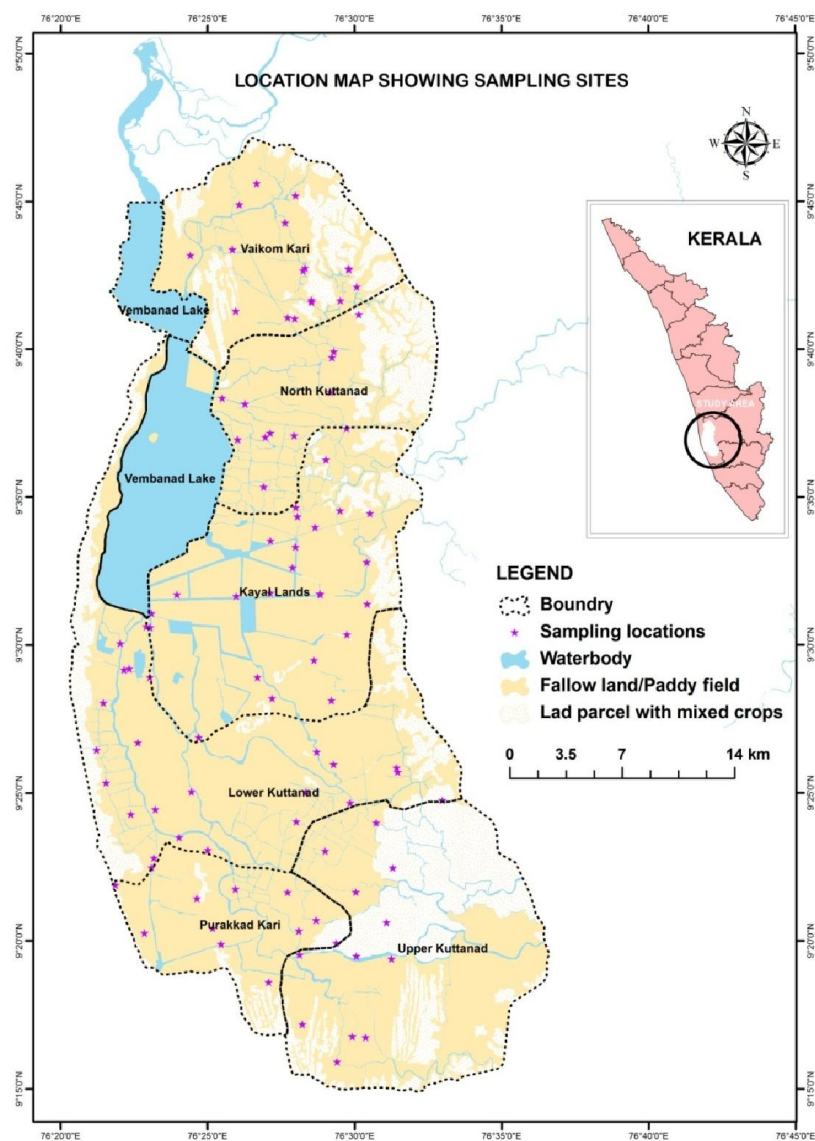
Agricultural wetlands, in particular those associated with rice cultivation, are one wetland category that has received little attention in terms of methyl mercury (MeHg) production (Marvin-DiPasquale *et al.*, 2013). Rice paddies constitute one of the most abundant wetland ecosystems in temperate and tropical latitudes worldwide. These habitats have been considered as paramount sites of Hg(II)-methylation owing to their highly dynamic hydroperiod (Alpers *et al.*, 2013). Mercury is extravagantly dispensed in aquatic ecosystems by virtue of anthropogenic activities and natural earth processes. Aquatic sediments act both as sinks and sources of mercury. Here, inorganic mercury is readily converted into methyl mercury through a complex web of transport and transformation process (Hsu-Kim *et al.*, 2013). Agricultural wetlands with varying biogeochemical conditions due to fluctuating water levels are better places for mercury methylation and release of Hg from sediments/soils (Ackerman and Eagles-Smith., 2010). The various factors affecting mercury methylation are available inorganic mercury (IM), temperature, pH,

organic matter, redox potential etc. Among these the major one is availability of IM and is mainly depend on the geochemical conditions and bonding with other elements. Hence it is important to understand the fractionation of mercury, which will indicate the quantity of mobile and available form of mercury in the system.

MATERIALS AND METHODS

Study area

The Kuttanad rice agroecosystem extends from 9° 17' – 9° 40' N and 76° 19' – 76° 33' E. It is a low lying area of costal Kerala situated 0.6 – 2.2 m below mean sea level (msl) and is the delta of four major river systems viz., Meenachil, Manimala, Pamba and Achancoil draining into the Vembanad Lake. The total geographical area of the Kuttanad is estimated as 1100 Km².



Sample collection and preparation

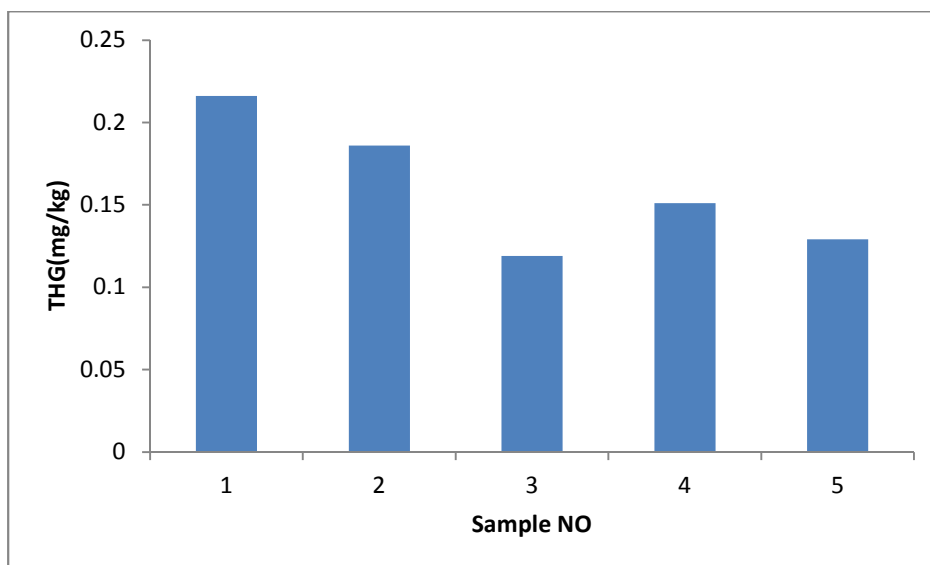
The soil samples were collected at 10-15 cm depth from representative sites of the study area. In the lab, soil samples were dried at controlled temperature (35⁰C) and then ground to fine powder using an agate mortar. Then the samples were separated to granulometric fraction, <63 μ using ASTM sieves. Total mercury was determined as per USEPA method 1631 using Cold Vapour Atomic Fluorescence Spectrophotometer (CVAFS, Brooks Rand, USA). Bloom's five-step sequential extraction scheme (Bloom *et al.*, 2003) was used to study the fractionation of mercury in the sediments.

RESULTS AND DISCUSSION

Total mercury content and various mercury fractionations detected for the soil samples collected from Kuttanad agricultural wetland ecosystem. The results are discussed in detail.

The total mercury values in the study ranged from 0.119 to 0.216 mg/kg. Among the five samples, the highest value for total mercury is obtained for sample 1 and least value is obtained for sample 3. Regarding the fractions, for samples 3,4 and 5 the highest value is gained for F1, which is the water soluble fraction. F1 includes mercury species present in pore water. The mercury present in this fraction is bound to dissolved organic matter (without a Hg-carbon bond) or suspended mineral particles (Biester and Scholz, 1997; Wallschlager *et al.*, 1998; Wasay *et al.*, 1998; Renneberg and Dudas, 2001), but may not be present in the form of water-soluble ionic species (Hg(OH)₂, OHHgCl, HgCl₂). This water-extracted portion of mercury may be easily transported by natural processes and serve as the substrate for mercury methylation process (Stein *et al.*, 1996; Ullrich *et al.*, 2001; Boszke *et al.*, 2003). Hence the mercury content in the soil is mobile. For samples 1 and 2, the dominant fraction is F3, which is the organochelated form. Organic matter plays a key role in the mobility of mercury in the environment, especially in the catchment areas. Important components of the organic matter are humus substances, whose contribution reaches up to 25% in the bottom sediments, 20% in marine water, 60% in river water and 70% in the wetlands (Weber, 1988). F3 is considered to be more potentially available for methylation compared to F4 and F5 (Frohne *et al.*, 2013).

The results showed that the major fraction of mercury found is organo-chelated followed by water soluble fraction. The total mercury concentration of only one sample was above the background concentration. The study further showed that the influence of organic matter, sulphur complexes and concentration of THg on the fractionation of mercury in the wetland soils. The percentage of mercury found in initial three fractions F1, F2 and F3 are more available and it may enhance the methylation potential of the Kuttanad agroecosystem. Mercury was closely associated with organic carbon. Information gained from this study is a useful tool for risk assessment of these sites. The concentrations of Hg is in the order F3>F1>F5>F4>F2, so it deserves special attention due to their high mobility and potential plant availability.



Sample	Fractions (mg/kg)				
	F1	F2	F3	F4	F5
1	0.07	0.026	0.294	0.024	0.125
2	0.38	0.166	0.401	0.116	0.107
3	0.08	0.041	0.062	0.052	0.073
4	0.07	0.024	0.051	0.069	0.04
5	0.07	0.022	0.066	0.035	0.067

CONCLUSION

The present study reviewed the significance of agricultural wetland ecosystems on the transport and transformation of mercury in the environment. The vast area and varying geochemistry of the agricultural wetland ecosystem greatly influences the speciation of mercury and thus toxic impacts. The study indicated the presence of total mercury in the soils. The fractionation studies showed that the presence of mobile and bioavailable mercury fraction, which indicates the availability of mercury for mercury methylation. Hence detailed investigations are needed for the mercury methylation process in the agricultural wetland ecosystems.

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