Competition for Mercury Between River Sediment and Bacteria

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Sediments bind very strongly to mercury, and the continuous process of sedimentation may be considered a way of decontaminating natural waters (D'ITRI, 1972a). From mass balance calculations the oceans (total volume 1.4×10^{21} litres) contain .03 ppb mercury representing 0.03% or less of the total amount that has entered the ocean through geological weathering and human activities (DAVIS and FERGUSON, 1972). In all surface waters, concentrations of mercury have remained below the levels which are toxic to life. The concentration of mercury in solutions in the ocean is not greatly different from that in fresh waters, suggesting that even in the presence of vast quantities of chloride ions adsorption of mercury to particulate matter and by sediments may be an effective sink (JONASSON, 1970 and HAWKES and WEBB, 1962). In highly polluted waters, sediment loads of >9000 ppm of mercury have been reported (D'ITRI, 1972

We have been interested in the relation between different species of mercury in solution, in the adsorption of these species on organic and inorganic substances and living organisms and in the competition between such substances for different forms of mercury. Recent studies show that Ottawa River water has a metal-binding capacity under equilibrium conditions of about 15 mg/l for Hg^{2+} ion (RAMAMOORTHY and KUSHNER, 1975a, 1975b). Most of the binding is du to low molecular weight (<1400) organic ligands. The actual mercur concentration in the unfiltered Ottawa River water column (.03 ppb) (Ottawa River Project Report No. 2) is very much lower than the tot binding capacity, but the huge mass of water involved makes this ph extremely important, especially as a medium of transport between compartments.

Sediment mercury concentrations have been studied extensively in sediments from the Ottawa River and its tributaries. The total mercury holding capacity of the sediment is enormous, about 1000 times the highest value found *in situ*, and desorption into river water is extremely slow, even in the presence of chelators (RAMAMOORTHY and RUST, 1976). For example, for Ottawa River sediments with a 10.1% organic content (RAMAMOORTHY and RUST, 1976) containin from 10-400 ppm of added mercury, the rate of desorption of added mercury was only 0.9 ng/cm^2/day.

Methods

Though exchange between the two-compartment system, water-sedi ment, has been studied, very little is known about mercury exchange in multicompartment systems. We have used a simple laboratory simu

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lation of an aquatic ecosystem to study competitive intercompartmental interactions. The compartments chosen were: river water, sediment, and biota, as represented by a suspension of bacteria. River water served as the fluid transfer medium, and the other compartments were separated by enclosing sediments and bacterial suspensions in dialysis sacs and suspending them in the continuously-stirred water.

In a typical experiment, seven sacs containing sediment (ca. 0.5 g dry wt., in 6 ml distilled water) and seven sacs containing bacteria (Pseudomonas fluorescens in amounts equivalent to 0.159 - 0.265 g dry weight in 6 ml distilled water) were suspended in 5.5 l of Ottawa River water. The water was stirred magnetically at room temperature (22°C) and the sacs rotated mechanically in a Multiple Dialyser (Pope Scientific Co., U.S.A.). Dialysis sacs and samples of river water were removed at intervals and analysed for total and inorganic mercury by flameless atomic absorption spectroscopy. Control values were obtained for background mercury levels in all compartments and in the dialysis tubing. The control levels were not significant in the experiments carried out. Mercury (as $Hg(NO_3)_2$) was added to one compartment and the ability of the other two to accumulate mercury was measured.

Results and Discussion

When 1.45 ppm Hg^{2+} was added to river water as the source compartment, mercury was accumulated by both bacterial and sediment compartments (Fig. 1). At first (at the time of the "Zero hr" reading, literally a few minutes after Hg^{2+} addition) more mercury entered the bags with sediment than those with bacteria. After the 1 hr reading, however, the bacterial samples contained considerably more mercury than the sediment samples; after 24 hr a steady state was reached in which the bacterial samples bound 5.8 times as much total mercury as the clay samples. These results seem to indicate that the sediment contained a relatively small number of binding sites with very high affinity for mercury, but that the bacteria contained many more binding sites. On a dry weight basis, the bacteria accumulated up to 20 times the amount of mercury accumulated by the sediment, over a 72 hr period. Within the limits of experimental error, the surface area of the bacteria is 1-3 times that of the sediment, per gram dry weight (Fig. 1, Legend). Thus, per unit surface area, bacteria were much more active in adsorbing Hg than were sediment particles.

Total amounts of Hg in all compartments are shown in Table 1. There was a considerable loss of mercury from this system (58% in 72 hr). Since the same sediment, incubated with sterilized or unsterilized river water showed no loss of Hg over a much longer period (RAMAMOORTHY and RUST, 1976), it may be concluded that the loss in the present experiments is due to the bacterial compartment possibly through conversion of Hg^{2+} to Hg^0 which is carried by several bacterial species including those from the Ottawa River. (Ottawa River Project Report No. 2, 1974, SUMMERS and SILVER, 1972, and KUSHNER, 1974).

TABLE 1

Distribution of Hg^{2+} in different fraction after addition of Hg^{2+} to water component in a multicomponent system.

Time (hrs)	pH	redox mV	AQ CONC. (mg) per litre	AQ CONC. (mg) total	CLAY (µg) per bag	CLAY (µg) total	P. fluorescens (µg) per bag	P. fluorescens (µg) total	Total Recovery in mg	Total Recovery As % ADDED Hg^{2+}
0	7.4	323	1.45	8.02	0.60	4.2	0.05	.322 (0.08)	8.02	100
1			--	--	3.46	21.36	3.91	28.51 (1.1)	--	--
6	7.396	254	1.04	5.71	28.80	148.05	94.08	474.36 (3.2)	6.33	79
12	7.435	215.2	1.11	6.11	30.48	154.78	111.00	542.04 (3.5)	6.8	85
24	7.452	229.1	0.94	5.19	25.31	139.27	201.00	812.04 (5.8)	6.14	76
48		201.3	0.60	3.29	30.68	150.01	232.90	874.04 (5.8)	4.31	54
72			0.42	2.30	44.16	163.49	297.2	940.14 (5.75)	3.40	42

Hg^{2+} added is 7.98 mg/5.51 ≈ 1.45 ppm; values in brackets represent the ratio of Hg^{2+} accumulated by P. fluorescens/sediment. AQ = aqueous (amounts in water compartment); Values for total (= inorganic) Hg; no

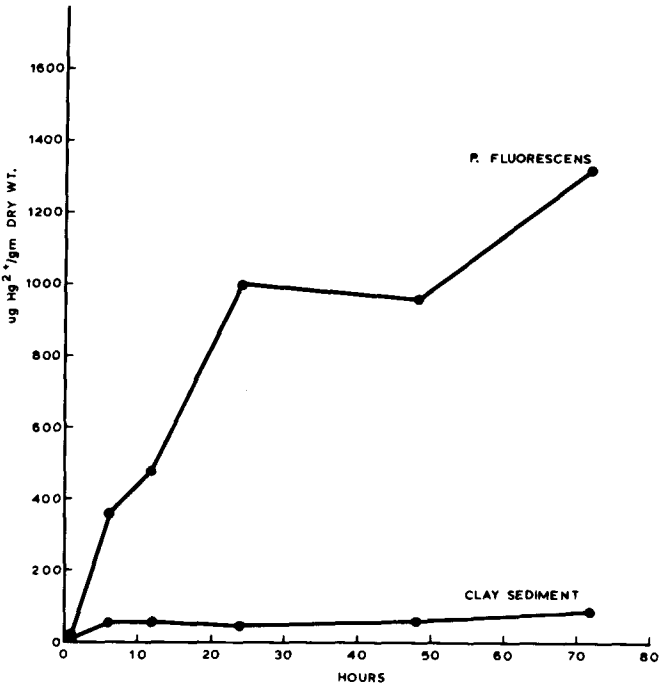

Fig. 1. Accumulation of mercury added to river water by bacteria and sediment.

Properties of the compartments studied.
Ottawa River water: Eh, + 345- + 430 mV; pH, 7.85 - 7.70; pCl, 3.80 - 3.68; Conductivity, 21 - 22 µmhos; Turbidity, 8 - 10 FTU; complexing capacity = 21 µM of Hg^{2+}. Sediment: Clay-type sediment from Ottawa River, mainly composed of poorly crystallized kaolinite and illite; surface area = 25.5 m^2/g dry wt. Organic content 10.1%; mean grain size 0.35 mm. Cation exchange capacity 18.58 mEq per 100 g dry wt. (RAMAMOORTHY and RUST, 1976). Bacteria: Cells of Pseudomonas fluorescens were grown to stationary phase for 72 h in Nutrient Broth at 30°C and washed thoroughly to remove growth medium. Total surface area (estimated by counting total numbers with a Coulter counter and multiplying by surface area of one bacteria): 40 ± 20 m^2/g dry weight-the variation is due to variation between sizes of individual cells at the time of harvesting.

The concentration of Hg added to water (1.45 ppm) in this experiment is much higher than is ever found naturally in the Ottawa River; however, it is well below the binding capacity of the river water (RAMAMOORTHY and KUSHNER, 1975a, 1975b). Sorption-desorption experiments have shown that Hg^{2+} added to a water sediment system will partition itself completely on the sediment (RAMAMOORTHY and RUST, 1976) (binding constant 10^{12}). Similar studies on a

number of different sediments with different physicochemical characteristics showed that the degree of sorption could be correlated (in descending order) to: surface area, organic content, cation exchange capacity (RAMAMOORTHY and RUST, 1976). The sediment used in the present experiments had the highest binding capacity of all those tested. Our results show that a thick suspension of bacteria can have a much greater binding capacity than the sediment, which normally provides a very efficient sink.

Similar experiments, in which the clay sediment was preloaded with high levels (400 ppm) of mercury and carefully washed to remove unadsorbed material, showed that bacteria can remove mercury from the sediment even when there are two dialysis membrane barriers between them. The accumulation of Hg by sacs of bacteria, and by the water around the sediment, over a 90 hr period, are shown in Fig. 2. The amount appearing in water (98 ppb) agrees well with that found in previous experiments (RAMAMOORTHY and RUST, 1976) in which sediment was incubated in river water with no added bacteria present (86 ppb). Thus, the presence of large amounts of bacteria can greatly accelerate the natural rate of desorption.

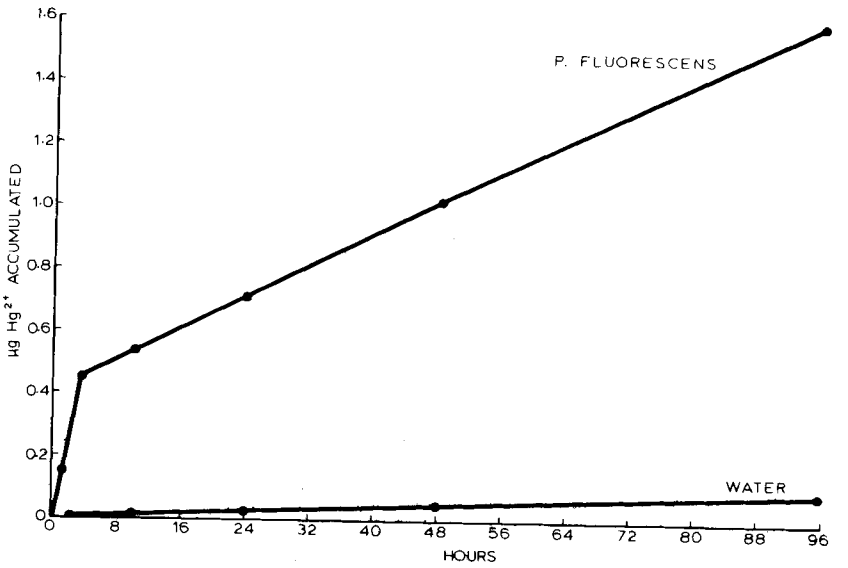

Fig. 2. Accumulation of mercury added to sediment by bacteria and river water. Properties of compartments studied as in Fig. 1.

Only limited balance measurements were carried out in this and similar experiments. The concentration of Hg in the sediment itself was so high (although such levels can be found in certain sediments below industrial outfalls) (D'ITRI, 1972b , MATIDA and KUMADA, 1969) that the loss of Hg to water and bacteria caused no detectible fall in the total amount. No definite effect on mercury transfer was observed in the presence of a chelation mixture of the fol-

lowing composition, added to the water compartment: Citric acid, 5 ppm; NTA, 1 ppm; Fulvic acid, 5 ppm; Cl^- (as NaCl), 3 ppm; PO_4 (as Na salt) 1 ppm; CO_3^{--} (as Na_2CO_3) 5 ppm.

The ability of microorganisms to bind heavy metals is well known. Adsorption of a number of heavy metals on the biological portion of activated sludge is recognized as a way of removing such ions from solution during sewage treatment (ADAMS et al. 1973).

Our experiments show that bacteria compete very effectively with sediment in accumulating mercuric ions from river water. The concentrations of bacteria used in these experiments are greater than those normally found in natural waters, but no grossly so: a total of about 1.4g (dry weight) in 5.5 l of river water. From estimations of the weight per cell (about 10^{-12} g from total cell counts) it is calculated that the concentration of cells for the whole water system studied was 2.5×10^8/ml. Viable counts (which are probably well below the total counts) of 1.7×10^7/ml were found in a badly polluted arm of the Ottawa River and 2.4×10^6 in a less polluted part (BLAISE and ARMSTRONG, 1973). Quite substantial numbers of bacteria and other microorganisms can exist in natural waters, and should have a significant effect on the mobilization of mercury from the presumed "sink" (the sediment) into food chains. No evidence was obtained for any conversion to organic forms of mercury in the system used, but it seems likely that any increase in the flux of mercury would promote interconversions to organic compounds.

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