DOCTORAL THESIS

The effects of mariculture on mercury distribution, speciation and transformation in the aquatic system around Hong Kong coastlines

Liang, Peng

Date of Award:
2011

The Effects of Mariculture on Mercury Distribution, Speciation and Transformation in the Aquatic System around Hong Kong Coastlines

LIANG Peng

A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor: Prof. WONG Ming Hung

Hong Kong Baptist University

August 2011

Abstract

The objectives of this study were to investigate the influence of mariculture on mercury (Hg) distribution, speciation, transformation, adsorption/desorption and chemical fractionations of Hg on sediments around Hong Kong and adjacent mainland China coastlines. In addition, the influences of salinity and humic acid on inorganic mercury (Hg^{2+}) adsorption by different iron (Fe) and manganese (Mn) oxides were evaluated. At last, the possible human risk on methylmercury (MeHg) exposure through consumption of Hg contained in cultured fish was assessed.

Sediments were collected from six mariculture sites, and the corresponding reference sites, 200 - 300 m away from the mariculture sites. Total Hg (THg) concentrations, organic matter (OM), carbon, nitrogen and sulfur contents in mariculture sediments (MS) were significantly higher ($p < 0.05$) than reference sediments (RS), possibly due to the accumulation of unconsumed fish feed and fish metabolisms. However, MeHg concentrations and the ratio of MeHg to THg (%MeHg) were significantly lower ($p < 0.05$) in MS than RS. The %MeHg in sediments was negatively correlated ($r = -0.579$, $p < 0.05$) with OM contents among all sites, indicating that the accumulation of OM may inhibit MeHg production in sediments. This is due to the complexation of Hg with OM in MS reduced Hg bioavailability to methylation bacteria, further leading to the decline of MeHg production in sediment.

The simulation experiments demonstrated that the higher the Hg^{2+} concentrations spiked in the sediment, the more MeHg was produced in sediment. This can be explained by the link between THg concentration in sediment and Hg bioavailability for methylation bacteria. MeHg levels in water and sediments decreased with time during the sediment culture period, which might be due to the decrease of methylation of Hg^{2+} or demethylation of MeHg in sediment and water. The decreasing percentages of MeHg were decreased with the increase of spiked Hg^{2+} concentration in sediment, which might be due to the *mer*-specific

function was inhibited by the high Hg concentration. The increase of salinity in the overlying water inhibited MeHg production in sediment and porewater, due to sea salt anions, such as Cl^-, S^{2-}, CO_3^{2-}, which inhibited Hg methylation by complexing with Hg^{2+} to form inorganic complex compounds, e.g., $HgCl_2$, HgS and $HgCO_3$. Significantly higher ($p < 0.05$) fluxes of THg and MeHg in MS than RS indicated that newly added Hg^{2+} and newly formed MeHg were easier to be evaporated in MS than RS.

The amount of adsorption and binding energy of Hg^{2+} were significantly higher ($p < 0.05$) on MS than RS. This may be explained by the strong complexation role that exists between Hg^{2+} and OM, which can be derived from unconsumed fish feed and fish metabolites. The amount of Hg^{2+} binding with Fe and Mn hydroxides in MS was significantly lower ($p < 0.01$) than in RS, which may have been caused by the decreasing amount of Fe and Mn hydroxide in MS, leading to the decrease of Hg^{2+} bound to them. On the contrary, the amount of residual Hg^{2+} was significantly higher ($p < 0.01$) in MS than in RS, which suggests that newly adsorbed Hg^{2+} was more stable in MS than in RS.

The adsorption of Hg^{2+} on Fe and Mn hydroxides in the marine system was significantly lower ($p < 0.01$) than the freshwater system, possibly due to the strong complexation between Hg^{2+} and Cl^-. The formation of stable, nonsorbing aqueous $HgCl_2$ complexes in solution would limit the amount of free Hg^{2+} available for sorption. The adsorption of Hg^{2+} on Fe and Mn hydroxides decreased with the increase of dissolved humic acid (DHA) concentrations in the freshwater system. The inhibition role of DHA on the adsorption of Hg^{2+} to Fe and Mn hydroxides might be attributed to the competition role between Hg^{2+} and DHA on adsorption to Fe and Mn hydroxides. In contrast, the adsorption of Hg^{2+} on Fe and Mn hydroxides decreased with the increase of DHA concentrations in the marine system, which means that DHA promoted the adsorption of Hg^{2+} on Fe and Mn hydroxides. This might be due to the addition of DHA resulted in the reaction between Cl^-

and DHA. The reduction of Cl^- promoted more Hg^{2+} to be adsorbed on the Fe and Mn hydroxides. As a result, the fish culture in the fresh water environment inhibited the adsorption of Hg^{2+} on the Fe and Mn hydroxides, but promoted the adsorption of Hg^{2+} on Fe and Mn hydroxides in the marine environment.

The fish consumption rate of the studied population was significantly correlated with THg and MeHg concentrations in human blood plasma, indicating that human blood plasma can serve as a biomarker for MeHg intake via fish consumption. The mean values of EDI_{Fish} and EDI_{Blood} were 0.47 and 0.39 μg/kg/week, respectively. Both of them were lower than the Provisional Tolerable Weekly Intake level (PTWI) of 1.6 μg/kg/week established by The Joint FAO/WHO Expert Committee on Food Additives (JECFA) and Reference Dose (RfD) of 0.7 μg/kg/week established by USEPA. Based on RfD of 0.7 μg/kg/week and a one-component biokinetic model, the potential human risk would be caused for Hong Kong residents when Hg concentration in blood exceeds 2.80 μg/L. Thus, this study recommended a reference value of 2.8 μg/L Hg concentration in whole blood for Hong Kong residents.

On the whole, the mariculture activities increased the accumulation of OM in sediments through the deposition of unconsumed fish feed and fish metabolisms, leading to higher accumulation and adsorption of Hg on sediment and metal hydroxides, but inhibit MeHg production in sediment. Through the consumption of mariculture fish, MeHg exposure for Hong Kong resident was lower than the PTWI of 1.6 μg/kg/week established by JECFA and RfD of 0.7 μg/kg/week established by USEPA.

Table of Contents