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Mercury Methylation and Partition in Aquatic Systems*

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The conversion of inorganic mercury into the more toxic monomethyl form has long been recognized as a potentially critical step in the environmental behaviour of this heavy metal (JENSEN and JERNELOV 1969). Although a large variety of mechanisms of transformation have been studied and described, we are still quite unable to make quantitative predictions of the rate at which such a conversion might take place in the environment (KRENKEL 1973, NAS 1978). Indeed, consideration of a "methylation rate" may be inappropriate, since reduction of organic mercury to inorganic and ultimately to elemental mercury certainly takes place (FURUKAWA et al. 1969, SUMMERS and SILVER 1972, reviewed by SUMMERS and SILVER 1978). In fact, an equilibrium distribution, or partitioning, at levels determined by the nature of the substrate, may be a better object of study (MILLER et al. 1977).

The work reported here was undertaken to determine whether the various processes involved could combine into a reproducible equilibrium in a model of a natural system, to examine partitioning of both methylmercury and inorganic mercury between sediment and water, and to determine the rate-limiting step in the process leading ultimately to uptake of methylmercury by fish. Specifically, we wished to investigate the effect of the presence of fish in the water column on the level of mercury found in water, and on the apparent rate of methylation by sediment.

METHODS

Inorganic mercury in the form of $^{203}HgCl_2$ was added to river sediments of three types, namely coarse sand, a mixture of fine silt and woodchips, and pure woodchips, taken from the Ottawa River, at the level of approximately 1.0 ppm on a dry-weight basis. 5 cm of labelled sediment was placed in glass tubes (inside diameter 8 cm) to which was added natural river water to a depth of 20 cm (1 L) and, in half of the tubes, four small goldfish. The fish were separated from the sediment by a plastic screen, since an earlier experiment had indicated substantial suspension of sedimentary

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material due to the activity of the fish themselves. At various intervals, sediment and water (whole and filtered) were extracted by benzene dithizonate, inorganic and methylmercury were separated by TLC and measured by gamma-counting. That the organic mercury was detected was indeed methylmercury was verified by GLC analysis.

RESULTS AND DISCUSSION

In Figure 1 is presented the percentage of mercury present in the methyl form in sediments and in the overlying water, for a three-week period. Results obtained earlier indicate equilibrium is essentially achieved within this time (unpublished).

The final concentrations of methylmercury and inorganic mercury in sediments and in overlying water are reported in Table I, along with partition coefficients. It may be observed that more organic mercury was produced in highly organic sediments than in sand; however, the partition coefficients are such that the methylmercury concentration in the water, i.e. the methylmercury actually available to the fish, was just as high over a coarse sand sediment as over an organic mixture and, in fact, lower over pure woodchips. To check this, actual mercury uptake of the fish per g of body weight during the 21-day experiment was compared to time-averaged water concentration to produce a coefficient of removal of (methyl)mercury from water averaging 2.9 g water/g fish/hr, in close agreement with published values (deFREITAS and HART 1975).

At the conclusion of the experiment, for the case of sand sediment, the fish (total weight roughly 10 g) contained approximately 10^{-6} g methylmercury, while the water column, (1 L at 0.1 ppb), contained roughly 10^{-7} g. Thus, although the equilibrium concentration of methylmercury in the water column is the same with or without fish, the amount of methylmercury produced in the systems including fish was more than tenfold higher. Methylmercury is produced in the sediment and desorbed quickly enough to maintain the water mercury level, even in this system in which the mass ratio of fish to water is much higher than in a natural system. One concludes that in a real sediment-water system, it is meaningful to consider equilibrium values of organic mercury levels, as well as ratios of organic to inorganic mercury, in the sediment-water system, rather than to consider production rates in the sediment. The rate of production of methylmercury in the sediment appears to be determined by the rate of removal from the water; the sediment and water characteristics determine the equilibrium partition, but not methylation rate.

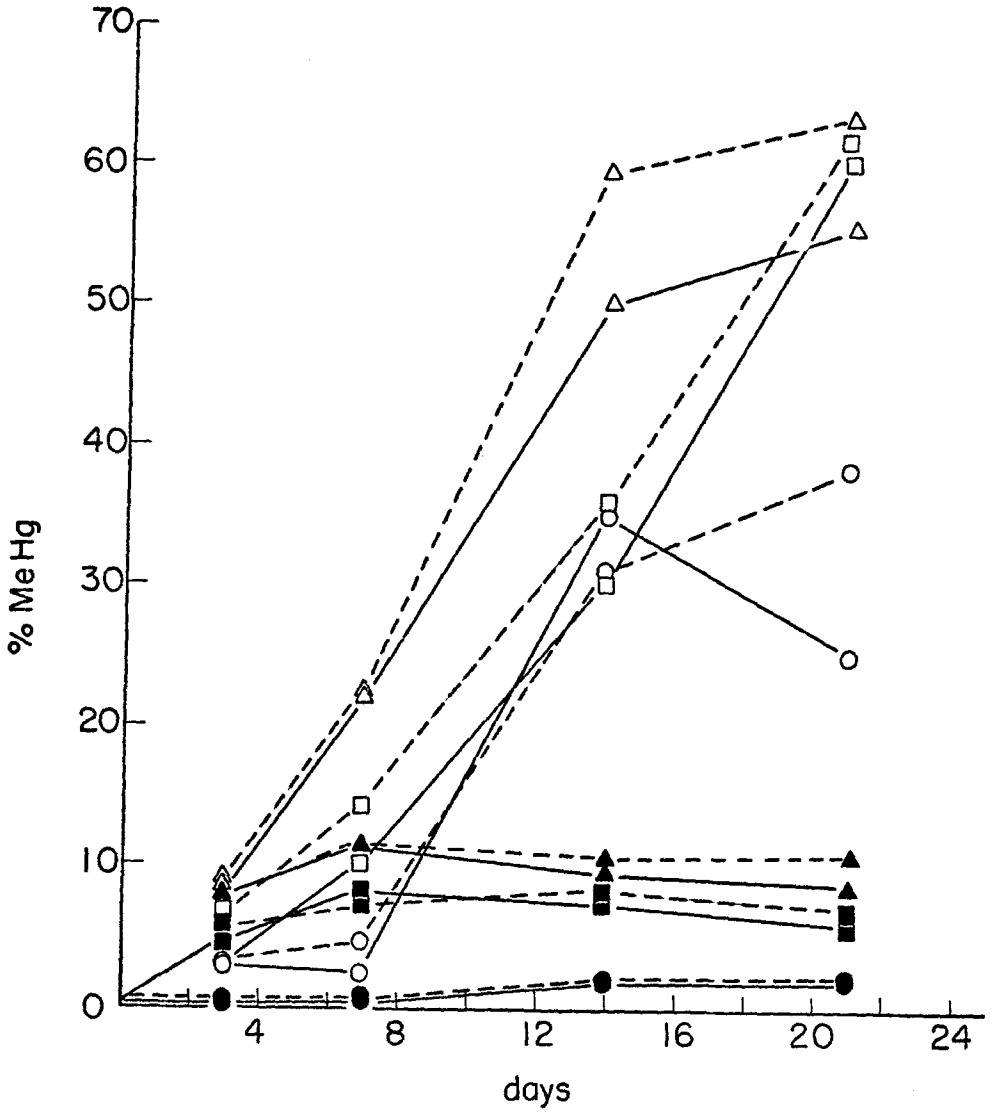

Figure 1. Fraction of mercury in methylmercury form in sediments and in overlying water. ● - sand. ■ - silt and woodchips. ▲ - woodchips. Open symbols: water. Dashed lines: systems including fish. Solid lines: systems without fish.

Table I. Equilibrium distribution of Hg in system. Partition coefficient is relative affinity for sediment measured as ppb Hg in sediment (dry weight)/ppb Hg in water.

Type of Sediment	Mercury in Sediment (ppb)			Sediment/Water Partition Coeff.		Hg in Whole Water (ppb)			Avg. Methyl Hg in Water (ppb)	Methyl Hg in Fish (ppb)	Methyl Hg Uptake Rate (hr^{-1})
	Inorg.	Methyl	% Methyl	Inorg.	Methyl	Inorg.	Methyl	% Methyl			
Sand	800	16.0	2.0	4,000	170	.204	.095	32	.063	92.9	2.9
Silt and Woodchips	960	69.4	7.2	9,800	760	.112	.103	48	.069	112.0	3.2
Woodchips	1048	93.5	8.9	50,000	4200	.023	.031	57	.021	28.1	2.7

The relatively high proportion of methylmercury in the water column is worthy of comment. MORTIMER and KUDO (1975) have shown rates of uptake of inorganic and of methylmercury from water by vascular plants to be quite similar, and subsequent field analyses of aquatic plants show organic mercury content in the neighbourhood of 30%, implying a similar concentration in natural water (MORTIMER, in preparation). Similar results have been reported by FITZGERALD and LYONS (1973) and by FOREBACK (1973). On the other hand, some investigators have reported an inability to detect organic mercury in natural water (CHAU and SAITOH 1973). The results remain to be reconciled, but it should be noted that the latter study measured only the methylmercury content of filtered water, while the present work includes suspended material. In any case, it seems clear that determination of partition coefficients is a necessary step if we are to predict effective methylation rates and actual availability of methylmercury in the food chain.

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