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MERCURY CYCLING IN A SMALL HAWAIIAN ESTUARY

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by

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ABSTRACT

Uptake from food and water and loss of $^{203}HgCl_2$ were studied in two detritus feeders, the polychaete **Nereis succinea** *and the shrimp* **Palaemon debilis**, *from a small Hawaiian estuary. During 1973 to 1974, total mercury analyses were also conducted on sediment and biota samples collected from the estuary. Detritus feeders concentrated dissolved ^{203}Hg from 160 to 310 times over the concentration in sea water. Little ^{203}Hg was accumulated from labelled estuarine sediment; the steady state concentration of ^{203}Hg in the animals was 0.0025 to 0.015 times the concentration in the sediment the animals ingested. Net excretion of ^{203}Hg was slow relative to accumulation in both species. The total mercury content of shrimp and worms collected from the estuary showed a temporal pattern of variation. Samples of shrimp collected at five day intervals were used, with a mathematical description of the accumulation and loss of metal by the shrimp to simulate biotic mercury dynamics in the estuary. The simulation showed that mercury levels in shrimp in the Ala Wai Canal were never at steady state over the 1973-74 sampling period, and indicated the most important source of biologically available mercury in the estuary was some inorganic, solute form of the metal.*

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INTRODUCTION

In water quality studies concerned with trace contaminants, it is important to both determine contaminant concentrations in various components of the ecosystem of interest, and to attempt to explain why contaminants are found where they are. The former approach, used throughout the Water Resources Research Center's "Quality of Coastal Waters" project study, helps define water quality as observed at a given point in time. The latter approach can be useful in (1) developing information necessary to facilitate prediction of what will happen to ecosystems should contaminant inputs change, and (2) providing information which might aid in the future design of monitoring studies and other field studies of trace substance contamination.

This portion of the QCW project was carried out primarily to investigate the two objectives of the second approach of determining why contaminants are found where they are. The general purpose was to develop some understanding of the cycling of heavy metals within subtropical aquatic ecosystems. The inland termination of Ala Wai Canal, a small urban estuary, was chosen as a study area (Fig. 1). Like Hawaii Kai and Pearl Harbor, water quality in Ala Wai Canal is influenced by storm runoff from an urban area. During periods of rainfall in the small watershed of the canal, untreated runoff from a densely populated portion of urban Honolulu directly enters the canal. Thus, a study of metal cycling in Ala Wai Canal might not only provide general information of predictive value, but might also specifically enhance prediction of the effects of future urban development in Hawaii on heavy metal contamination of estuarine resources.

To facilitate an in-depth analysis of estuarine metal cycling, a single metal (mercury) was chosen for study. Mercury has been found in relatively high concentrations (>1000 ppb) in the smaller fractions of sediment swept from city streets (Sartor and Boyd 1972) and, thus, may be a significant pollutant associated with urban development. Reliable, sensitive methods for analysis of stable mercury in sediment, animal tissue, and water have been developed, and a radioisotope is readily available for use in laboratory experimentation. The environmental chemistry of mercury is complex (Fig. 2). The metal usually enters aquatic environments as $(C_6H_5)_2Hg$, $CH_3OCH_2CH_2Hg$, Hg^{o} or Hg^{++}. Jernelov (1972) and Wood (1974) have shown that, in aquatic systems, inorganic mercury (Hg^{++}) may be bound enzymatically or by covalent processes to methyl groups and, thus, converted to highly toxic monomethyl mercury ($CH\ Hg^{+}$) or to relatively nontoxic, highly volatile dimethyl mercury, $(CH_3)_2Hg$. Andern and Harriss (1973) have suggested macrofauna may also convert inorganic mercury to methylated mercury.

Several physical characteristics of the Ala Wai Canal indicate that inorganic mercury, rather than methyl mercury, was probably the form of the metal most important in the physical cycling of mercury within this estuary: (1) the sediments of the canal were highly anaerobic, a condition which inhibits the conversion of inorganic mercury to methyl mercury (Fagerstrom and Jernelov 1972; Gillespie 1972); (2) in the area of the canal chosen for this study (Fig. 1), the estuary was shallow, enhancing sunlight induced

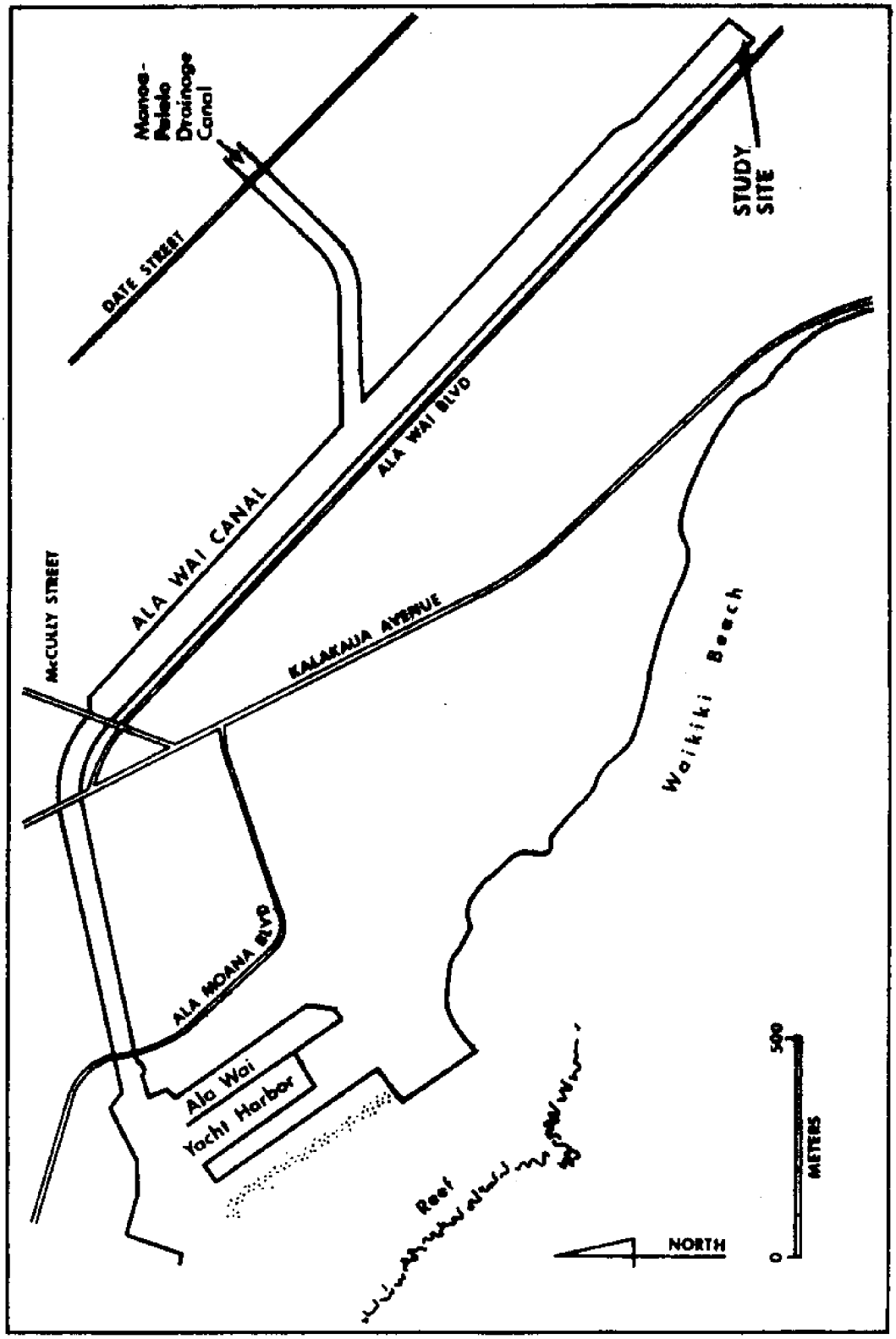

FIGURE 1. LOCATION OF THE ALA WAI CANAL STUDY SITE.

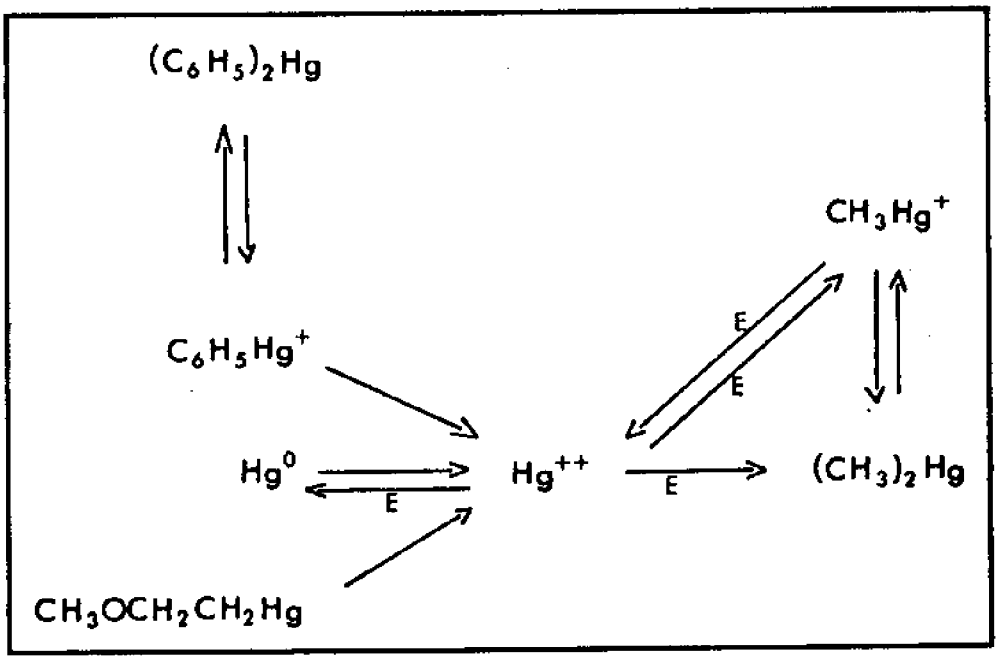

FIGURE 2. A MODEL OF THE ENVIRONMENTAL MERCURY CYCLE (ADAPTED FROM BAUGHMAN ET AL. 1973). DIVALENT MERCURY (Hg^{++}) MAY ALSO FORM SOLUBLE AND INSOLUBLE CHEMICAL COMPLEXES AS DESCRIBED IN THE TEXT. ONE WAY ARROWS INDICATING REACTION RATES IN THE OPPOSITE DIRECTION ARE EXTREMELY SLOW AND ARE PROBABLY INSIGNIFICANT. REACTIONS LETTERED E HAVE BEEN SHOWN TO BE ENZYMATICALLY CATALYZED.

degradation of methylmercury to mercuric sulfide (Baughman et al. 1973); and (3) the pH of the Ala Wai Canal water also consistently exceeded 7.0, a condition which favors formation and volatilization of dimethyl mercury, overformation of the toxic, more persistent, monomethyl form of the metal (Jernelov 1972). Thus, laboratory experiments in this study were conducted using divalent inorganic mercury in chloride form, $HgCl_2$. Samples of organisms and sediment collected from the canal were analyzed for total mercury--the sum of all forms of the metal described in Figure 2.

OBJECTIVES

This study, then, specifically involved a study of inorganic mercury cycling in a small, urban Hawaiian estuary. The objectives of the study were:

(1) to provide general information about what happens to mercury when it is released into an ecosystem,
(2) to help develop improved methods for future studies of heavy metal contamination in Hawaiian coastal (especially estuarine) ecosystems, and
(3) to facilitate prediction of the effects of coastal urban development in Hawaii on heavy metal contamination of marine and estuarine biotic resources.

METHODS AND MATERIALS

Radiomercury Analyses

A combination of laboratory and field experiments was used to approach the problem of mercury cycling in the Ala Wai Canal. In the laboratory, all studies were conducted using ^{203}Hg in chloride form, $^{203}HgCl_2$. The specific activity of the ^{203}Hg was such that no carrier mercury, other than that in the processed radioisotope, was needed to reach the desired concentrations in the medium.

The ^{203}Hg activity in individuals from three species of detritus feeders, in dissected crab organs, in water, and in sediment, were measured using liquid scintillation. The ^{203}Hg activity in water was determined from 1 mℓ Millipore filtered (0.45μ) samples without digestion. The polychaetes were digested individually at each sampling interval in scintillation vials using 75 percent nitric:perchloric acid (17:3) for three hours at 50° C. Crab organs and individual shrimp and fish were digested in 2 or 3 mℓ concentrated nitric:perchloric acid at room temperature. The sediment was digested in 5 mℓ of the concentrated acid at 50° C for 24 hours. No loss of mercury occurred using these procedures, because at low pH all mercury is present as nonvolatile Hg^{++}. Recoveries of known amounts of ^{203}Hg added to sediment were 99%±1% (SD) using these techniques.

After digestion or extraction, liquid scintillation was used to measure the ^{203}Hg in an aliquot of tissue digest or extract. The liquid samples were all made to 1 mℓ with distilled water or ascorbic acid and 10 mℓ of the liquid scintillation cocktail, Aquasol (New England Nuclear) were added to each. The samples were allowed to stand (to stabilize any chemiluminescence) and the activity was then measured using a Beckman LS100 ambient temperature liquid scintillation counter. Counting efficiency was determined by plotting the external standard ratio from quenched standards, made by adding varying amounts of acid digested, nonradioactive, animal tissue, to known ^{203}Hg samples. Disintegrations per minute were corrected for decay, then converted to parts per billion (ppb) mercury using the formula

$$\text{ppb } ^{203}Hg = \frac{(\text{DPM/Decay}) \times \text{SpAct}}{\text{g worm}} \qquad (1)$$

where DPM = disintegrations per minute,
Decay = percent of activity remaining after decay, since the nuclide was processed (all samples were corrected to the activity on the day of processing),
SpAct = specific activity or ng Hg/DPM ^{203}Hg on processing day,
g worm = weight of the worm analyzed.

The time course of ^{203}Hg whole body uptake by the crab, *T. crenata*, and by the shrimp, *P. debilis* were determined by placing whole animals on a lead-shielded NaI gamma scintillation crystal and counting by gamma scintillation on a Nuclear Chicago Model D181 gamma counter. Although no variable pulse height analyzer was used, the resulting background (2000-5000 cpm) was insignificant in terms of total activity of the samples.

Total Mercury Analyses

Organisms and sediment were also periodically collected from the Ala Wai Canal and analyzed for total mercury. For each of the detritus feeding species (polychaete, shrimp, and fish), one sample represented a number of individuals pooled to a weight of 2-5 grams. Thus, while only three samples of each species were usually taken at each time period, the mean of the mercury concentration in the three samples represented the mean wholebody mercury concentration from 10 to 50 individual organisms of that species. The crabs were dissected so that four organs or groups of organs were analyzed from each individual: chela muscle, body muscle, viscera, and gills.

Sediment samples were scraped from the upper 5 mm of intertidal sediment, and 1 g (wet wt.) was separated for digestion and analysis. The water content of the sediment was determined by drying 5 grams of the material. These values were also used to calculate dry weight mercury concentrations. Oven dried sediment samples were not analyzed directly for total mercury because such treatment may result in volatilization of mercury from the sample (Thompson and McComas 1973).

The analysis for total mercury in samples employed the digestion techniques suggested by Knauer and Martin (1972). To each sample, 7 mℓ of concentrated sulfuric:nitric acid (2:1) was added. After the reaction had cooled, the mixture was kept overnight at 80° C (in a drying oven), then samples were stored, if necessary. Prior to analysis, an excess of 6 percent potassium permanganate (usually about 10 mℓ) plus 2 mℓ potassiumpersulfate were added to each sample to assure oxidation of all organic matter. This mixture was left overnight. The excess permanganate was then reduced with several drops of hydrogen peroxide and back titrated with permanganate until light pink; Knauer and Martin (1972) found this process important in removing gaseous oxides of nitrogen which otherwise caused peak suppression during mercury determination. Samples were then washed into standard BOD bottles and distilled water was added to a total volume of 100 mℓ. At this point, all mercury was in oxidized form. Hydroxylamine hydrochloride was added to reduce the permanaganate and remove any interference from Fe^{++} (Thompson and McComas 1973). To these samples, 5 mℓ of stannous chloride (88 g/ℓ in 0.5N H_2SO_4) were added to reduce all Hg^{++} to the volatile species Hg^{o}, and the BOD bottle was immediately connected to a closed cold vapor mercury analysis chamber (Manning 1970). The Hg^{o} was purged from solution in this system by bubbling air through the mixture. Mercury was determined by flameless atomic absorption using either a Perkin-Elmer Atomic Absorption Spectrophotometer (Model 305A) fitted with a hollow cathode mercury lamp or by using a Coleman Mercury Analyzer. Preliminary experiments in this laboratory and work by other authors (Siegel 1973; Tuna Research Foundation 1971) indicated similar results are obtained from either type of instrumentation. The detection limit of mercury was 0.01 µg. All samples were corrected for contamination using reagent blanks. Instruments were calibrated before and during every run using Hg^{++} in chloride form. Recoveries, using digested animal tissue spiked with known concentrations of mercury, showed this method to be 103±5% (SD) efficient.

Organic Mercury Analyses

Organic mercury analyses were conducted acoording to the methods of

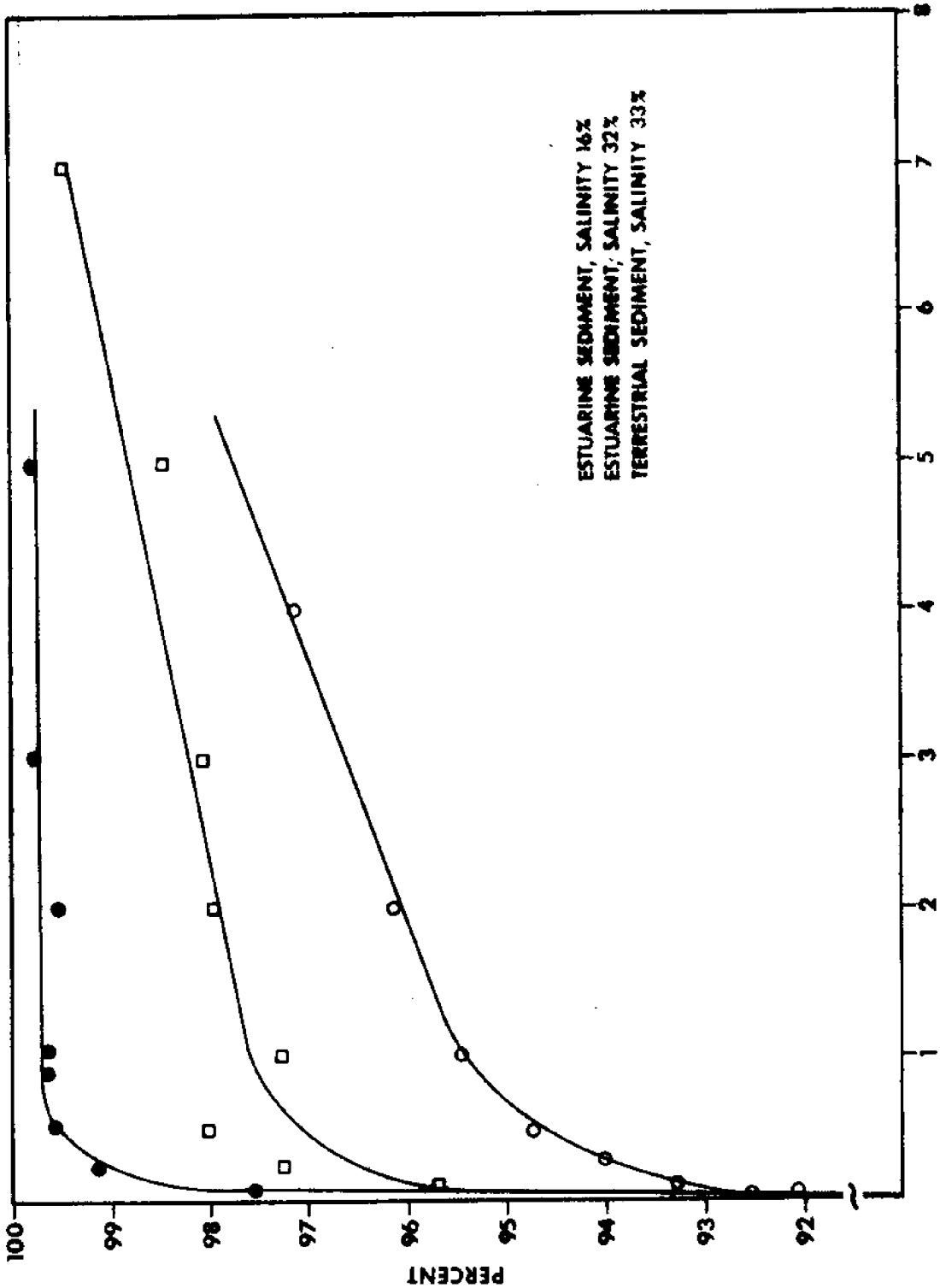

FIGURE 3. LOSS OF ^{203}Hg FROM SEA WATER AFTER EXPOSURE TO SEDIMENT AS A FUNCTION OF TIME.

Rivers, Pierson, and Schultz (1972). Briefly, tissue samples were homogenized in a Waring Blender with an equal volume of distilled water. Each sample was made-up to a volume of 70 mℓ with 10 g of NaCl and distilled water. The sample was then extracted in 65 mℓ of benzene, and centrifuged until the benzene phase was clear. From the benzene phase, 50 mℓ was pipetted into a 125 mℓ separatory funnel with 7 mℓ of 1 percent cysteine solution (1 g L-cys, 0.775 g sodium acetate, and 12 g sodium sulfate in 100 mℓ distilled water). After extraction and phase separation (by centrifuging several times), 4 mℓ concentrated HCl and 10 mℓ 6 percent potassium permanganate were added to 4 mℓ of the cysteine extract. After 30 minutes oxidizing time, the samples were analyzed for Hg^{++} using cold vapor atomic absorption techniques.

RESULTS AND DISCUSSION

Metal-Sediment Interactions

Divalent mercury (Hg^{++}) is an highly electropositive cation with an extremely strong affinity for binding to inorganic and organic particulates within aquatic ecosystems. In a simple laboratory experiment, ^{203}Hg was dissolved in sea water then exposed to either estuarine sediment, at salinities of 16.8‰ or 32‰, or to terrestrial sediment. Figure 3 shows that, under all three conditions, greater than 90 percent of the mercury, once in solution, had become adsorbed to the particulate material within less than two minutes. When equilibrium was reached, in all three treatments, only 0.5 percent of the initial concentrations of dissolved ^{203}Hg remained in the water column. Little of the ^{203}Hg bound to the sediments in these experiments moved from sediment back to the water column when fresh sea water was placed in the experimental aquaria. In eight different experiments, the concentration of mercury in the sediment exceeded that in the water by an average of $1.42 \pm 0.85 \times 10^5$ (SD) times (Table 1), after equilibration of the sediment with the unlabelled sea water. Thus, the fixation of ^{203}Hg to sediment in these experiments was not only rapid but also relatively irreversible. It is not surprising, then, that in field studies of mercury, concentrations in sediment and water from aquatic ecosystems concentrations of the dissolved metal in most water samples are below the limits of detectability (<0.1 ppb), while mercury is usually readily detectable (>100 ppb) in even the most pristine aquatic sediments.

Because mercury preferentially associates with sediments, this portion of the ecosystem tends to integrate over time to the degree of mercury contamination to which an aquatic system is subject. Many authors have used sediment concentrations of mercury as an indicator of mercury contamination in an aquatic ecosystem. Table 2 compares mercury concentrations in the sediment of the Ala Wai Canal with concentrations of the metal observed in sediments of some other nonurban Hawaiian marine and estuarine ecosystems included in the QCW study. Although standard deviations were large in all studies, mean total mercury in sediments from the Ala Wai Canal were significantly higher than found in the nonurban aquatic environment studies. This suggested there was some localized input of mercury into the canal, and indicated that input might result from the urban location of the estuary.

TABLE 1. COMPARISON OF THE CONCENTRATION OF ^{203}Hg IN SEDIMENT AND SEA WATER IN EXPERIMENTS USING ALA WAI CANAL SEDIMENT. SEA WATER WAS ADDED TO ^{203}Hg-LABELLED SEDIMENT AND MEASUREMENTS WERE TAKEN AFTER 24 HRS OF EQUILIBRATION. THE DISTRIBUTION COEFFICIENT IS THE RATIO OF DRY WEIGHT ^{203}Hg CONCENTRATION IN SEDIMENT VERSUS THE CONCENTRATION OF ^{203}Hg IN AN EQUAL WEIGHT OF SEA WATER.

Concentration of ^{203}Hg (ppb)		Distribution Coefficient
Sediment	Sea Water	
344	0.122	2.82×10^4
914	0.096	9.52×10^4
801	0.076	1.05×10^5
1171	0.071	1.65×10^5
1292	0.086	1.50×10^5
1425	0.068	2.10×10^5
1834	0.225	8.10×10^4
2086	0.070	2.98×10^5

Accumulation and Retention of Mercury by Detritus Feeders

TOTAL MERCURY IN DETRITUS FEEDERS FROM THE ALA WAI CANAL. To determine the degree to which the mercury observed in the Ala Wai Canal might be cycled into the macrobiotic portion of this estuary, experiments were initiated with three species of organisms from the canal: the shrimp, *Palaemon debilis;* the polychaete worm, *Nereis succinea;* and the poecilid fish, *Mollienesia latipinnia.* Preliminary studies showed the three species were detritus feeders, ingesting organic and inorganic particulates associated with the sediments of the canal while feeding, and presumably gaining nutrition from the organic matter associated with these particles. Thus, these organisms would be directly exposed to both the concentrated sedimentary pool of mercury in the estuary, and to any mercury entering the canal in dissolved form, making them potentially excellent indicators of the extent and the nature of mercury cycling within this estuary. The three detritus feeding species were also an important food source for predator species in the estuary and might provide a link in the transfer of mercury into the economically important portion of this detritus-based food web.

As one approach to the study of mercury cycling into the detritus-based food web of the Ala Wai Canal, total mercury concentrations were determined in sediment and in two of the detritus feeding species (shrimp and worm) during 1973-74. Figure 4 shows that the mean concentration of total mercury in sediments from the canal varied considerably between samples over the sampling period. However, no readily obvious temporal pattern of change in total mercury levels in the sediment was observed. Total mercury concentrations in the two detritus feeders during the same period are shown in Figure 5. In contrast with results observed with sediment, there was an obvious pattern of temporal variation in the concentration of mercury observed in both the worm and the shrimp throughout the 1973-74 sampling period. During months when rainfall in the Ala Wai watershed normally occurs more frequent-

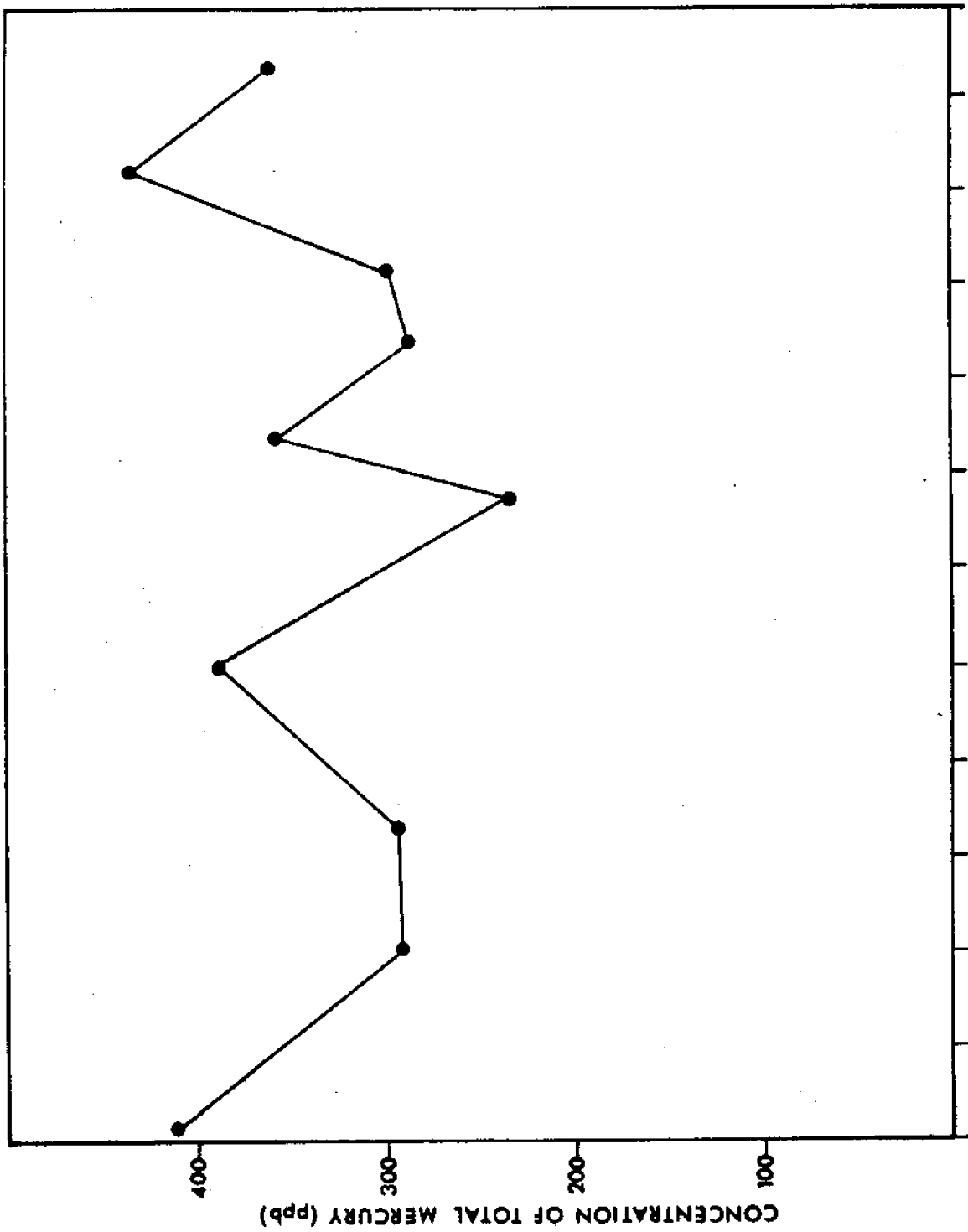

FIGURE 4. TOTAL MERCURY CONCENTRATIONS IN SEDIMENT FROM ALA WAI CANAL DURING 1973-74. EACH POINT REPRESENTS THE MEAN OF AT LEAST THREE SAMPLES.

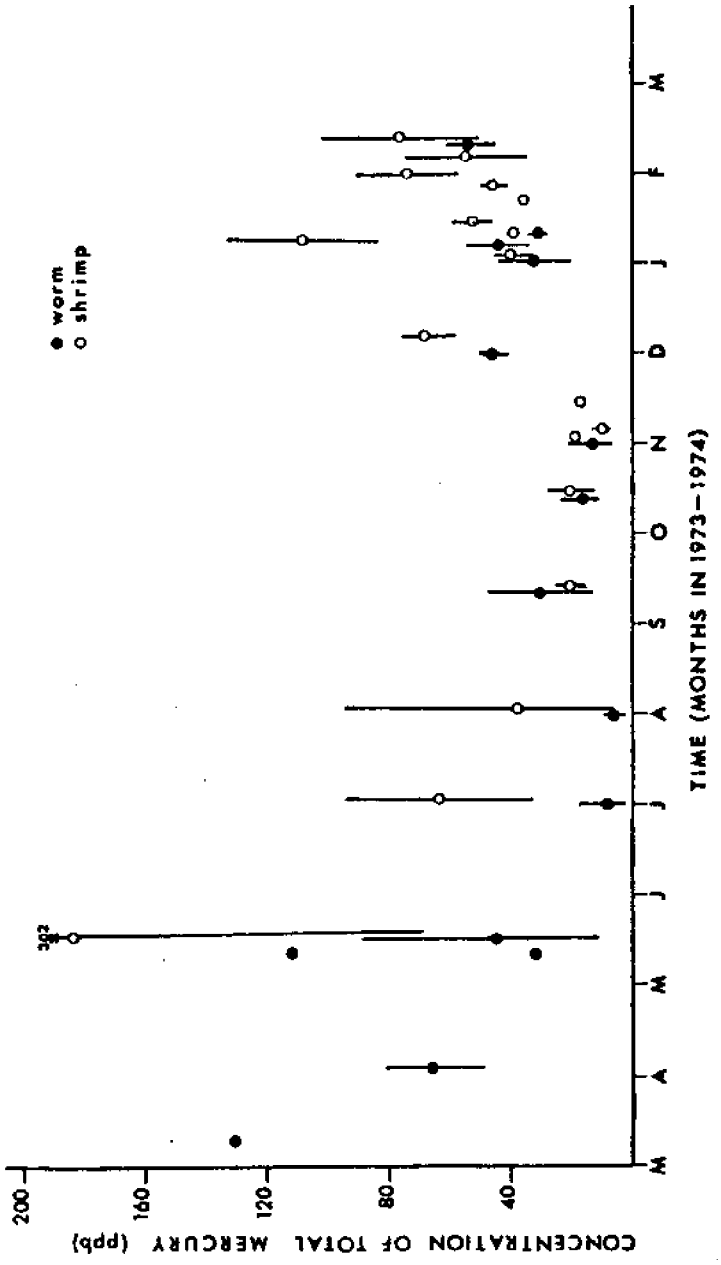

FIGURE 5. TOTAL MERCURY CONCENTRATION IN *P. DEBILIS* AND *N. SUCCINEA* PERIODICALLY COLLECTED FROM ALA WAI CANAL THROUGH 1973-74. (MERCURY VALUES REPRESENT WET WEIGHT CONCENTRATIONS.)

TABLE 2. TOTAL MERCURY CONCENTRATIONS IN SEDIMENT OF SEVERAL HAWAIIAN AQUATIC ECOSYSTEMS.

Location	Type of System	Total Hg in Sediment (ppb dry wt.)
Kahana Bay, Oahu*	Marine (pristine)	72 ± 65 (12)
Kalihiwai Bay, Kauai*	Estuarine (adjoining agricultural discharge)	125 ± 75 (11)
North Kauai*	Marine (agricultural sugarcane mill waste, and nonpoint discharge)	94 ± 83 (27)
Pearl Harbor, Oahu*	Estuarine (harbor, military, urban, agricultural, and industrial discharge)	194 ± 102 (7)
Waikiki, Oahu*	Marine (recreation, urban, and nonpoint discharge)	128 ± 234 (22)
Ala Wai Canal, Oahu†	Estuarine (urban runoff)	386 ± 383 (30)
Ala Wai Canal, Oahu‡	Estuarine (urban runoff)	334 ± 108 (31)

NOTE: Numbers in parentheses indicate the number of samples from which means were calculated.
* Lau 1972.
† Siegel 1973.
‡ This study.

ly (December-May), mercury concentrations in both detritus feeding species were higher than observed during normally drier months (July-November). The strong dissimilarity between the temporal pattern of fluctuation in the concentration of mercury within detritus feeders and the pattern of fluctuation of the concentration of the metal in the sedimentary food of these organisms suggested sedimentary-bound mercury might not provide the most significant contribution to the body burden of the metal observed in worms and shrimp collected from the canal.

UPTAKE OF ^{203}Hg FROM FOOD. To directly investigate the uptake of sediment-bound mercury by detritus feeders, sediment was collected from the Ala Wai Canal and labelled in the laboratory with ^{203}Hg. The sediment used in these experiments was highly organic (24.5 percent weight loss after 12-hr ashing at 550° C). Because of the strong affinity of mercury for organic binding sites (Vallee and Ulmer 1972), the metal will bind preferentially to the organic fraction of the substrate when organic matter is abundant in the sediment (Jenne 1968). Thus, in these experiments, the ^{203}Hg label was probably bound to the organic fraction of the Ala Wai Canal sediment, that portion of the sediment which comprised the food of the detritus feeders.

All three detritus feeding species, the worm, the shrimp, and the fish, were exposed to the ^{203}Hg-labelled Ala Wai Canal sediment in different experiments. Before analysis for ^{203}Hg in its tissue, each animal was allowed to defecate any radioactive sediment in its intestinal tract. Complete defecation of sediment seldom took longer than 6 hours. Correction for any loss of ^{203}Hg from the tissues of the animal over the defecation period was made by using data from efflux experiments. Figure 6 shows that after sufficient exposure to the nuclide, all three animals reached a steady state

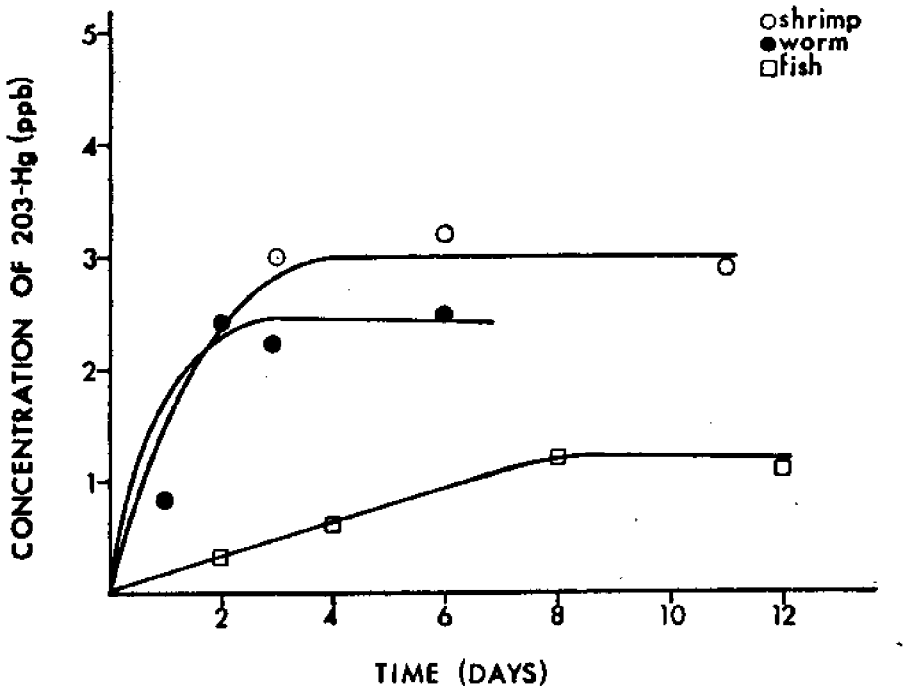

FIGURE 6. UPTAKE OF ^{203}Hg BY THE DETRITUS FEEDERS *N. SUCCINEA* (WORM), *P. DEBILIS* (SHRIMP), AND *M. LATIPINNIA* (FISH) FROM LABELLED ESTUARINE SEDIMENT AS A FUNCTION OF TIME.

concentration of the metal. Table 3 show the magnitude of that steady state. When worms were exposed to 344 ppb ^{203}Hg (the approximate concentration of total mercury observed in the Ala Wai Canal sediment), they accumulated a steady state concentration of the metal of only 2 ppb. Shrimp and fish exposed to 1172 ppb and 1374 ppb ^{203}Hg, respectively, accumulated only 2-3 ppb of the metal. The footnotes in Table 3 show that the concentration of the nuclide in the feces of both the worm and the fish exceeded ^{203}Hg concentrations in the food of the animals. Thus, while these three species were ingesting the ^{203}Hg-labelled portion of the sediment, they were unable to assimilate significant amounts of the ingested mercury into their tissues. Steady state organismic ^{203}Hg concentrations ranged from only 0.006 to 0.015 of the concentration of the metal in the sediment upon which these species fed. Thus, it would take very large changes in the concentration of mercury in the sediment to result in any significant change in the mercury content of these detritus feeders. Large changes in the concentration of total mercury in sediments from the Ala Wai Canal were not observed during the 1973-74 sampling period. These results then indicated that mercury associated with estuarine sediment in the Ala Wai Canal contributed little to the body burden of the metal observed in sediment-ingesting organisms in this estuary.

TABLE 3. UPTAKE OF ^{203}Hg FROM LABELLED SEDIMENT BY THREE DETRITUS FEEDERS: THE WORM, *N. succinea;* THE SHRIMP, *P. debilis;* AND THE POECILID FISH, *M. latipinnia*

Species	Mean Concentration of ^{203}Hg ± One Std. Dev. (ppb)		CF_{cs}*
	Sediment (dry wt.)	Feeding Organism at Steady State (wet wt.)	
Worm	344 ± 93 (4)	2 ± 1 (14)	0.010
Worm	915 ± 397 (4)	11 ± 5 (16)	0.012
Worm†	1475 ± 75 (2)	22 ± 7 (7)	0.015
Shrimp	1172 ± 268 (3)	3 ± 2 (28)	0.0025
Fish‡	1354 ± 125 (2)	2 ± 2 (18)	0.0016
Worm§	1292 ± 439 (3)	12 ± 5 (11)	0.0094

NOTE: Organic content of the sediment was 24.5% weight loss after ashing, except where noted otherwise. Numbers in parentheses indicate the number of samples from which each value was determined.

* Steady state concentration of ^{203}Hg accumulated by the organism relative to the concentration of the nuclide in estuarine sediment (concentration factor relative to estuarine sediment).

† Concentration of ^{203}Hg in the feces of the worm was 2487 ppb (dry wt.).

‡ Concentration of ^{203}Hg in the feces of the fish was 3325 ppb (dry wt.).

§ Organic content of the sediment in this experiment was 11.5% weight loss after ashing.

UPTAKE OF ^{203}Hg FROM SOLUTION. Since food (sediment) appeared to contribute little to mercury levels observed in detritus feeders from the Ala Wai Canal, it was important to an understanding of mercury cycling in the canal to determine the role other sources or processes may play in mercury uptake by these organisms. Aquatic organisms may accumulate heavy metals from solution. To investigate the significance of this phenomenon, ^{203}Hg was dissolved in sea water of 32 ‰ salinity. The worm and the shrimp were then exposed to the labelled sea water. Nuclide concentrations in the medium

were held constant. Figure 7 shows that after exposure to the labelled water for a sufficient period of time (13 hrs for the worm, 3 days for the shrimp), both species reached a steady state concentration of the metal. In Figure 8, it can be seen that as the concentration of ^{203}Hg in the sea water was increased from 0.5 ppb to 6 ppb, steady state ^{203}Hg concentrations in the worm increased from less than 100 ppb to 1400 ppb. Similar results were observed with the shrimp. Table 4, calculated from Figure 8, shows these two species concentrated dissolved mercury to body levels which exceeded the concentration of the metal in the water column by 160-310 times. The results indicated that, although only very low concentrations of mercury normally exist in solution due to the affinity of the metal for particulate material, it would take only a very small increase in the concentration of this small dissolved pool of the metal to result in a large and rapid increase in the concentration of mercury in either the worm or the shrimp. Small temporal changes in the concentration of mercury dissolved in the water of the Ala Wai Canal could then result potentially in the temporal changes in the mercury content of detritus feeders from the canal as observed during 1973-74.

TABLE 4. CONCENTRATION FACTOR, C_{SS}/C_{WO}, FOR THE WORM, *N. succinea*, AND THE SHRIMP, *P. debilis*, AS A FUNCTION OF THE CONCENTRATION OF ^{203}Hg IN SEA WATER

Concentration of ^{203}Hg in Sea Water (ppb)	C_{SS}/C_{WO}* (*N. succinea*)	C_{SS}/C_{WO} (*P. debilis*)
1	160	270
2	180	275
3	203	240
4	236	200
5	310	181

NOTE: Calculated from data presented in Figure 2.
* C_{SS} = organismic steady state concentration of ^{203}Hg; and C_{WO} = initial concentration of ^{203}Hg in sea water.

EFFECTS OF VARIATIONS IN PHYSICAL PARAMETERS WITHIN THE ESTUARY. Estuaries are characterized by spatial and temporal fluctuations in various physical parameters. Changes in the physical environment of an organism may affect the ability of that organism to accumulate mercury.

Salinity. Several authors have shown that the rate of accumulation of mercury by estuarine organisms may be affected by salinity (e.g., Wolfe and Coburn 1970). Salinity in the Ala Wai Canal is influenced by rainfall (Gonzalez 1971). Thus, the body burden of mercury observed in biota from the canal could be indirectly affected during the rainy season through the influence of rainfall on salinity in the estuary. To test this, worms and shrimp were acclimated for four hours (to test the effects of short-term salinity changes) or for four days (to study the effects of long-term changes in salinity) to a given salinity. The animals were then exposed to ^{203}Hg-labelled sea water at the salinity to which they were acclimated. Similar results were observed after both four-hour and four-day acclimation periods. Figure 9 shows that down to salinities of 6 ‰, this variable had

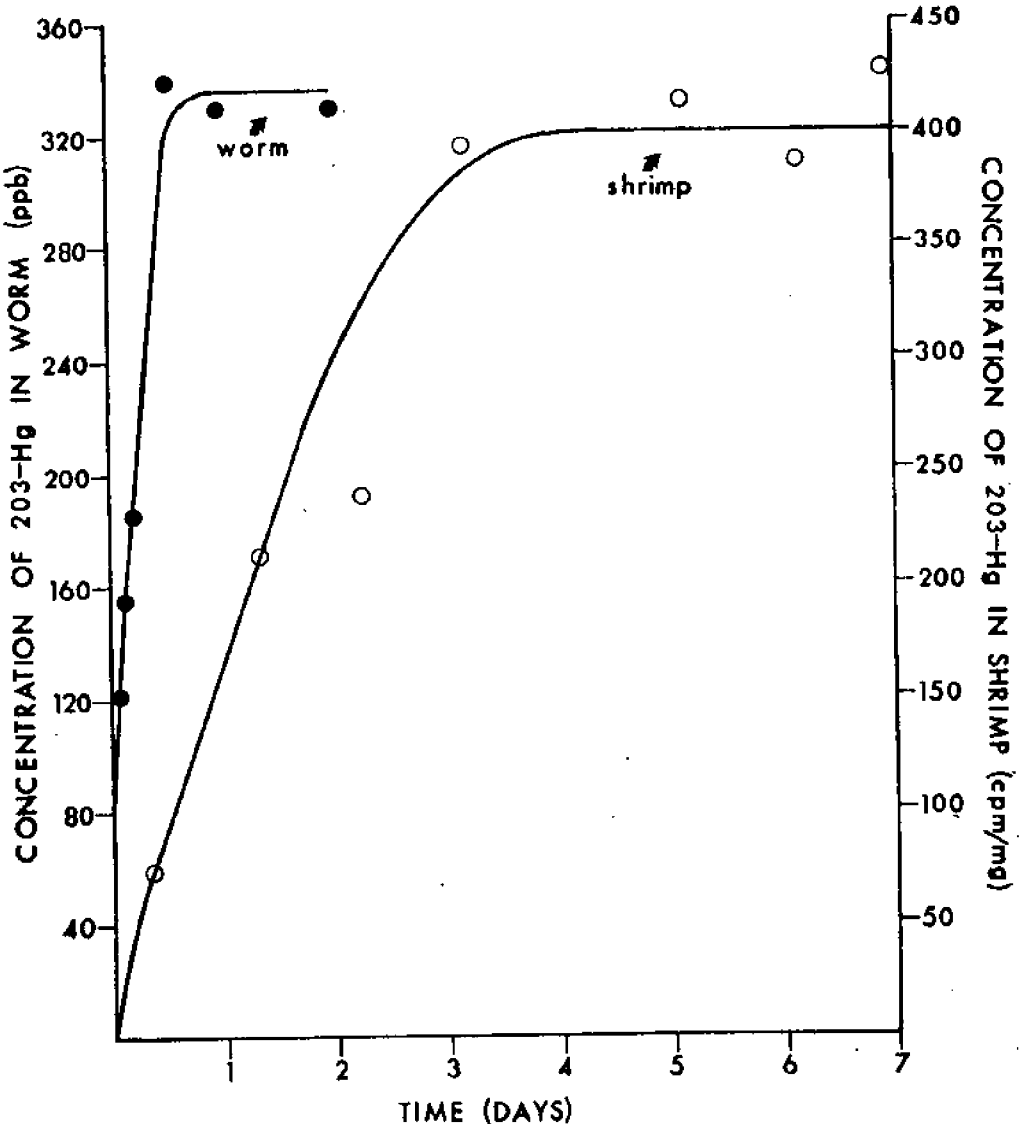

FIGURE 7. UPTAKE OF ^{203}Hg FROM SEA WATER BY *N. SUCCINEA* AND *P. DEBILIS* AS A FUNCTION OF TIME. THE MEDIUM CONTAINED 1.0 PPB ^{203}Hg IN EXPERIMENTS WITH SHRIMP AND 1.88 PPB ^{203}Hg IN EXPERIMENTS WITH WORMS. EACH POINT REPRESENTS THE MEAN MERCURY CONCENTRATION IN AT LEAST FIVE ANIMALS. LINES WERE FIT BY EYE.

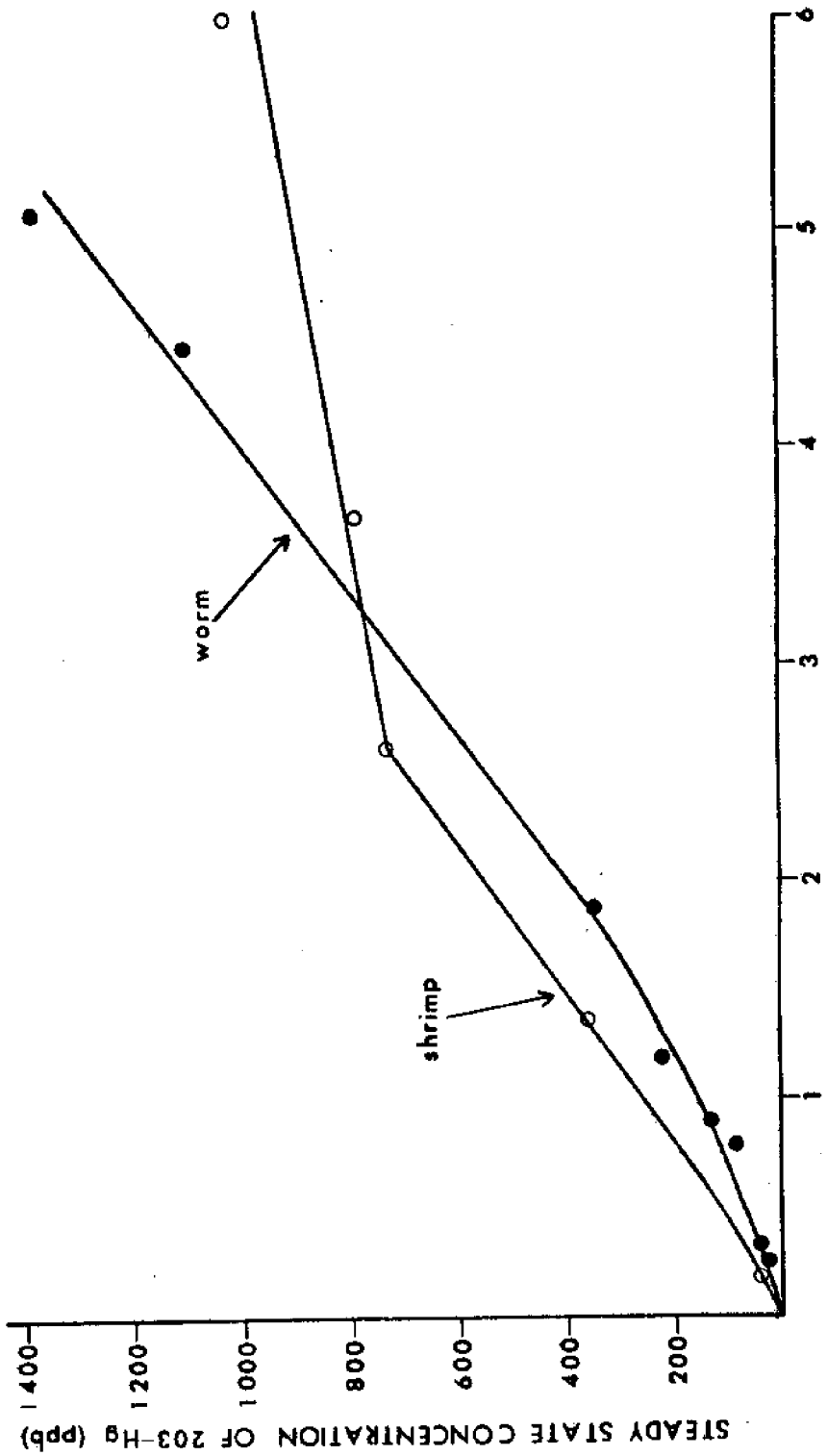

FIGURE 8. STEADY STATE CONCENTRATION OF ^{203}Hg IN *N. SUCCINEA* AND *P. DEBILIS* AS A FUNCTION OF THE CONCENTRATION OF ^{203}Hg IN SEAWATER. LINES WERE FIT BY EYE.

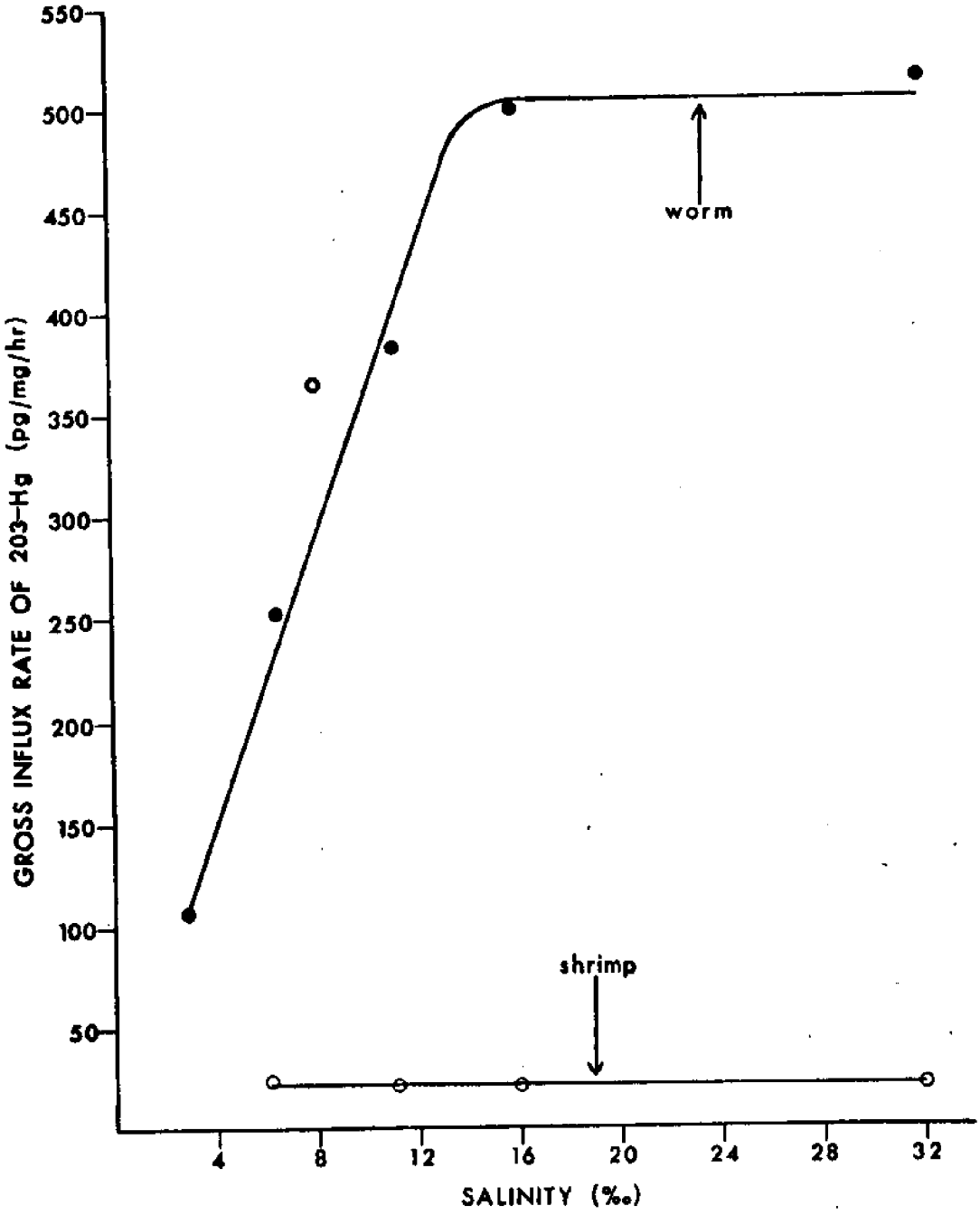

FIGURE 9. THE RATE OF UPTAKE OF DISSOLVED ^{203}Hg BY *N. SUCCINEA* AND *P. DEBILIS* AS A FUNCTION OF THE SALINITY OF THE MEDIUM AFTER ANIMALS WERE ACCLIMATED TO A GIVEN SALINITY FOR FOUR HOURS. CONCENTRATION OF ^{203}Hg IN THE MEDIUM WAS 1 PPB. STARRED POINT REPRESENTS THE RATE OF UPTAKE OF ^{203}Hg BY *N. SUCCINEA* AFTER FOUR DAYS ACCLIMATION TO THE GIVEN SALINITY.

no effect on the rate of ^{203}Hg accumulation by the shrimp. However, the rate of mercury accumulation by the worm decreased as salinity decreased below 16‰. Salinities below 6‰ have not been recorded in the portion of the Ala Wai Canal where this study was conducted (Harris 1972; Gonzalez 1971; personal observation). Mercury concentrations in samples of the worm and the shrimp collected from this study area were *highest* during periods when the Ala Wai watershed was subject to more frequent rainfall (and, thus, frequent *decreases* in salinity). Such decreases in salinity probably had no effect on the body burden of mercury observed in shrimp from the canal, but may have inhibited accumulation by the worm of any biologically available mercury which was present during periods of storm runoff. Salinity changes, alone, could not have accounted for the elevated mercury concentrations observed in the worm and the shrimp during the rainy season.

Dissolved Organic Molecules. Estuaries tend to be relatively productive ecosystems. This is especially true of the terminal part of the Ala Wai Canal, where poor circulation and heavy nutrient input combine to produce highly eutrophic conditions (Harris 1972; Gonzalez 1971). In such highly productive ecosystems, energy cycles tend to be inefficient and organic matter accumulates both in the sediments and in dissolved form in the water column. The presence of dissolved organic material has been shown to reduce the toxicity of dissolved copper (Morris and Russell 1973), and dissolved mercury (Corner and Rigler 1958) in aquatic organisms. Reductions in the toxicity of metals in sea water containing dissolved organic material may result from binding of the metals to organic molecules and a reduced uptake of the metal ions in this bound form. To test this, 1 m*M* cysteine was dissolved sea water. The sea water was then labelled with from 1*NM* (0.2 ppb) to 25*NM* (4 ppb) ^{203}Hg. Cysteine is an amino acid which contains a sulfhydryl end group. Because mercury has a strong affinity for binding to sulfhydryl groups (Vallee and Ulmer 1972), and because of the large number of cysteine molecules in solution relative to the number of dissolved atoms of mercury, it was presumed that most of the ^{203}Hg in solution was bound to amino acid in these experiments. In a similar experiment, a high concentration of a large protein (100 mg/ℓ bovine serum albumin [BSA]) was also dissolved in sea water, and this solution was labelled with ^{203}Hg. BSA is also characterized by a large number of sulfhydryl groups and should readily bind mercury. When the worm, *N. succinea*, was exposed to dissolved ^{203}Hg bound to either the dissolved amino acid or the dissolved protein, this species accumulated steady state concentrations of the metal which were only 4 to 7 times higher than the concentration of ^{203}Hg in the organic molecule-laden sea water (Table 5). In contrast, dissolved mercury was concentrated by the worm 124 - 235 times over similar concentrations of the metal in sea water to which no organic molecules were added (Table 5). Thus, it appeared that the biological availability of mercury was reduced when the metal was bound to dissolved organic molecules.

Because of the low concentration of dissolved organic material in sea water, the extent and significance of the formation of complexes between heavy metals and organics in nature remains a subject of some controversy (Robertson 1971). To determine if sufficient dissolved organic matter occurred in Ala Wai Canal water to affect the biological availability of mercury, uptake of the metal by the worm from the Ala Wai Canal water was compared with uptake from open ocean water. Water from both sources was

TABLE 5. CONCENTRATION OF ^{203}Hg ACCUMULATED BY *N. SUCCINEA* RELATIVE TO THE INITIAL CONCENTRATION OF THE NUCLIDE IN SEA WATER (CF_W) WHEN THE WORM WAS EXPOSED TO ^{203}Hg IN SEA WATER CONTAINING DISSOLVED CYSTEINE (1 mM) OR DISSOLVED BSA (100 mg/ℓ), COMPARED WITH THE DEGREE TO WHICH THE WORM CONCENTRATED ^{203}Hg FROM SEA WATER ALONE.

C_{WO} (ppb)	Cysteine-Bound ^{203}Hg (CF_W)	BSA-Bound ^{203}Hg (CF_W)	^{203}Hg in Sea Water Alone (CF_W)
0.21		7	124
0.45	4		129
1.14		5	158
2.12	4		180
4.12		4	235

NOTE: CF_W is the concentration factor of ^{203}Hg from sea water, C_{SS}/C_{WO}, where C_{SS} = organismic steady state concentration of ^{203}Hg, and C_{WO} = initial concentration of ^{203}Hg in sea water.

of the same salinity (32‰) and was Millipore filtered before labelling. The canal water sample was taken in summer when productivity was high (Harris 1972), but the direct influence of storm runoff on water quality was minimal. Figure 10 shows that ^{203}Hg uptake by the worm from the more eutrophic canal water was considerably less than uptake from the more oligotrophic open ocean water over a range of dissolved ^{203}Hg concentrations from 0.2 to 6.8 ppb. Thus, during the summer, the availability of dissolved mercury to the biota of the Ala Wai Canal appeared to be less than the biological availability of the metal dissolved in open ocean water, due apparently to the abundance of dissolved organic matter in the waters of the estuary. Temporal fluctuations in dissolved organic matter within the canal could, then, also have affected the concentration of mercury observed in worm and shrimp samples collected from the Ala Wai Canal during 1973-74.

Terrestrial Sediment. All estuaries are subject to a periodic influx of terrestrial sediment coincident with storm runoff from their watersheds. Because of its urban watershed, much of the terrestrial sediment which enters the Ala Wai Canal in storm runoff probably originates from streets and other urban sources. The physical characteristics of particulates washed into the estuary in this runoff may be quite different from the characteristics of the particulates which make up the sediment of the Ala Wai Canal. Darnell (1967) has shown that the inorganic and organic particulates of which estuarine sediment is composed are characterized by an adsorbed "coat" of organic molecules, microflora, and microfauna. Inorganic terrestrial particulates, which are found in storm runoff, probably lack much of this organic coating. Similarly, sulfur, associated with terrestrial sediment, most often occurs in oxidized form (with no affinity for mercury), while reduced sulfur (with a high affinity for mercury) is dominant in heavily organic estuarine sediment*. Any physical and/or

* A.W. Andern 1973: personal communication.

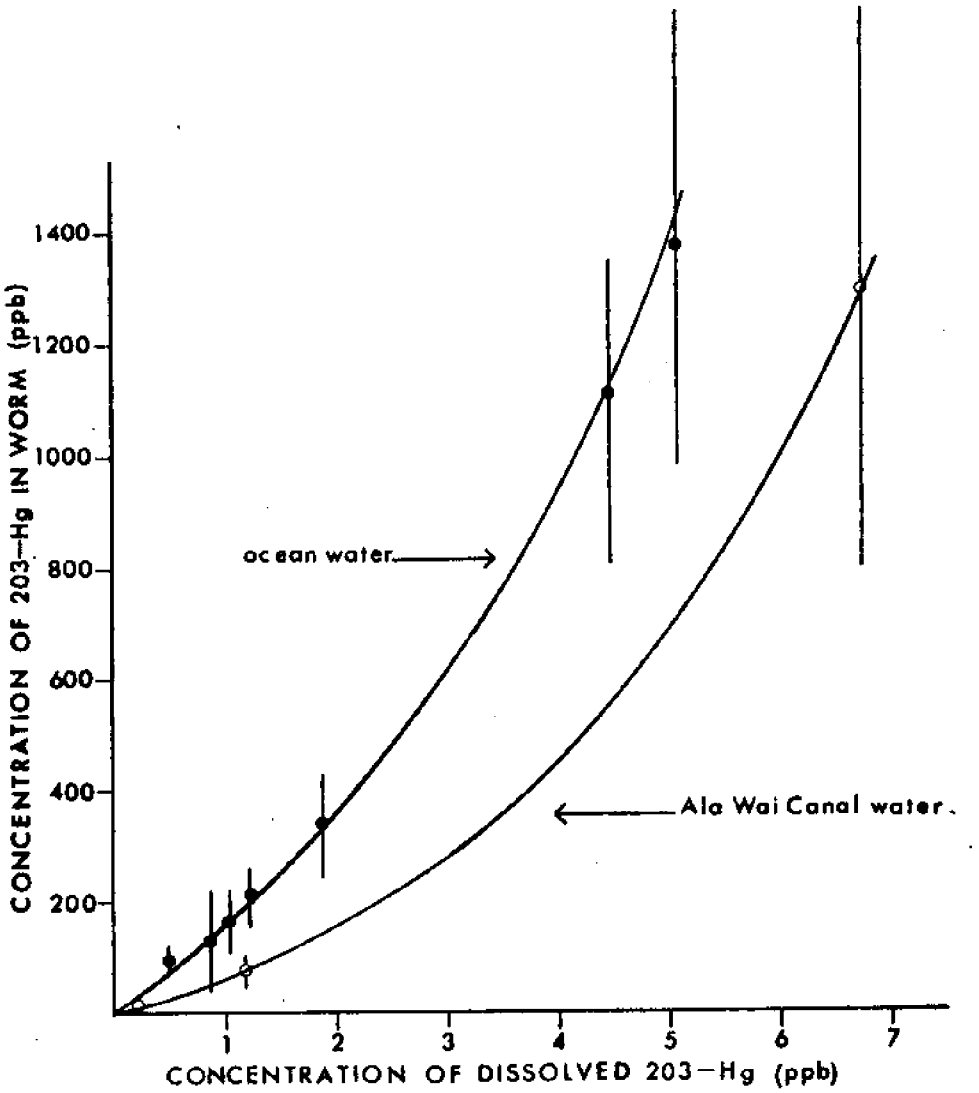

FIGURE 10. THE CONCENTRATION DEPENDENCE OF STEADY STATE ^{203}Hg CONCENTRATIONS IN *N. SUCCINEA* EXPOSED TO LABELLED ALA WAI CANAL WATER AND LABELLED OPEN OCEAN WATER. VERTICAL BARS REPRESENT ± ONE STANDARD DEVIATION.

chemical differences between terrestrial and estuarine sediments could result in differences in the way mercury is bound to sedimentary particulates or in differences in the chemical form of the metal. Such physicochemical differences in the form of mercury in different sediments could affect the ability of particulate-ingesting organisms to assimilate the metal into their tissues. To test this, sediment was swept from streets in the Ala Wai Canal watershed. Particles greater than 1 mm were removed and the sediment was labelled in sea water with ^{203}Hg. The detritus-feeding worm and shrimp were then exposed to the labelled terrestrial sediment in sea water. The terrestrial material was the only food available to these animals in the experiments. Figure 11 shows that, after a sufficient period of exposure to the labelled sediment, both the worm and the shrimp reached a steady state whole body concentration of ^{203}Hg. Table 6 shows the magnitude of that steady state. When worms were exposed to 391 ppb terrestrial sediment-bound ^{203}Hg, they accumulated 341 ppb of the metal. Exposure to a similar concentration of ^{203}Hg bound to estuarine sediment in previous experiments resulted in accumulation of only 2 ppb of the metal by this species (Table 3). Similar results were observed in mercury uptake by the shrimp. Animals exposed to 321 ppb ^{203}Hg fixed to terrestrial sediment accumulated 35 ppb of the metal, whereas shrimp exposed to 1172 ppb ^{203}Hg adsorbed to estuarine sediment accumulated only 3 ppb mercury. Mercury uptake from terrestrial sediment by the worm was considerably greater than uptake from this source by the shrimp. This may be, at least partially, due to differences in dissolved mercury concentrations in the microhabitats of these two species. The concentration of ^{203}Hg in the interstitial water, in which the worms resided, ranged around 0.375 ppb (Table 6). Concentrations of the nuclide above the sediment-water interface, the habitat of the shrimp, range around only 0.05 ppb. The failure of worms to accumulate significant levels of ^{203}Hg when exposed to labelled estuarine sediment indicated little, if any, enrichment of mercury concentrations in interstitial waters occurred in those experiments.

The experiments with terrestrial sediment suggested that the biological availability of mercury associated with terrestrial material was significantly greater than the availability of mercury associated with estuarine sediment. The enhanced availability of terrestrial sediment-bound ^{203}Hg appeared to result from both an elevation of mercury levels in interstitial waters and from the presence of mercury in a more biologically available physiochemical form when it was associated with terrestrial material. The influx of mercury into the Ala Wai Canal in association with the influx of sediment from urban storm runoff, might then result in an increase in the biological availability of mercury to sediment-ingesting biota coincident with rainstorms in the Ala Wai Canal watershed.

Implications of Changes in the Biological Availability of Mercury. Results in the previous two sections imply that the biological significance of the concentration of either dissolved mercury or of mercury associated with sediment in an aquatic ecosystem may be modified by the abundance of organic matter (or the productivity) within the system. Mercury dissolved in eutrophic water from the Ala Wai Canal was much less available to the polychaete *Nereis succinea* than was a similar concentration of the metal dissolved in oligotrophic open ocean water (Fig. 10). Likewise, ^{203}Hg associated with the heavily organic Ala Wai Canal sediment was much less available than were similar concentrations of the nuclide associated with

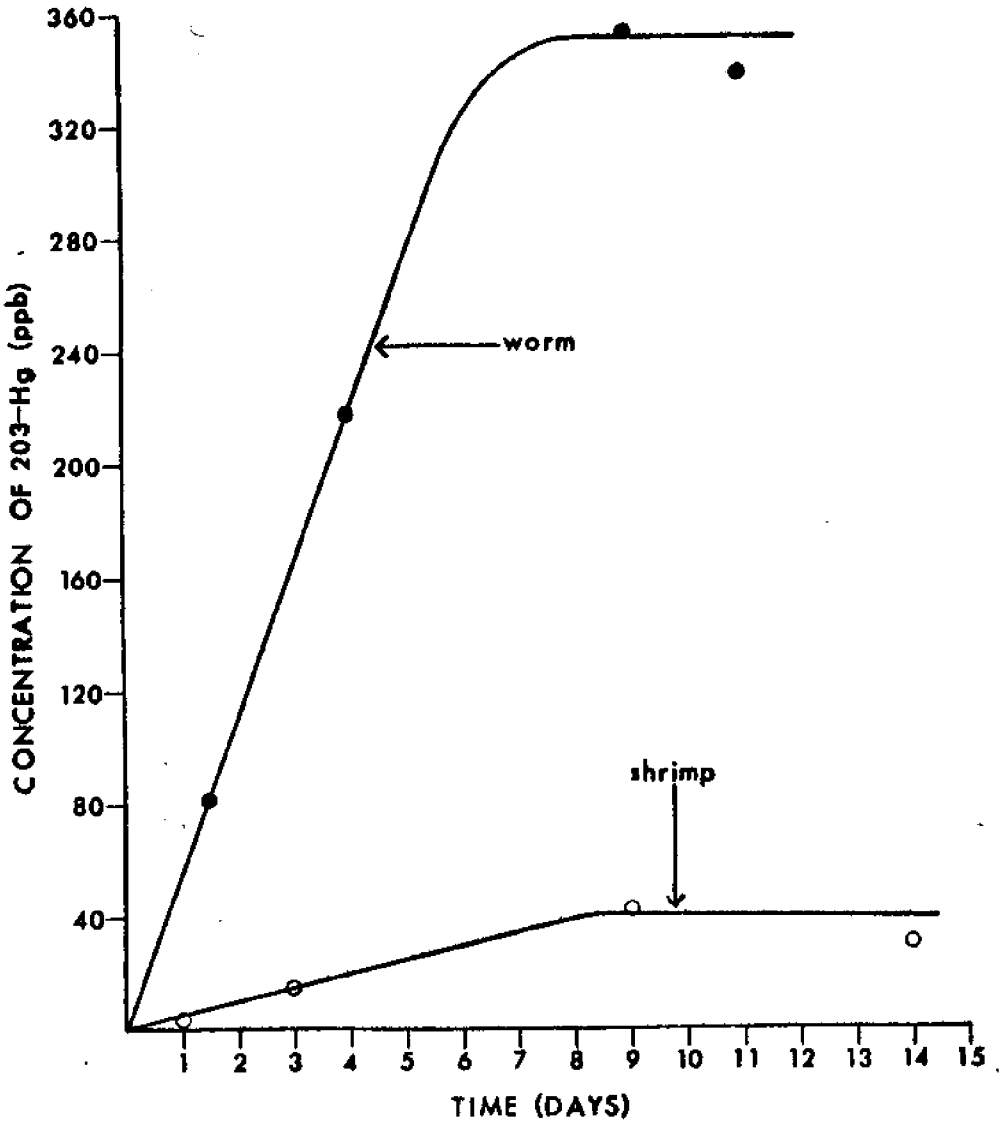

FIGURE 11. UPTAKE OF ^{203}Hg BY *N. SUCCINEA* AND *P. DEBILIS* PROVIDED LABELLED TERRIGENOUS SEDIMENT AS FOOD AS A FUNCTION OF TIME.

TABLE 6. STEADY STATE WHOLE BODY CONCENTRATIONS OF ^{203}Hg IN THE WORM, *N. SUCCINEA*, AND THE SHRIMP, *P. DEBILIS*, AFTER FEEDING ON ^{203}Hg LABELLED SEDIMENT OF TERRESTRIAL ORIGIN

Organism	Concentration of ^{203}Hg ± One Std. Dev. (ppb)			CF_{ts} †	CF_{ts}/CF_{es} ‡
	Sediment	Organism	I_{wo}*		
Worm	1625 ± 628 (5)	810 ± 232 (9)	0.380	0.498	33.2
Worm	391 ± 141 (3)	343 ± 90 (13)	0.374	0.878	87.8
Shrimp	321 ± 93 (2)	35 ± 35 (11)		0.109	44.0

NOTE: Numbers in parentheses indicate the number of samples from which each value was determined.

* I_{wo} = the concentration of ^{203}Hg in the interstitial water 4 days after the experiment was begun.

† CF_{ts} = the steady state concentration of ^{203}Hg accumulated by the organism relative to the concentration of the nuclide in terrigenous sediment (concentration factor relative to terrigenous sediment).

‡ CF_{ts}/CF_{es} = a comparison of the concentration factor relative to terrestrial sediment and the concentration factor relative to estuarine sediment.

terrestrial sediment, where inorganic particles were abundant. This suggests that in any study of the significance of mercury contamination within aquatic systems, conclusions based upon measurement of the concentration of mercury in sediment and/or water alone may be misleading. The same concentration of dissolved or sedimentary mercury in an oligotrophic ecosystem may be biologically much more significant than would observation of that level of the metal in a highly productive eutrophic ecosystem. Likewise any increase in mercury contamination is likely to have much more significant biological effects in pristine oligotrophic waters than in a more eutrophic body of water. Any attempt to predict the effects of an increase in mercury discharge into an aquatic system must, then, consider not only the concentration of the metal to be discharged but also the biological availability of the metal in its various forms and the type of ecosystem into which the metal will be released.

The Temporal Dynamics of Biologically Available Mercury in Ala Wai Canal

In results reported to this point, three detritus feeders have been used as indicators to study the biological availability of mercury in Ala Wai Canal. Field analyses of total mercury concentrations in two of the species indicated biotic concentrations of mercury fluctuated seasonally, increasing when rainfall occurred most frequently. Laboratory experiments showed such increases did not result from mercury uptake from estuarine sediment or from salinity changes, but may have been the result of:

(1) changes in concentrations of dissolved organic material, (2) the influx into the canal of mercury bound to terrestrial sediment during periods of storm runoff, and/or (3) a small increase in biologically available dissolved mercury in the estuary occurring in conjunction with storm runoff.

TOTAL MERCURY IN SHRIMP OVER JANUARY-FEBRUARY, 1974. Since the watershed of Ala Wai Canal is small and is primarily an urban area, runoff begins to enter the canal soon after a rainstorm begins and influx of the runoff ceases soon after the rainstorm ends. Any biologically available mercury entering the canal in association with such runoff would then be present in only relatively short term pulses. It was hypothesized that organisms subjected to such periodic, short-term exposures to mercury should show a relatively high degree of temporal variability in mercury content, if biota samples were taken at short time intervals over a period of intermittent rainfall in the watershed of the canal. To test this hypothesis, nine sets of shrimp samples were collected at approximately 5- to 8-day intervals between 2 January and 12 February 1974. The results of total mercury analyses conducted on these samples can be observed on the right side of Figure 5. As hypothesized, there was a readily observable degree of variability between mean mercury concentrations determined at each sampling time. This implied that mercury levels observed in shrimp samples did not represent steady state concentrations of the metals. Rather, it suggested, a shrimp sample taken at any one point in time represented only a point during a period of net accumulation or net loss of the metal by the species.

A MODEL OF ACCUMULATION AND LOSS OF INORGANIC MERCURY BY THE SHRIMP. Accumulation of mercury by the shrimp from either food or from a dissolved source has been shown to follow a similar course as a function of time (see Figs. 6, 7, and 11). Such a time course curve can be described mathematically by the general equation

$$C_t = C_{ss}(1 - e^{-kt}) \qquad (2)$$

where: C_t = concentration of ^{203}Hg in the animal at any time t;
C_{ss} = concentration of ^{203}Hg in the animal at steady state;
k = rate constant describing accumulation.

The rate of loss of mercury from the shrimp was also determined experimentally. Shrimp and worms were preloaded by exposure to dissolved ^{203}Hg until they reached a steady state concentration of the metal. Organisms were then placed in a ^{203}Hg-free aquarium with unlimited food, and loss of the nuclide as a function of time was observed. Figure 12 shows that both the shrimp and the worm lost mercury at a rate that appeared to be the sum of at least two mono-exponential processes. Such loss can be described mathematically by the general equation

$$C_t = AC_o e^{-k_f t} + BC_o e^{-k_s t} \qquad (3)$$

where: C_t = concentration of ^{203}Hg in the shrimp at any time t;
A and B = constants representing the proportion of the total body burden of ^{203}Hg made up by the fast component and the slow component of loss, respectively;
C_o = concentration of ^{203}Hg in the shrimp when efflux began;

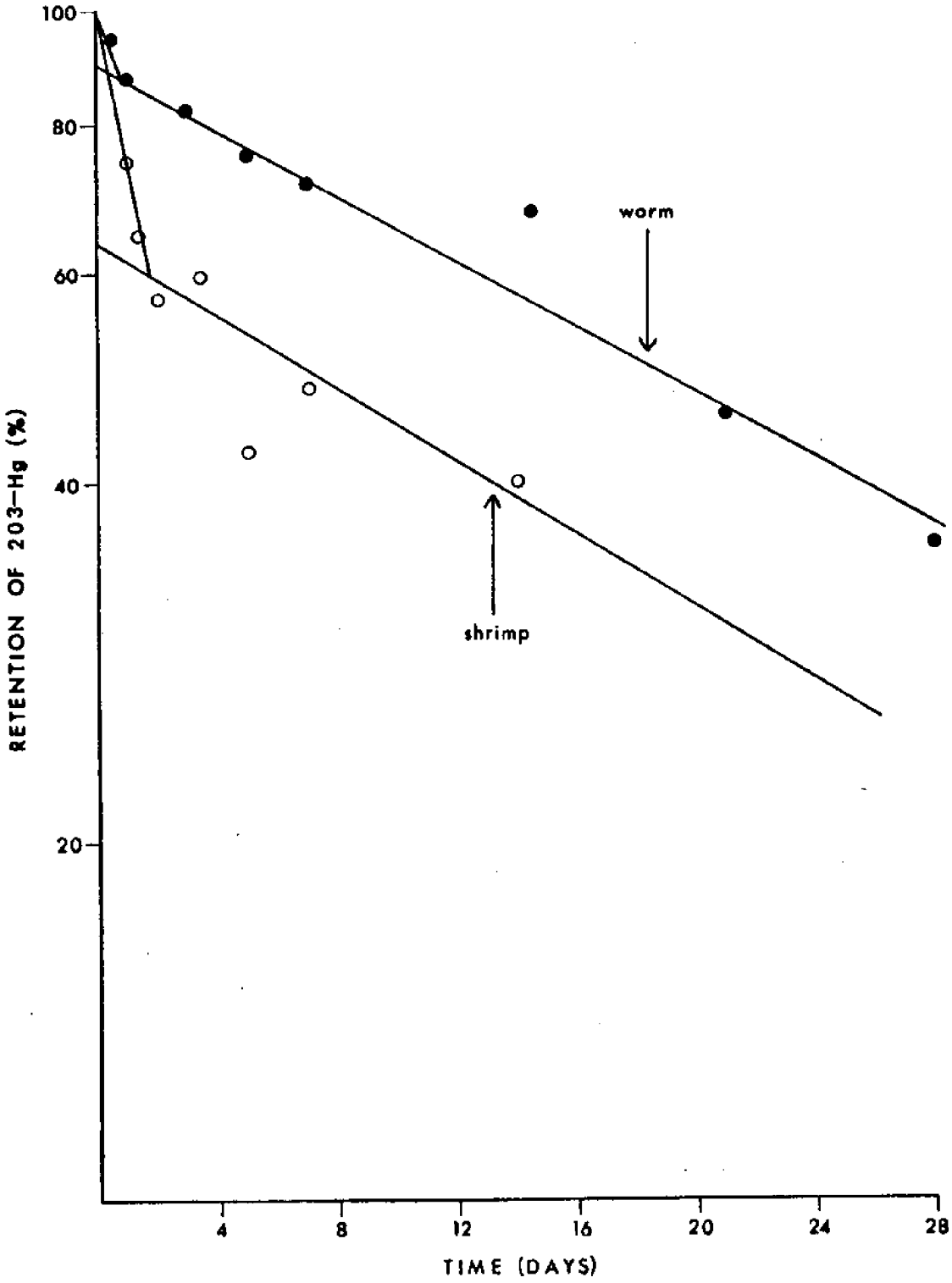

FIGURE 12. LOSS OF ^{203}Hg FROM *P. DEBILIS* AND *N. SUCCINEA* AS A FUNCTION OF TIME.

k_f and k_s = rate constants describing loss from the fast component and the slow component of loss.

For the shrimp the rate of loss best fit (as determined by log regression) the equation

$$C_t = 0.39C_o e^{-1.49t} + 0.63C_o e^{-0.044t} \quad . \qquad (4)$$

From these laboratory experiments, then, a simple mathematical model of the accumulation and retention of inorganic mercury by the shrimp was constructed, as shown in Figure 13. In this model

$k_a = 0.91\ day^{-1}$ = rate constant describing net accumulation of dissolved mercury;

k_{es} = rate constant describing accumulation of mercury from estuarine sediment. (Since the degree of accumulation from this source was negligible, this process can be ignored);

$k_{ts} = 0.19\ day^{-1}$ = rate constant describing accumulation of mercury from terrestrial sediment;

k_f and k_s = rate constants describing loss of mercury from the shrimp (as shown in Equation [4]).

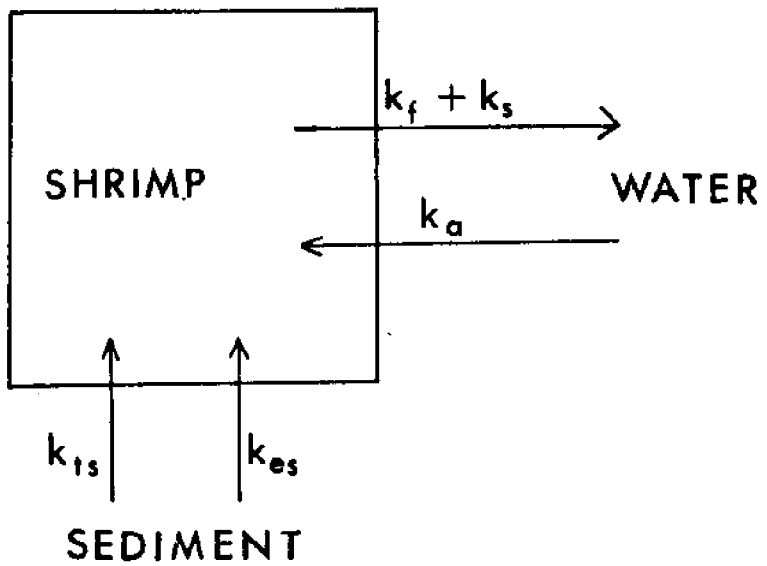

FIGURE 13. MODEL OF THE DYNAMICS OF THE ACCUMULATION AND RETENTION OF ^{203}Hg BY THE SHRIMP, *P. DEBILIS*.

If the concentrations of total mercury observed in shrimp collected from the Ala Wai Canal represent points during periods of net accumulation or net loss of the metal by this species, then this model might allow continuous simulation of the mercury levels in the shrimp and permit determination of the temporal dynamics of biologically available mercury in the canal.

SIMULATION OF MERCURY DYNAMICS IN SHRIMP. To test for any correlation

between the occurrence of rainfall in the Ala Wai Canal watershed and the concentration of total mercury in shrimp from the canal, the simplest hypothesis possible was initially chosen. It was hypothesized that: (1) each rainstorm in the watershed of the estuary resulted in the influx into the canal of a pulse of biologically available mercury, and (2) at the end of each rainstorm (when influx of runoff into the canal ceased), all significant biologically available mercury was flushed from the estuary by tidal flushing. According to this hypothesis, the influx of mercury in the shrimp by processes described by k_a, k_{es}, and k_{ts} (Fig. 13) should equal zero at any point between rainstorms. Therefore, over a period when no rain fell in the watershed of the canal, the concentration of mercury in the shrimp, as a function of time, should follow Equation (4) alone. This hypothesis could be tested if two shrimp samples were collected at points between which there was no rainfall in the watershed of the estuary. Two such determinations were made on 14 January and 21 January (see Fig. 14). Mercury concentrations observed in shrimp samples on 14 January ranged from 47 - 59 ppb with a mean of 53 ppb. Mercury in the shrimp on 21 January ranged from 34 - 37 ppb with a mean of 36 ppb. There was no significant rainfall in either Waikiki or Manoa between these two dates, thus, loss of mercury during this interval should have followed Equation (4). To test the hypothesis, the mean mercury concentration in the shrimp on 14 January was made equal to C_t in Equation (4). The time of efflux (t) prior to the observation of C_t was taken from the morning of 14 January, since the last rain observed in the watershed fell prior to the morning of this date. The shrimp sample of 14 January was taken in the afternoon, so t = 0.25 days. Equation (4) was solved for C_o and predicted C_o = 58 ppb on the morning of 14 January. Applying this C_o, it was then possible to solve Equation (4) for C_t on 21 January, using t = 7 days, and to compare this value with the mercury concentration observed in the shrimp on that date. The calculated value of C_t on 21 January was 27 ppb and the observed concentration of mercury in the shrimp on that date was 36 ppb. The calculation appeared to underestimate the observed concentration of the metal. However, only a small amount (0.15 in.) of rain fell in the Ala Wai watershed on 13 January. If this rainfall was not sufficiently intense to result in a measureable release of mercury into the canal, then net loss of mercury from the shrimp would have begun on the morning of 13 January. Under this condition, using t = 1.25 days, Equation (4) was then solved as C_o = 82 ppb on the morning of 13 January. Applying the value of C_o, the equation predicted C_t = 37 ppb on 21 January. The excellent fit between the observed (36 ppb) and the calculated (37 ppb) data in this case implied the basic hypothesis of the model, that the disappearance of biologically available mercury after significant rainfall ended could explain the observed variability in organismic mercury content.

It was possible to test the model and hypothesis in a second case. Mercury concentrations were determined in shrimp on 31 January, during a three day rainfall, and on February 6, four days after the storm ended. The mercury concentrations in shrimp ranged from 92 - 56 ppb on 31 January with a mean of 74 ppb. On 6 February, mercury values ranged from 75 to 35 ppb with a mean of 55 ppb. If it is assumed efflux (following Equation [4]) began in the morning of 2 February, then using C_t = 55 ppb (observed on 6 February) and t = 4 days, C_o on 2 February should have equaled 104 ppb. Three days elapsed between the beginning of this storm and the morning of 2 February. Shrimp reached steady state when exposed for three days

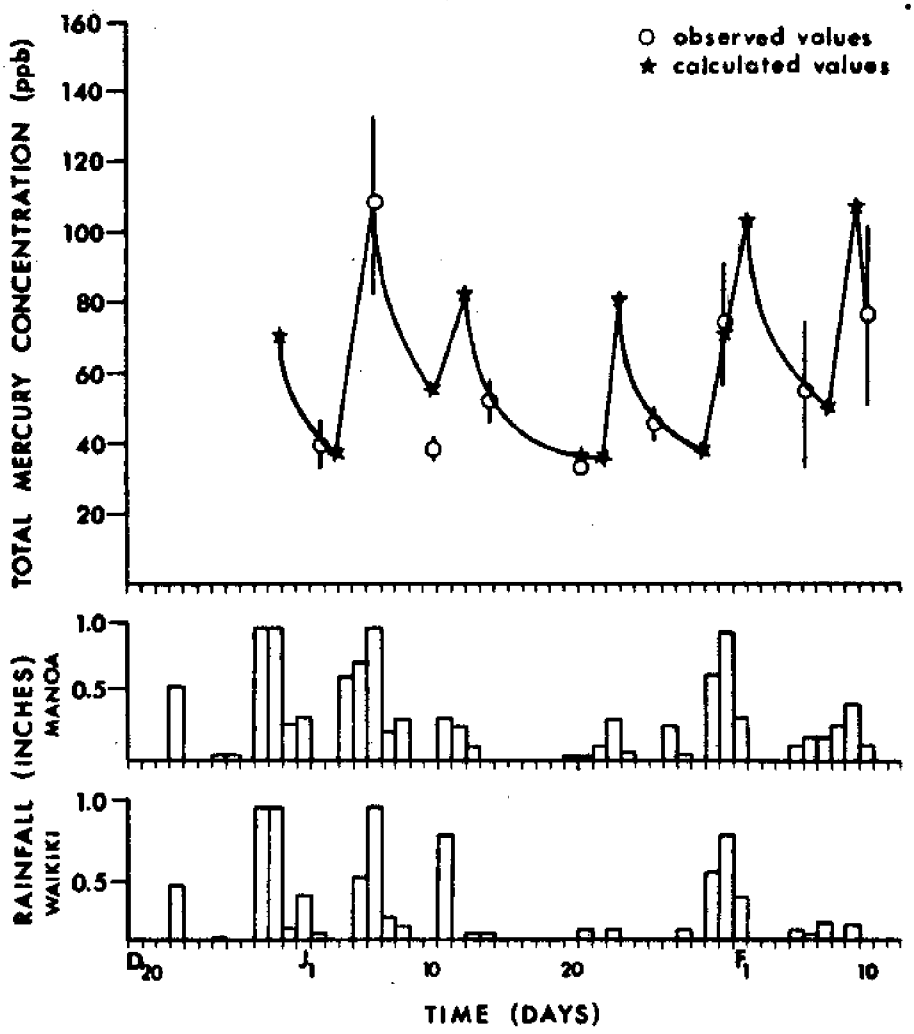

FIGURE 14. MERCURY CONCENTRATIONS IN *P. DEBILIS*, JANUARY-FEBRUARY 1974, AS OBSERVED AT NINE COLLECTING DATES, AND CALCULATED FROM THE MODEL OF MERCURY ACCUMULATION AND RETENTION IN THE SHRIMP. VERTICAL LINES IN THE FIGURE REPRESENT THE RANGE OF OBSERVED TOTAL MERCURY VALUES. LOWER HISTOGRAM GIVES DAILY RAINFALL IN THE MANOA AND WAIKIKI WATERSHEDS OF ALA WAI CANAL.

to dissolved mercury (Fig. 7). If the source of mercury of the shrimp in the canal were in dissolved form, then C_o on 2 February could have equalled C_{ss} in Equation (2). It would then be possible to solve Equation (2) for C_t on 31 January using t = 1.5 days (time from the beginning of the storm until the 31 January sample was taken), and k_a (rate constant determined in the laboratory for uptake of dissolved mercury by the shrimp) and to compare this value with the mercury concentration observed in the shrimp on that date. The solution showed C_t = 71 ppb, compared to an observed concentration 74 ppb mercury on 31 January. Again the fit between values predicted by the simulation curve and those observed in the field were excellent. These results suggested:

(1) The model describing the accumulation and retention of inorganic mercury by the shrimp fit mercury dynamics observed in shrimp collected from the estuary;
(2) Sufficient rainfall in the watershed of Ala Wai Canal resulted in an influx into the canal of a pulse of biologically available mercury;
(3) All biologically available mercury was flushed from the canal after each rainstorm; and
(4) The best fit between the simulation curve describing accumulation of mercury and the concentrations of total mercury observed in shrimp over a period of accumulation was found when the equation describing accumulation of dissolved mercury was used.

The hypothesis of post-rainstorm flushing of mercury from the Ala Wai Canal was fundamental in allowing the calculation of the simulation curve in the test cases. If this hypothesis had been incorrect (if there had been a constant supply of available mercury beyond the date chosen for C_o), the calculated C_t would have always underestimated the observed C_t, because of the inhibition of *net* efflux due to backflux (influx) from the source of mercury. The excellent fit observed in both test cases implied there was no significant influx of mercury from any source in the shrimp during periods between rainstorms over the January - February sampling period. Thus, this hypothesis and Equations 2 and 4 were used with rainfall data to generate simulation curves describing mercury concentration in shrimp continuously during January - February 1974 (Fig. 14), and during the 1973 sampling period (Fig. 15). There were several instances where there was insufficient field data to calculate mercury peaks in Figure 15. In these instances, blanks were left in the curve.

The simulation curves showed that at no time during the 1973-74 sampling period were mercury concentrations in shrimp at steady state. Rather, mercury levels in this species appeared to fluctuate continuously with time, apparently in response to periodic, short-term pulses of biologically available mercury which entered the canal in conjunction with storm runoff. As might be expected under such circumstances, larger and/or longer storms resulted in higher biotic concentrations of mercury than did shorter or smaller storms. More frequent large storms during the rainy season resulted in a higher probability of observing higher biotic mercury concentrations in monthly samples collected during this time of the year than might be observed during drier months.

Temporal fluctuations in the concentration of total mercury observed in shrimp from the Ala Wai Canal appeared to follow the equations developed in

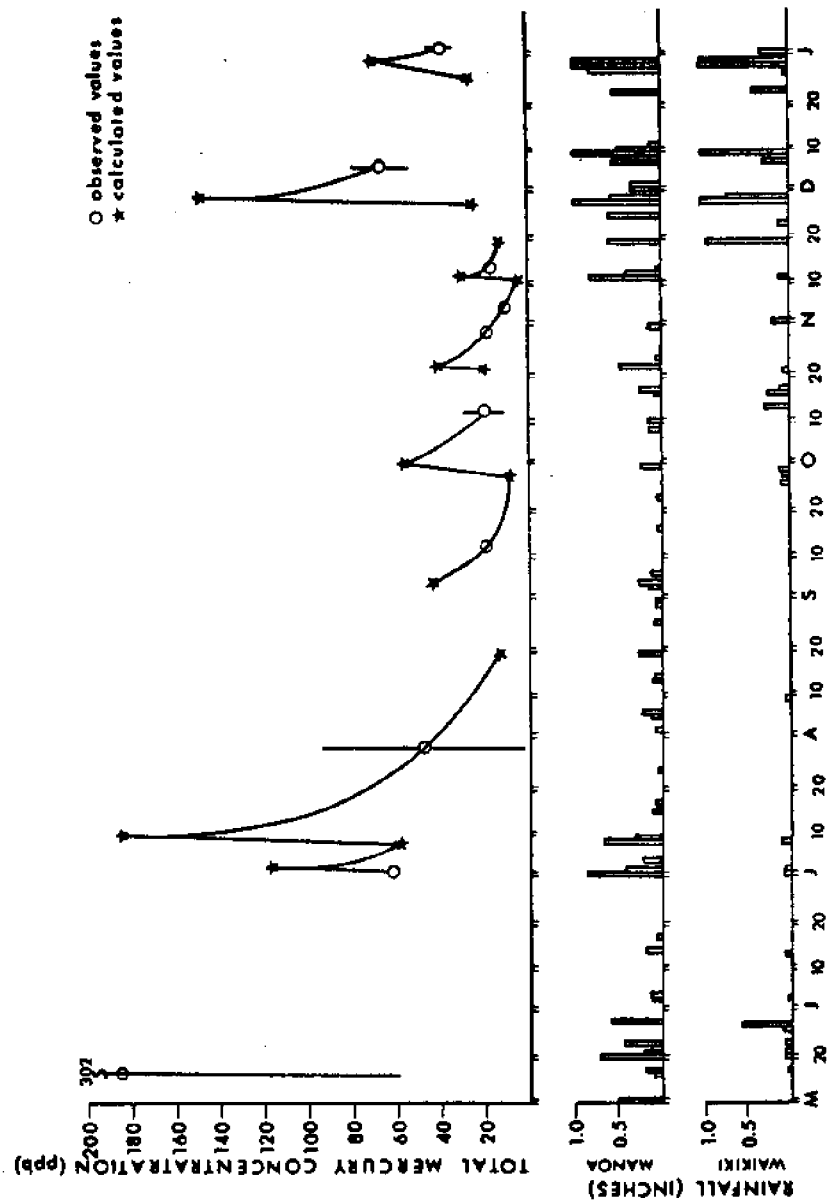

FIGURE 15. MERCURY CONCENTRATIONS IN *P. DEBILIS* IN 1973 AS OBSERVED AT TEN COLLECTING DATES, AND CALCULATED FROM THE MODEL OF MERCURY ACCUMULATION AND RETENTION IN THE SHRIMP. VERTICAL LINES REPRESENT THE RANGE OF OBSERVED TOTAL MERCURY VALUES; LOWER HISTOGRAM GIVES DAILY RAINFALL IN THE MANOA AND WAIKIKI WATERSHEDS OF THE ALA WAI CANAL.

the laboratory describing accumulation and retention of inorganic mercury by the shrimp. This suggested, as originally hypothesized, that the most important physical source of mercury in this estuary was some inorganic form of the metal (rather than a methylated species of mercury). Thus, any methylated mercury which might be observed in organisms from the canal must have originated through methylation of the metal by macrofauna themselves, or through exposure to sources of methyl mercury originating outside the canal (e.g., ingestion by predators in the canal of species which may have entered the estuary from other locations).

The simulation curves best fit observed data when it was hypothesized that each pulse of available mercury in the Ala Wai Canal was flushed out of the estuary after each rainstorm, and when the equation describing uptake of dissolved mercury was used to simulate accumulation of the metal by shrimp in the estuary. The terrestrial sediment which enters the Ala Wai Canal in storm runoff is not flushed from the estuary after each rainstorm. As much as 30 cm of runoff sediment accumulated in portions of the Ala Wai Canal used in this work during the 18-month period of the study. Thus, it is unlikely that mercury bound to the terrestrial sediment which remained in the Ala Wai Canal was a significant source of the metal for this species; rather, it appeared that dissolved mercury (which could be easily flushed from the canal after the influx of runoff ceased) was responsible for mercury concentrations observed in the shrimp. Laboratory experiments have shown that pulses of mercury at concentrations of less than 1 ppb could account for the magnitude of the concentrations of mercury observed in shrimp from the canal (Fig. 8). Measurement of low levels of dissolved mercury in the study area used in this work was often impeded by interference from aromatic hydrocarbons in the street runoff. However, at the end of a storm in July, 0.24 ppb was measured in the Ala Wai water. Siegel (1973) detected 0.6 ppb dissolved mercury in a sample collected March 1971 below the Manoa-Palolo Streams. Mercury in the water of the canal was never detectable in samples collected between storms in this study or in the study conducted by Siegel (1973). A sampling program which averaged the results of total mercury analyses of Ala Wai water during 1973 would probably have concluded that no significant mercury existed in solution in this estuary. Yet, as this study has shown, short-term increases in the concentration of dissolved mercury were responsible for mercury concentrations observed in lower trophic level organisms from the canal. Thus, the dynamics of dissolved mercury concentrations, rather than the mean concentration of the dissolved metal, was the most significant parameter determining the degree of mercury contamination in this estuary.

Data from the simulation curves also indicated that the source of the short-term pulses of dissolved inorganic mercury may have been mercury contaminated sediment originating from city streets in the watershed of the canal. During rainstorms, runoff from a large, densely populated urban area directly enters Ala Wai Canal. The smaller fractions of particulates found on urban streets can contain as much as 1000 ppb mercury (Sartor and Boyd 1972). The suspended sediment load in urban street runoff increases asymptotically with the intensity of rainfall (Sartor and Boyd 1972), i.e., the sedimentary load of the runoff increases with increased rainfall intensity to the point where the maximum possible amount of sediment has been washed from the street. Any increase in intensity beyond that point removes little or no further sediment. The relationship observed between the

magnitude of maximum mercury concentrations in the shrimp observed or predicted after each rainstorm and the sum of rainfall occurring in the Ala Wai Canal watershed for three days prior to observation of peak biotic mercury concentrations are shown in Figure 16. Predicted peak mercury concentrations in the shrimp also showed an asymptotic relationship to the amount of rain which fell in a given storm in the urban Ala Wai watershed. Temperature, the effects of the tide on the residence times of storm runoff in the canal, and variation in the intensity of rainfall during each storm probably all contributed to the wide variation of the data. However, the similarity between the nature of the relationship describing sediment loads in urban street runoff as a function of rainfall of different intensities, and the general relationship describing peak mercury concentrations in the shrimp as a function of precipitation, suggested that the increase in biologically available mercury in the Ala Wai Canal occurred in association with the influx into the canal of sediment originating from urban streets.

Desorption of some forms of particulate-bound mercury has been observed as mercury-laden sediment is transferred from fresh water to saline water (Feick et al. 1972; Reimers and Krenkel 1972). The desorbed form of mercury in the saline water appeared to be a chloride complex of the metal, $Hg(Cl_4)^{-2}$, which showed little resorption to particulates in sea water (Reimers and Krenkel 1972). Thus, desorption of particulate-bound mercury as sediment washed from city streets by fresh water storm runoff entered the saline waters of Ala Wai Canal could have resulted in an influx into the canal of a pulse of dissolved mercury in conjunction with the runoff. If this dissolved mercury occurred in a form that was not resorbed to particulates in the estuary, sufficient exposure time for biotic uptake of the metal could occur, and would explain the results observed in this study.

CONCLUSIONS

At no time during the course of this study did the concentration of total mercury in any organism from the Ala Wai Canal included in this work exceed the federal standards (500 ppb) for permissable mercury levels in edible tissue. Thus, the storm runoff from urban areas which enters this estuary had not significantly contaminated the canal with mercury during 1973-74. However, several qualifications to this conclusion must be added before these results may be extrapolated to conclusions concerning the effects of urban runoff in general:

(1) Runoff from adjacent urban areas into the Ala Wai Canal did result in some influx of biologically available mercury into the estuary. Other toxic metals (especially Pb and Cd) also occur in significant concentrations in sediment from urban streets (Sartor and Boyd 1972). Because of the chemical similarity of Pb, Cd and Hg, the dynamics of lead and cadmium in the Ala Wai Canal may be similar to those of mercury. Before concluding that heavy metal contamination from urban storm runoff entering Ala Wai Canal is not a problem, a temporal study of at least lead and cadmium concentrations in either indicator species or in important resource species in the canal should be conducted. A comparison and analyses of the results of the work reported here and the results of the work with other metals may provide conclusive evidence concerning the potential for heavy metal contamination of estuarine re-

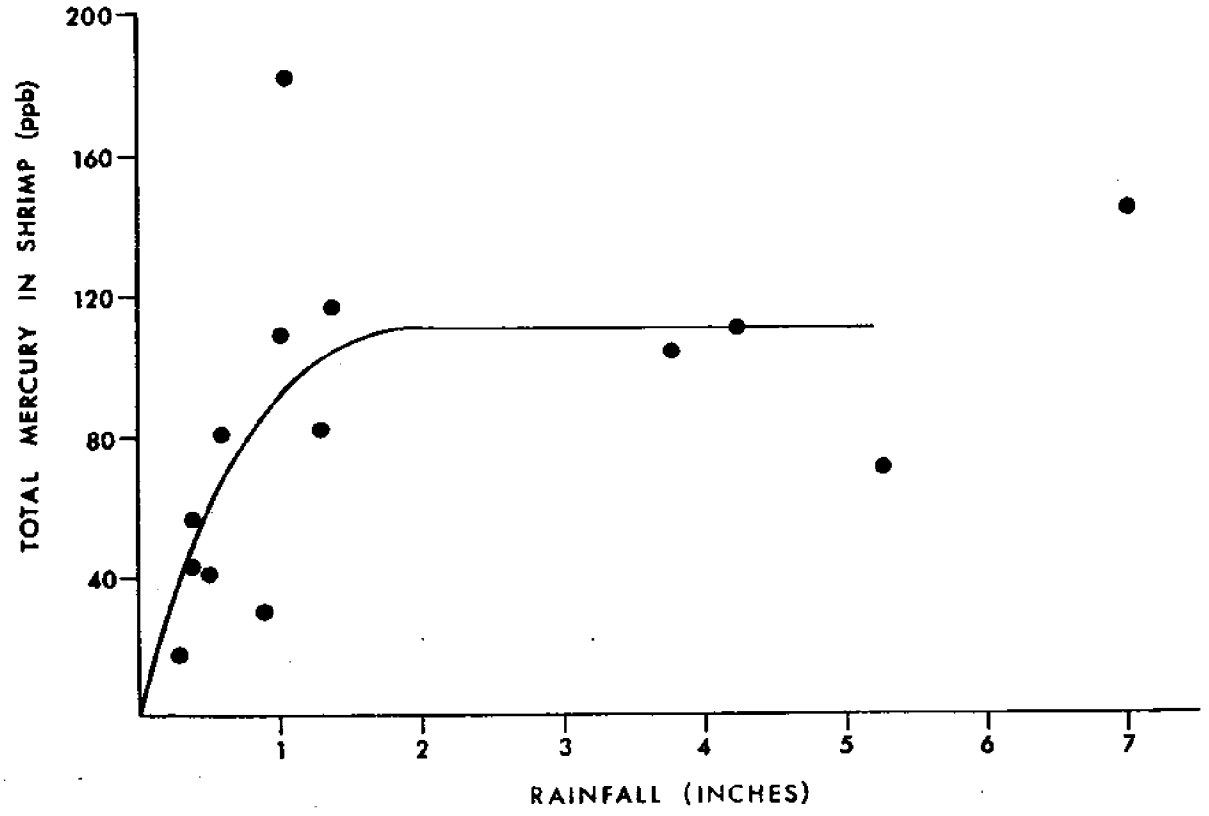

FIGURE 16. THE MAXIMUM TOTAL MERCURY CONCENTRATION IN *P. DEBILIS* OBSERVED OR CALCULATED AFTER EACH RAINFALL, AS A FUNCTION OF THE SUM OF THE PRECIPITATION OBSERVED IN THE WAIKIKI AND MANOA WATERSHEDS OF ALA'WAI CANAL OVER THE THREE DAY PERIOD PRIOR TO EACH TOTAL MERCURY PEAK. (MERCURY VALUES REPRESENT WET WEIGHT CONCENTRATIONS.) LINE WAS FIT BY EYE.

sources by urban runoff.

(2) Conclusions from laboratory experiments conducted here indicated the biological availability of mercury may be reduced in eutrophic waters, where organic matter is abundant. The Ala Wai Canal is a highly eutrophic estuary. It is quite possible that the biological effects of the influx of urban runoff-associated mercury into the canal may have been damped by the abundance of organic matter in the estuary. Oligotrophic ecosystems, however, may be highly susceptible to mercury contamination. Thus, release of urban runoff into more pristine or more oligotrophic water might result in significantly greater biotic contamination of those systems than was observed in the Ala Wai Canal. Similar conclusions may also be relevant in terms of the biological effects of industrial discharge of metals into potentially heavy metal-sensitive oligotrophic ecosystems. Further information about the relative biological availability of metals in oligotrophic ecosystems is especially relevant to the maintenance of water quality in Hawaii. Important economic and recreational resources are associated with the oligotrophic coastal waters and the open ocean waters of the outer islands. Results from this study indicate the potential for disruption of those possibly sensitive resources by industrial development (e.g., deep sea mining and its accompanying industry) or by urban development may be high. The importance of further work to clarify such a conclusion is obvious.

Although this work describes the cycling of only small quantities of biologically available mercury in the Ala Wai Canal, it does point to several general conclusions which may be relevant to other studies of metal contamination. Continuous simulation of mercury concentrations in shrimp from the canal illustrated the extremely dynamic nature of biotic mercury concentrations in organisms from this estuary. Interpretation of the degree of mercury contamination in an aquatic ecosystem may be significantly influenced by such temporal variations in biotic mercury concentrations. Conclusions drawn from samples of biota from the canal taken only at one time of the year could have resulted in significant misinterpretations of the meaning of the observed mercury concentrations. Fluctuations in the concentrations of mercury in shrimp from the canal appeared to result from periodic, short-term increases in biologically available mercury in the estuary. In this case measurement of mercury concentrations in water and/or in sediment alone would not have detected factors resulting in changes in biotic mercury concentrations and, thus, would have given no indication of the biologically important aspects of the dynamics of metal concentrations. The largest and most obvious physical pool of mercury in the Ala Wai Canal (sedimentary bound pool) had little influence on mercury concentrations in detritus feeders; while small short-term changes in dissolved mercury, which were difficult to detect and interpret directly, appeared to be responsible primarily for observed biotic mercury fluctuations. Previous experiments have emphasized that important changes in biotic mercury uptake may even occur without changes in concentrations in physical mercury pools if the biological availability of the metal changes.

These results illustrate that detection of changes in the biological availability of mercury, and interpretation of the significance of observations of mercury in physical pools of the metal are difficult using anal-

yses of the physical environment (water and sediment) alone. The relatively rapid flux rates of mercury in the worm and the shrimp used in this study made these species excellent indicators of even short-term changes in the biological availability of mercury in the Ala Wai Canal. Such indicator species were shown to be an important aid in interpreting the biotic importance of complex physical processes, and were useful in enhancing an understanding of the role of these processes in an ecosystem subject to mercury contamination.

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