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Distribution of Arsenic in the Sediments and Biota of Hilo Bay, Hawaii[1]

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ABSTRACT: Sediment samples collected from the Waiakea Mill Pond, Wailoa River, and Hilo Bay were analyzed for arsenic. Arsenic was detectable in 10 of 11 sediment samples, and ranged in concentration from 2 to 715 ppm. Two species of plant and seven species of animal were collected from the Waiakea Mill Pond and analyzed for arsenic. No arsenic was detected in the plants, whereas four of the seven animal species had arsenic concentrations ranging from a trace to 1.3 ppm.

Sediments of the Wailoa River estuary have much higher concentrations of arsenic than those of Hilo Bay, indicating that most arsenic is located near the original source of pollution, a factory that once operated on the shores of the Waiakea Mill Pond. Much of the arsenic is found in anaerobic regions of the sediment where it has been relatively undisturbed by biological activity. The low levels of arsenic in the biota of the estuary suggest that there is little remineralization of the region's arsenic and that it is trapped in anaerobic sediment layers.

HILO BAY, LOCATED on the northeast coast of the Island of Hawaii, has historically served as a sink for human-related pollutants from numerous point sources (M&E Pacific, Inc. 1980). The bay and adjoining Wailoa River estuary system are severely polluted with arsenic as a result of dumping of arsenic trioxide (used as an antitermite agent) into the Waiakea Mill Pond and Wailoa River by a canec (a building material made from sugar cane waste) manufacturing plant during the years 1932–1963 (Kelly, Nakamura, and Barrere 1981). Arsenic concentrations in the sediments of Hilo Bay have been found to be as high as 6370 ppm, approximately 34 times higher than anywhere else in the state (Department of Health 1978*a*).

In addition to its presence in the sediments of the region, arsenic has been detected in the biota of the Waiakea Mill Pond and Hilo Bay (Department of Health 1978*a*, *b*). The Department of Health examined a filamentous algae (no taxonomic designation listed) commonly consumed by mullet, and found detectable levels of arsenic (1.84 ppm). The tissues and viscera of the Samoan crab (*Scylla serrata*), white crab (*Portunus sanguinolentus*), mullet (*Mugil cephalus*), and a goby (no taxonomic designation listed) were also analyzed. No arsenic was detectable in the goby, but the mullet had arsenic in their viscera (1.67–6.64 ppm), the white crab had detectable levels of arsenic in muscle tissue (0.17 ppm), and the Samoan crab had detectable levels of arsenic in the viscera (0.39 ppm)

The purpose of the present investigation was twofold. First, we sought to determine the extent and pattern of movement of arsenic out of the Wailoa estuary from its original source into Hilo Bay. Second, we wished to examine biota of the Wailoa estuary system for the presence of arsenic in visceral and muscle tissues. Although it is generally hypothesized that arsenic does not concentrate in higher

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trophic levels via food chain magnification (Kennedy 1976, Klumpp and Peterson 1978, Spehar et al. 1980), it can be efficiently passed along to higher trophic levels (Wrench, Fowler, and Unlu 1979). In light of the magnitude of arsenic pollution in the estuary, we suspected that much of the biota of the estuary might have measurable levels of arsenic in their tissues.

MATERIALS AND METHODS

Core samples of sediments were collected in June and July 1983 from nine stations located throughout the Waiakea Mill Pond, the Wailoa River, and Hilo Bay (Figure 1). Cores were collected by means of a 2-in.-diameter piston corer. Each core had a 2-cm subsample removed from the top and bottom for arsenic content analysis. In addition to the core samples, two sediment grab samples were collected in deep water (approx. 20 m) at the mouth of the bay in April 1983. Also, dredge spoils from dredging of the mouth of the Wailoa River were collected in July 1984. All sediment samples were digested directly with a nitric/sulfuric/perchloric acid mixture, and then reacted with hydrazine sulfate/ammonium molybdate solution to produce arsenomolybdenum blue for spectrophotometric analysis (Sandell 1959).

All biological material was collected in the Wailoa River or Waiakea Mill Pond during June and July 1983. Samples were collected by hand, hand net, and hook-and-line. Samples collected included benthonic blue-green algae, which serves as a food base for mullet in the estuary; *Elodea* sp., an aquatic embryophyte; *Theodoxus vespertinus*, a small brackish-water gastropod common to the region; *Eleotris sandwicensis*, a small benthonic fish eaten by larger fishes; and several species regularly consumed by people, including *Mugil cephalus*, a mullet; *Lutjanus fulvus*, a snapper; *Kuhlia sandvicensis*, a moderate-sized perchlike fish; *Mulloides vanicolensis*, a moderate-sized goatfish; and *Portunus sanguinolentus*, the white crab.

Specimens were stored on ice after capture and frozen within 3 hr of capture. They were later thawed for analysis. Specimens were eviscertated and filleted with stainless steel instruments. Viscera (gastrointestinal tract and associated organs) and muscle tissue (epaxial and hypaxial musculature in the fish, foot and part of visceral hump in the gastropod, appendage musculature in the crustaceans) were analyzed separately.

Because of the small size of many of the specimens collected, tissue samples from several individuals were sometimes pooled into larger, monospecific analytical samples. Weights of analytical samples were as follows: 50.1960 g of blue-green alga; 21.0645 g of *Elodea* sp.; 40 specimens of *Theodoxus vespertinus* ranging in size from 19 to 27 mm maximum shell dimension produced a total of 29.3270 g muscle tissue; 4 specimens of *Eleotris sandwicensis* ranging in size from 90 to 120 mm standard length (SL) produced a total of 2.2150 g visceral tissue and 9.0515 g muscle tissue; 6 specimens of *Lutjanus fulvus* ranging in size from 95 to 125 mm SL produced a total of 4.655 g visceral tissue and 29.3515 g muscle tissue; 3 specimens of *Kuhlia sandvicensis* ranging in size from 95 to 110 mm SL produced a total of 5.0180 g visceral tissue and 10.7215 g muscle tissue; 1 specimen of *Mulloides vanicolensis* (155 mm SL) produced 3.6745 g visceral tissue and 19.1450 g muscle tissue; 3 visceral samples from *Mugil cephalus* weighing 63.1490, 63.0405, and 139.7935 g, respectively (donated by a local fisherman, sizes unknown); and 1 specimen of *Portunus sanguinolentus* (95 mm carapace width) produced 17.7435 g visceral tissue and 5.4015 g muscle tissue. All biological material was subjected to the same analytical technique used for sediment samples.

Temperature and salinity changes in the Wailoa estuary system were monitored throughout an entire spring tidal cycle (25 hr) on 25–26 February 1983. Four stations located along the course of the Wailoa River between the Waiakea Mill Pond and the river mouth were monitored every 2 hr (Figure 2).

Temperature and salinity were recorded at 25-cm intervals between the surface and the bottom at each station with a YSI Model #33 S-C-T meter.

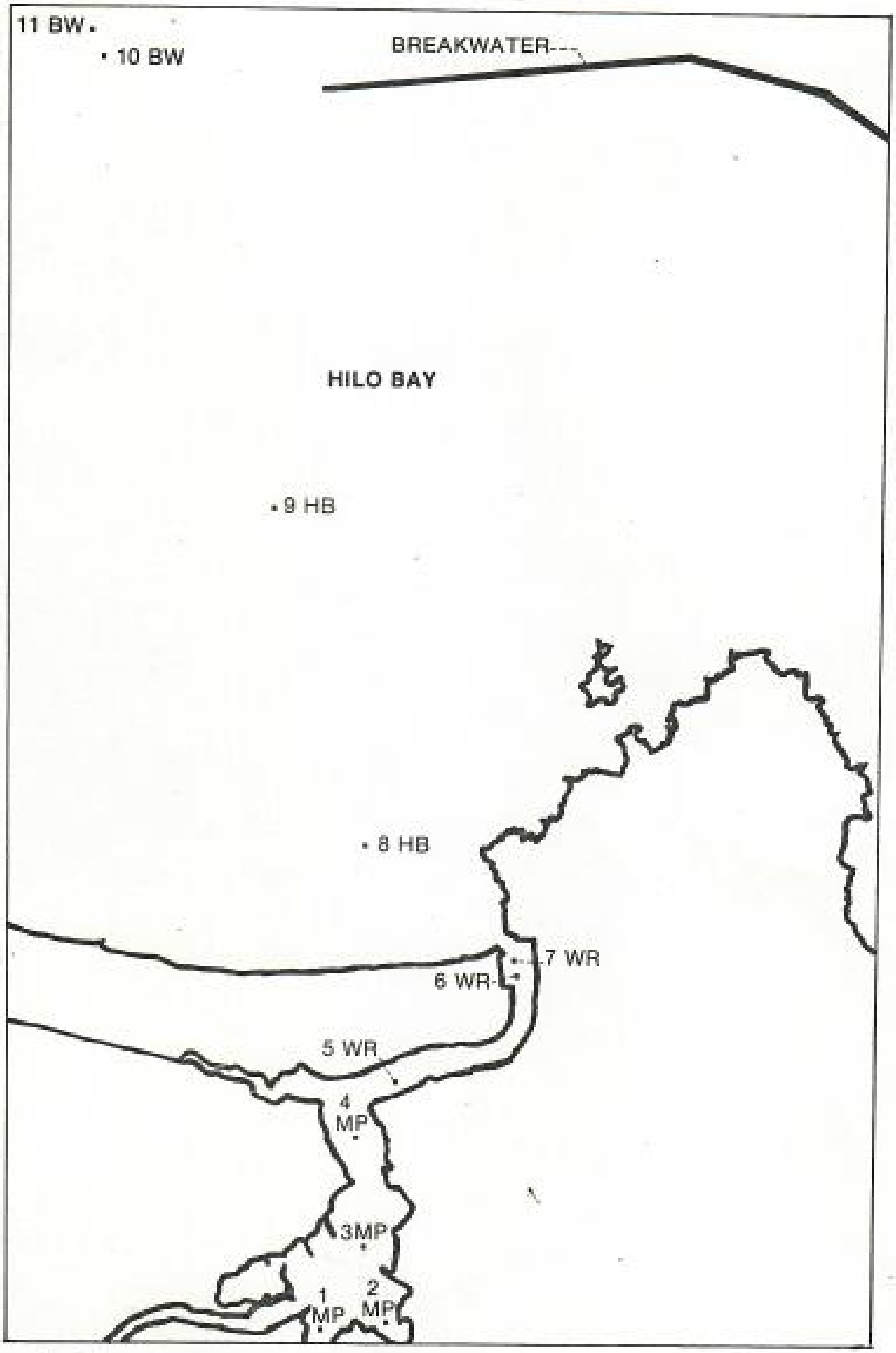


FIGURE 1. Coring station locations in the Waiakea Mill Pond (MP), Wailoa River (WR), Hilo Bay (HB), and the mouth of Hilo Bay (BW).

RESULTS

Detectable levels of arsenic were found in 10 of the 11 sediment samples examined, with 6 cores having arsenic concentrations in excess of 50 ppm (Table 1). Extremely high arsenic concentrations were present in the sediments of the Waiakea Mill Pond and Wailoa River, with cores from those locations registering maximum concentrations of 550 ppm and 715 ppm, respectively (Table 1). Sediments from cores taken in Hilo Bay had much lower levels of arsenic present, the highest concentration being 63 ppm, and generally showed little variation from site to site (Table 1, Figure 3).

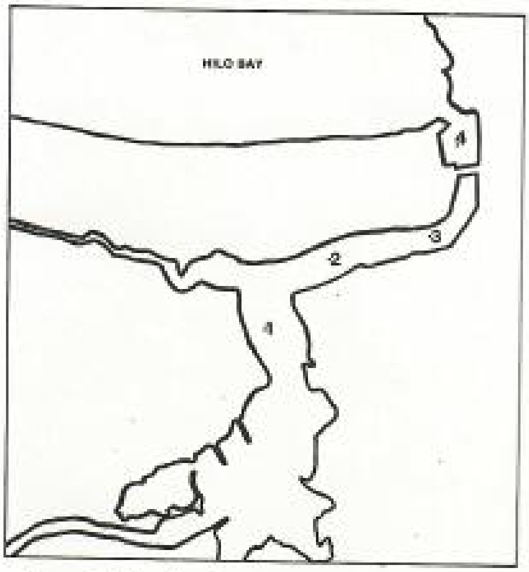


FIGURE 2. The location of tidal cycle monitoring stations from the Wailoa River.

Most cores collected had sediment arsenic concentrations that varied throughout their length. Two cores examined (6-WR and 8-HB) showed slightly higher (26–29 ppm) arsenic concentrations at a depth of approx. 60 cm below the surface than on the surface of the sediment. Two cores (2-MP and 5-WR) showed markedly higher (299–564 ppm) arsenic concentrations at a depth of approx. 60 cm than on the sediment surface. Conversely, five cores (1-MP, 3-MP, 4-MP, 7-WR, and 9-HB) had an inverse relationship between sediment depth and arsenic concentration, with arsenic concentrations showing modest declines (2–115 ppm) with increasing sediment depths of approx. 20–110 cm (Table 1).

All cored sediments were black in color just a few centimeters below the surface, gave off a strong hydrogen sulfide odor, and contained pieces of undecomposed vegetation in the black-colored region. This indicates that the sediments of the Waiakea Mill Pond, Wailoa River, and Hilo Bay are anaerobic just below the sediment surface.

Dredge spoils taken from a mixed sediment depth (max. depth 3–6 m) at the mouth of the

TABLE 1

ARSENIC LEVELS IN SEDIMENTS COLLECTED FROM THE WAIAKEA MILL POND (MP), WAILOA RIVER (WR), HILO BAY (HB), AND THE MOUTH OF HILO BAY (BW)

SAMPLE	TOP	BOTTOM
1-MP	2 ± 0.4 (8–10 cm)	ND (16–18 cm)
2-MP	251 ± 25.7 (4–6 cm)	550 ± 6.1 (56–58 cm)
3-MP	27 ± 6.7 (6–8 cm)	3 ± 1.1 (108–110 cm)
4-MP	115 ± 2.0 (10–12 cm)	ND (52–54 cm)
5-WR	151 ± 10.3 (4–6 cm)	715 ± 32.8 (57–59 cm)
6-WR	34 ± 0.7 (3–5 cm)	60 ± 0.2 (61–63 cm)
7-WR	43 ± 0.6 (3–5 cm)	17 ± 0.1 (103–105 cm)
8-HB	34 ± 0.3 (3–5 cm)	63 ± 0.3 (66–68 cm)
9-HB	56 ± 0.2 (3–5 cm)	19 ± 0.1 (50–52 cm)
10-BW	ND (surface)	
11-BW	40 ± 1.5 (surface)	

NOTE: All values are in parts per million wet weight, and are followed by their standard errors. Numbers in parentheses represent the depths in centimeters below the surface of the sediment from which the analyzed sample was collected. ND = not detected.

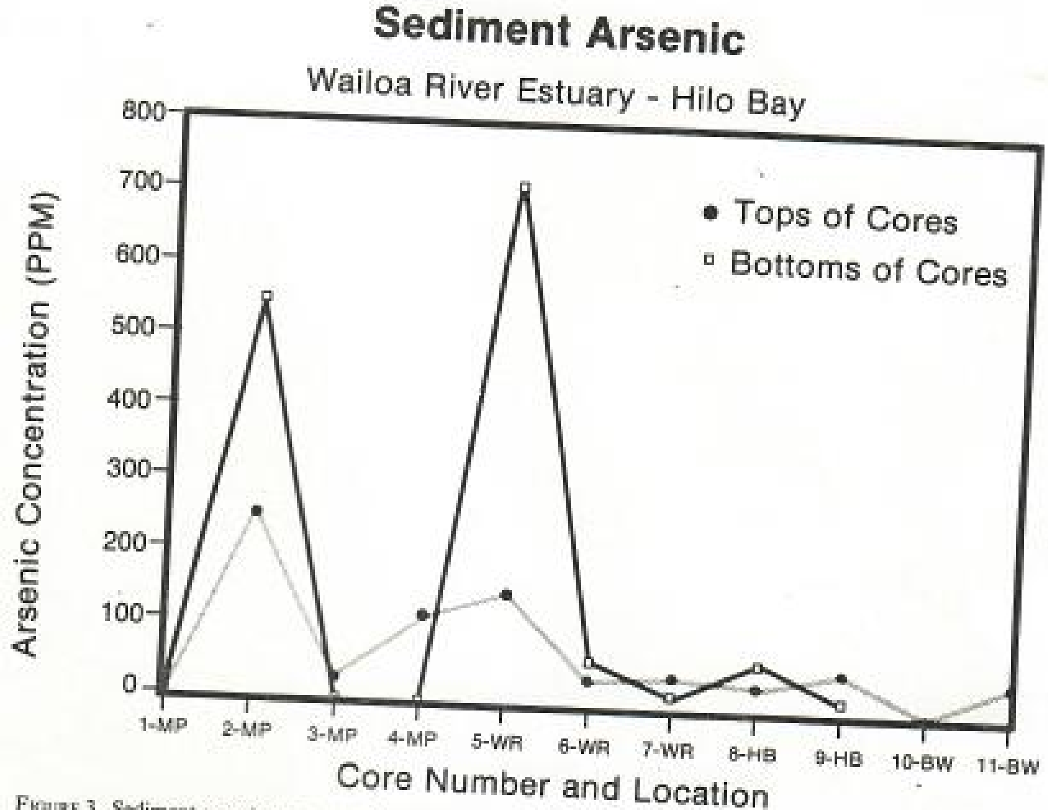


FIGURE 3. Sediment arsenic concentrations from cores collected from the Waiakea Mill Pond (MP), Wailoa River (WR), Hilo Bay (HB), and the mouth of Hilo Bay (BW).

TABLE 2

ARSENIC LEVELS IN ORGANISMS COLLECTED FROM THE WAIAKEA MILL POND AND WAILOA RIVER

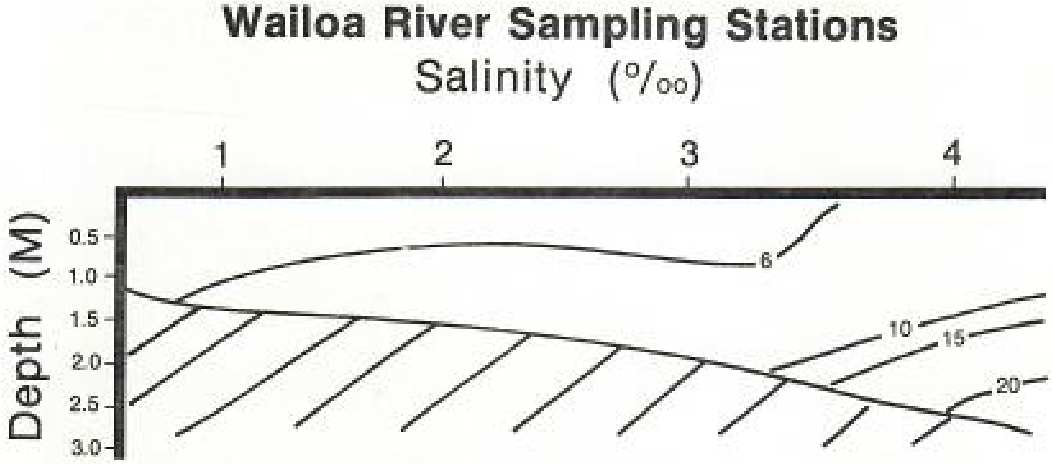
SAMPLE	VISCERAL AS CONTENT	TISSUE AS CONTENT
Blue-green algae	NA	ND
Elodea sp.	NA	ND
Theodoxus vespertinus	NS	Trace
Eleotris sandwicensis	1.1	0.2 ± 0.04
Lutjanus fulvus	0.8 ± 0.3	0.2 ± 0.03
Kuhlia sandvicensis	ND	ND
Mulloides vanicolensis	ND	ND
Mugil cephalus, #1	1.3 ± 0.4	NS
Mugil cephalus, #2	1.2 ± 0.02	NS
Mugil cephalus, #3	1.2 ± 0.1	NS
Portunus sanguinolentus	ND	ND

NOTE: All values are in parts per million wet weight. NA = not applicable, ND = not detected, NS = not sampled.

Wailoa River had an arsenic concentration of 13 ppm ± 0.7 ppm standard error (SE).

Of the nine species of organisms examined by us, four had detectable levels of arsenic in their tissues (Table 2). Arsenic levels were much lower than those recorded in the sediment samples, with biological material having arsenic concentrations ranging from trace amounts to 1.3 ppm. Highest biological arsenic levels were obtained from visceral tissue of the mullet *Mugil cephalus* (1.3 ppm max.). Three species had detectable levels of arsenic in their muscle tissue, the brackish water gastropod *Theodoxus vespertinus* (trace), the snapper *Lutjanus fulvus* (0.2 ppm), and the eleotrid *Eleotris sandwicensis* (0.2 ppm). Neither of the plants that thrive in the Wailoa estuary system had detectable levels of arsenic (Table 2).

Salinity changes that occur in the Wailoa



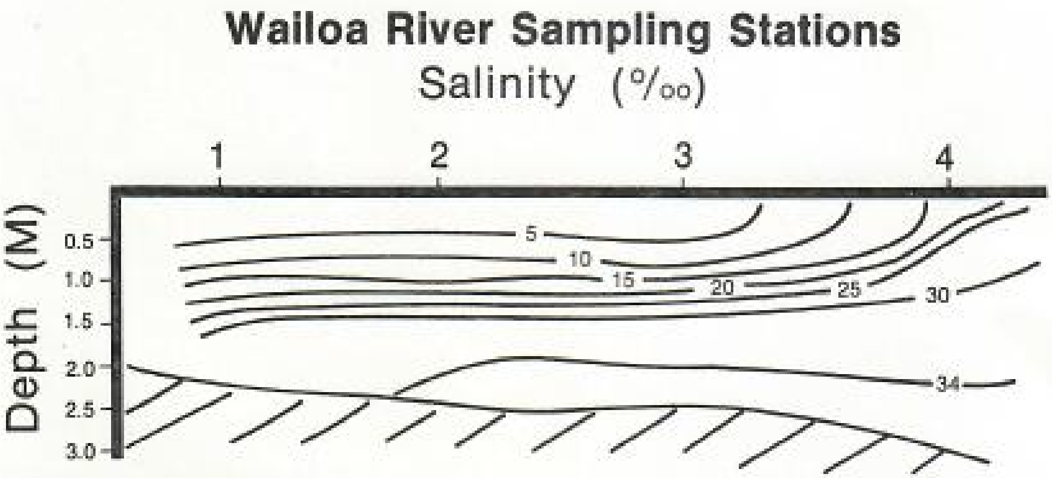


FIGURE 4. Spring tidal range cross sections of water salinity (in parts per thousand) from four stations along the course of the Wailoa River between the Waiakea Mill Pond (station 1) and the mouth of the Wailoa River (station 4) for 25–26 February 1983. The upper profile is at LLW (−7 cm), while the lower profile is at HHW (+70 cm).

estuary during tidal cycles are pronounced, with at least one station (1) showing more than a 25 ppt increase in salinity near the bottom during high tide (Figure 4). During the 25-hr observation period, an extremely well-developed salt wedge was observed to penetrate the estuary, leading to the maintenance of a well-defined stratification. This stratification is apparently tidally controlled under conditions of low input of fresh water.

DISCUSSION

Arsenic was present in 10 of 11 of the sediment samples collected from the Wailoa River estuary system and Hilo Bay during this study. This observation suggests that arsenic is a ubiquitous contaminant of the sediments in these systems (Table 1, Figure 3). However, although arsenic is present well out into the bay and is easily measurable in sediments collected beyond the breakwater, it is found in much lower concentrations in sediments of these areas than in the estuarine sediments. The arsenic contamination of the sediments of Hilo Bay that has occurred is apparently the result of transport of some of the arsenic-laden sediments out of the Wailoa estuary.

It has been suggested that arsenic is transported out of the Wailoa estuary system into Hilo Bay during periods of high freshwater runoff (M&E Pacific, Inc. 1980). If this is the case, our data suggest that sediments are not immediately redeposited but instead are transported out of Hilo Bay. Recent studies of salinity profiles from Hilo Bay show surface freshwater plumes extending well past the breakwater at the mouth of Hilo Bay (Bernard et al. 1983). Fine-grained sediments may remain suspended in turbulent low-salinity surface waters until exiting the bay, where reduced flow intensity would permit settling.

We believe that it is also possible that relatively little seaward transport of arsenic has occurred. Although we have observed high seaward freshwater flow rates out of the Wailoa River estuary, much of this flow is confined to a thin surface lens. Conversely, we have recorded the movement of a salt wedge up the Wailoa River into the Waiakea Mill Pond, which during spring tidal cycles has a salinity in excess of 33 ppt near the bottom (Figure 4). Furthermore, the sediments of the estuary are anaerobic just a few centimeters below the surface. This condition results in reduced biological disturbance of the arsenic-contaminated sediments because few organisms burrow into the anaerobic strata. It seems possible that limited seaward transport of sediment by freshwater runoff and low biological disturbance of the anaerobic sediments have resulted in much of the arsenic that has been dumped into the estuary remaining in relatively undisturbed estuarine sediments.

Arsenic in the sediments of the estuary is remarkably localized in its distribution. Core 2-MP had an arsenic concentration that was approx. 5 times higher than any of the other cores taken in the Waiakea Mill Pond (Figure 3). According to historical records, the location of this coring station corresponds to the location of the canec manufacturing plant on the shores of the mill pond (Department of Health 1978*b*). Similarly, core 5-WR, located in an area where an effluent pipe dumped arsenic-laden waste-water from the canec plant into the Wailoa River (Department of Health 1978*b*), had an arsenic concentration approx. 12 times higher than any of the other cores (all downstream) taken in the Wailoa River (Figures 1, 3).

The variation in arsenic concentration with depth suggests that the sediments of the region have been subjected to some degree of localized mechanical disturbance. Four cores (2-MP, 5-WR, 6-WR, and 8-HB) had higher arsenic concentrations at increased depth, whereas five cores (1-MP, 3-MP, 4-MP, 7-WR, and 9-HB) showed the opposite pattern (Table 1). Differences in variation in arsenic concentration with depth can occur between stations that are located close together. Cores 6-WR and 7-WR were taken within 10 m of each other, yet exhibit inverse patterns in the vertical distribution of arsenic. These cores were taken near the mouth of the Wailoa River, an area that is frequently dredged to keep the boat channel open. Therefore, it is possible that dredging may account for the disturbed sediments in this area. Other sources of sediment disturbance in Hilo Bay and the Wailoa River estuary are not as easily identified, although some mixing may have occurred as a result of tsunami action.

To summarize, our data suggest that much of the arsenic remains in sediments located near the sites of the canec mill and its effluent pipe in the Waiakea Mill Pond and Wailoa River, although some arsenic-bearing sediment has been transported to Hilo Bay. Furthermore, much of this arsenic apparently is confined to anaerobic sediment layers, and is probably in a reduced inorganic form that is potentially hazardous to humans (Fowler 1977). Physical disturbance of the sediments, particularly near the old effluent sites, could cause the release of substantial amounts of arsenic into the water or surface sediment layers.

The results of our analyses for arsenic in the tissues of specimens collected from the Waiakea Mill Pond and Wailoa River do not support our early hypothesis that the biota of the region would be severely contaminated with arsenic. Instead, the analyses indicate that remarkably little arsenic has been transferred from the arsenic-contaminated sediments into the biota of the region. Much of the biota sampled by us had no detectable arsenic in their tissues, and those species that did have measurable levels of arsenic had reasonably low concentrations (max. 1.3 ppm; Table 2)

Our analysis of biological material produced results comparable to previous work done by the Department of Health (1978*b*). Three species examined by us and also by the Department of Health were found by us to have lower arsenic concentrations. *Mugil cephalus* had visceral arsenic concentrations that were all approx. 1 ppm, whereas the Department of Health reported a range from 1.67 to 6.64 ppm. The blue-green algae that represents a food base for mullet was reported by the Department of Health to have 1 ppm arsenic, whereas we were unable to detect arsenic in our samples. Furthermore, we did not find detectable arsenic in *Portunus sanguinolentus* (white crab), whereas the Department of Health found 0.17 ppm arsenic in white crab muscle tissue. These data showing low arsenic contamination of biota are compatible with the hypothesis that much of the arsenic of Hilo Bay and the Wailoa River estuary is trapped in relatively undisturbed anaerobic sediment layers.

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