Pacific Science (1995), vol. 49, no. 4: 511–525

Mercury Accumulation in Sediments of the Ala Wai Canal and in Soils and Stream Sediments of the Central Honolulu Watershed[1]

LAURENCE M. RAINE,[2,3] BARBARA Z. SIEGEL,[2] AND GARY M. MCMURTRY[4]

ABSTRACT: In this study we determined the historical trend of both natural and anthropogenic sources of mercury deposition as preserved in anoxic estuarine sediments of the Ala Wai Canal, an estuary situated within a heavily urbanized area of Honolulu. Analysis of sediments from the Ala Wai Canal revealed that the total mercury content is highest at the Ala Wai Yacht Harbor (0.054–2.810 μg/g) and decreases exponentially toward the most distal portion of the canal (0.009–0.237 μg/g). In contrast, the mercury content of soil and stream samples taken from the central Honolulu watershed ranges from only 0.001 to 0.058 μg/g. This pattern suggests tidal transport of mercury into the canal from the Ala Wai Yacht Harbor. A chronological analysis of core samples shows a peak in mercury concentrations in the late 1950s, which corresponds to the use of antifouling paints on boats in the harbor and is the probable source of the majority of the mercury found in the Ala Wai Canal. High mercury accumulation ends in the early 1970s in two of the cores investigated, suggesting that antifouling paint–based accumulation ceased rapidly after the U.S. Environmental Protection Agency (EPA) ban. An exception is noted in a comparatively smaller peak coincident with 1986, the last year of a 3-yr intense fire-fountaining period of the ongoing Pu'u 'Ō'ō eruption of nearby Kīlauea Volcano.

THE PUBLIC HEALTH TRAGEDY of mercury contamination of Minimata Bay, Japan, in the 1950s resulted in a global awareness of the deleterious effects of this heavy metal (Clark 1992). Since 1972, regulatory controls have limited its use worldwide; however, the past widespread utilization of this heavy metal as well as its natural accumulation may affect the environment for generations to come (Nriagu 1979, Gerlach 1981).

Much of the background mercury found in the Hawaiian Islands is of volcanic origin and is a result of magmatic degassing and rock weathering, with soil cycling by degassing and biogenic processes (Siegel and Siegel 1978*a*, 1987, Nriagu 1979, Holcomb 1987, Clark 1992). The active volcano Kīlauea, located on the island of Hawai'i, has been observed to increase its mercury output by as much as 100-fold during eruptions (Eshleman 1973, Siegel and Siegel 1978*a,b*). An increase of air mercury levels can occur during full-scale volcanic eruptions both locally and at considerable distances from the volcanic site (Siegel and Siegel 1978*b*, Nriagu 1979). Anthropogenic introduction of mercury in Hawai'i may have resulted from a number of sources, including agricultural pesticides, antifouling paints, mercury fulminate in percussion caps, mercurous chloride in fireworks, and both the legal and illegal dumping of laboratory equipment as well as batteries (Nriagu 1979, Clark 1992).

[1] This is University of Hawai'i School of Public Health (DHHS) contribution no. 240-93-0035, UNIHI-SEAGRANT contribution no. JC-94-32, and School of Ocean and Earth Science and Technology contribution no. 3544. This study was funded in part by the NSF Young Scholars Program and the NOAA-UH Sea Grant College Program. Manuscript accepted 25 April 1994.

[2] School of Public Health, University of Hawai'i at Mānoa, Honolulu, Hawai'i 96822.

[3] To whom all correspondence should be addressed.

[4] Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawai'i at Mānoa, Honolulu, Hawai'i 96822.

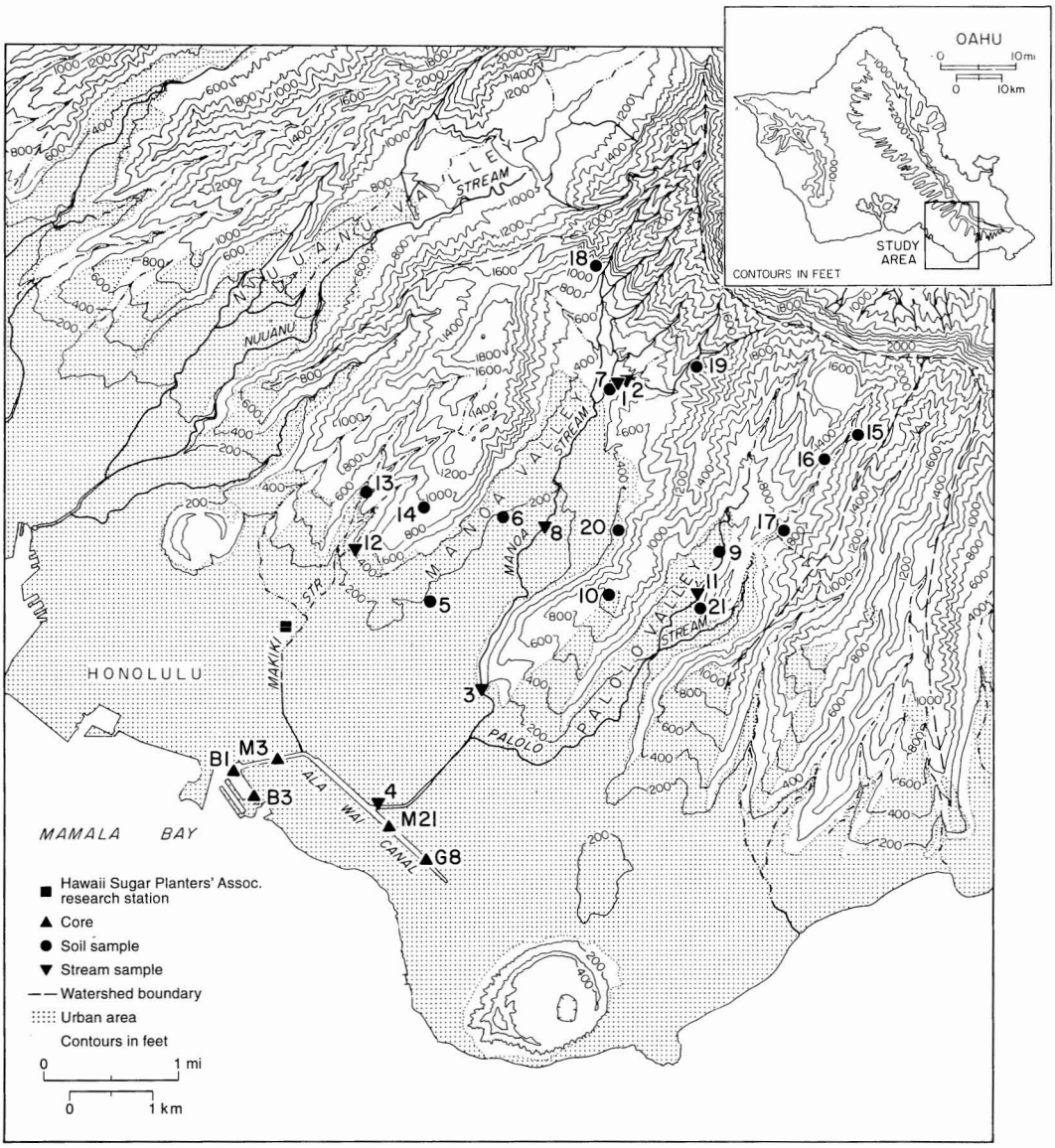

FIGURE 1. Sample sites of the Ala Wai Canal and greater Honolulu watershed.

This study represented a unique opportunity to determine the historical distribution of mercury deposition as preserved in anoxic estuarine sediments of the Ala Wai Canal. The canal, a long, narrow estuary located within a heavily urbanized area of Honolulu, was constructed from 1921 to 1929 to drain swamplands near the resort area of Waikīkī (Figure 1). Since its completion, portions of the canal have remained relatively undisturbed by dredging, and bioturbation is minimal to nonexistent because of the anoxic conditions within the sediments and overlying waters.

Three cores were taken from the canal, the longest of which probably represents a

relatively complete history of sedimentation dating back to canal construction. The canal not only lies within a densely populated urban area but is in relatively close proximity to two active volcanoes on the island of Hawai'i, Kīlauea and Mauna Loa, some 200 km to the southeast. This unique geographic feature should reveal contamination of the environment by both natural as well as anthropogenic sources of mercury. Although the current population of O'ahu (ca. 800,000) is relatively small in comparison with other metropolitan areas of the United States, it does exhibit similar patterns of mercury consumption and concomitant pollution of the environment. In this study, we determined the quantity of mercury contained in the Ala Wai Canal sediments and in soil and stream samples taken from the surrounding watershed; stratigraphic distributions and comparative concentrations of this metal were used to determine its source.

MATERIALS AND METHODS

Five sediment core samples were recovered in 1991: three from the canal and two from the Ala Wai Yacht Harbor basin (Figure 1). These cores were obtained as part of a research program conducted by various researchers of the University of Hawai'i at Mānoa (Fryer 1995). The cores were obtained by pushing ca. 6.1 m of 8.9-cm-diameter plastic core-liners into the shallow sediment of the canal from a small boat. Coring disturbance was minimized by keeping the removed cores vertical at all times. These cores were then coded as Miller-3 or M3 (length = 90 cm), Miller-21 or M21 (length = 163 cm), Gonzalez-8 or G8 (length = 200 cm), Basin-1 or B1 (length = 62 cm), and Basin-3 or B3 (length = 67 cm). The M3, M21, and G8 cores were sectioned into 2-cm segments; subsamples for mercury were then placed in plastic bags, stored at 4°C, and analyzed on a wet basis. The B1 and B3 core samples were freeze-dried and stored at ambient room temperature. Stream sediment and soil samples were taken for mercury determination within the watershed area (Figure 1). The stream sediment samples were analyzed on a wet basis after wet size sieving. The soil samples were stored in plastic self-sealing bags at ambient room temperature and, to avoid any potential loss of mercury, were not air-dried to remove moisture before analysis.

The wet, moist, and freeze-dried samples were analyzed for their mercury content using a flameless atomic absorption spectrophotometer (Perkin-Elmer model no. 50B), with a sensitivity of 0.005 μg, following standard HNO_3-H_2O_2 digestion (Pickard and Martin 1960, Siegel et al. 1980). A standard curve using $HgCl_2$ (J. T. Baker Chemical Co., analytical grade mercury; 1000 μg/g; lot no. 138179) was used to calibrate the instrument at the initiation of and during analyses of the samples. Data are presented as averages of duplicate determinations, except for the canal cores, which are averages of four determinations (two adjacent 2-cm samples). Fallout ^{137}Cs dating techniques were utilized to determine the sedimentation rates of the M3, M21, and G8 cores (McMurtry et al. 1995).

RESULTS

The M3 core was taken from a section of the Ala Wai Canal that lies between the Ala Wai Yacht Harbor and the entrance of Makiki Stream (Figure 1). The total mercury of this sample ranges from 0.100 to 1.076 μg/g (Table 1). The M3 core was the shortest of the three canal cores (total length = 90 cm). Fallout ^{137}Cs dating yielded an average sedimentation rate of ca. 2.5 cm/yr for M3. Apart from the Ala Wai Yacht Harbor cores, this core exhibits the highest concentration of total mercury. The M3 core mercury distribution shows relatively low and consistent concentrations from 1991 until about 1972 (Figure 2). The total mercury for this time period ranges from 0.100 to 0.247 μg/g. This stable period is preceded by sharp increases in total mercury exhibiting two peaks in about 1966 (0.567 μg/g) and in about 1959 (1.076 μg/g). The 1959 peak is preceded by a decrease in total mercury to a low of 0.188 μg/g, in about 1957, before

TABLE 1

MERCURY ACCUMULATION RATE, DETRITUS FRACTION-NORMALIZED, AND TOTAL MERCURY CONTENTS OF ALA WAI CANAL SEDIMENT CORES M3, M21, and G8

DEPTH (cm)	CORE M3			CORE M21			CORE G8		
	ACM[a]	DF[b]	Hg[c]	ACM	DF	Hg	ACM	DF	Hg
0–4	0.249	0.120	0.105	0.099	0.077	0.065	0.010	0.107	0.089
4–8	0.134	0.118	0.100	0.088	0.065	0.054	0.105	0.094	0.077
8–12	0.185	0.146	0.116	0.031	0.071	0.061	0.060	0.078	0.065
12–16	0.262	0.150	0.121	0.029	0.061	0.054	0.087	0.102	0.084
16–20	0.292	0.126	0.109	0.227	0.088	0.077	0.097	0.109	0.088
20–24	0.246	0.161	0.129	0.200	0.076	0.067	0.119	0.170	0.136
24–28	0.273	0.128	0.111	0.242	0.104	0.090	0.087	0.136	0.101
28–32	0.266	0.147	0.128	0.204	0.080	0.069	0.047	0.101	0.063
32–36	0.173	0.122	0.110	0.224	0.084	0.072	0.053	0.108	0.084
36–40	0.345	0.198	0.177	0.309	0.102	0.084	0.057	0.120	0.089
40–44	0.294	0.219	0.184	0.325	0.107	0.088	0.059	0.107	0.088
44–48	0.259	0.294	0.247	0.353	0.113	0.093	0.061	0.116	0.072
48–52	0.536	0.565	0.487	0.284	0.096	0.083	0.084	0.138	0.097
52–56	0.635	0.672	0.561	0.254	0.098	0.084	0.091	0.125	0.105
56–60	0.642	0.664	0.553	0.240	0.106	0.089	0.067	0.123	0.108
60–64	0.715	0.603	0.487	0.169	0.093	0.079	0.076	0.139	0.120
64–68	0.503	0.481	0.412	0.156	0.088	0.075	0.091	0.166	0.145
68–72	0.717	0.646	0.507	0.172	0.094	0.081	0.095	0.166	0.146
72–76	1.501	1.647	1.070	0.234	0.145	0.125	0.075	0.158	0.137
76–80	1.085	1.067	0.775	0.217	0.112	0.100	0.109	0.169	0.148
80–84	0.636	0.545	0.443	0.167	0.083	0.073	0.122	0.201	0.178
84–88	0.176	0.207	0.188	0.242	0.109	0.096	0.122	0.164	0.145
88–92	0.773	0.787	0.670	0.234	0.106	0.094	0.165	0.229	0.197
92–96				0.208	0.094	0.083	0.157	0.244	0.209
96–100				0.208	0.092	0.080	0.155	0.202	0.179
100–104				0.176	0.079	0.069	0.168	0.213	0.185
104–108				0.179	0.082	0.071	0.223	0.278	0.237
108–112				0.203	0.094	0.086	0.209	0.281	0.230
112–116				0.188	0.084	0.078	0.123	0.170	0.136
116–120				0.227	0.094	0.089	0.126	0.164	0.130
120–124				0.122	0.062	0.057	0.066	0.082	0.067
124–128				0.198	0.098	0.082	0.059	0.100	0.071
128–132				0.177	0.092	0.081	0.056	0.084	0.065
132–136				0.146	0.089	0.065	0.050	0.057	0.047
136–140				0.164	0.103	0.059	0.050	0.053	0.044
140–144				0.098	0.048	0.039	0.055	0.047	0.042
144–148				0.134	0.069	0.062	0.045	0.048	0.042
148–152				0.234	0.141	0.127	0.041	0.048	0.038
152–156				0.206	0.109	0.098	0.048	0.050	0.045
156–160				0.203	0.116	0.105	0.042	0.045	0.040
160–164				0.157	0.079	0.073	0.026	0.049	0.025
164–168							0.022	0.038	0.014
168–172							0.025	0.039	0.015
172–176							0.016	0.035	0.013
176–180							0.027	0.046	0.017
180–184							0.020	0.041	0.015
184–188							0.017	0.030	0.009
188–192							0.011	0.021	0.009
192–196							0.022	0.037	0.017
196–200							0.037	0.046	0.021

[a] ACM, Mercury accumulation rate (μg/cm^2 mo) calculated using sedimentation rate and dry bulk density data from McMurtry et al. (1995).

[b] DF, Detritus fraction-normalized Hg (μg/g) calculated using data from McMurtry et al. (1995).

[c] Bulk Hg (μg/g).

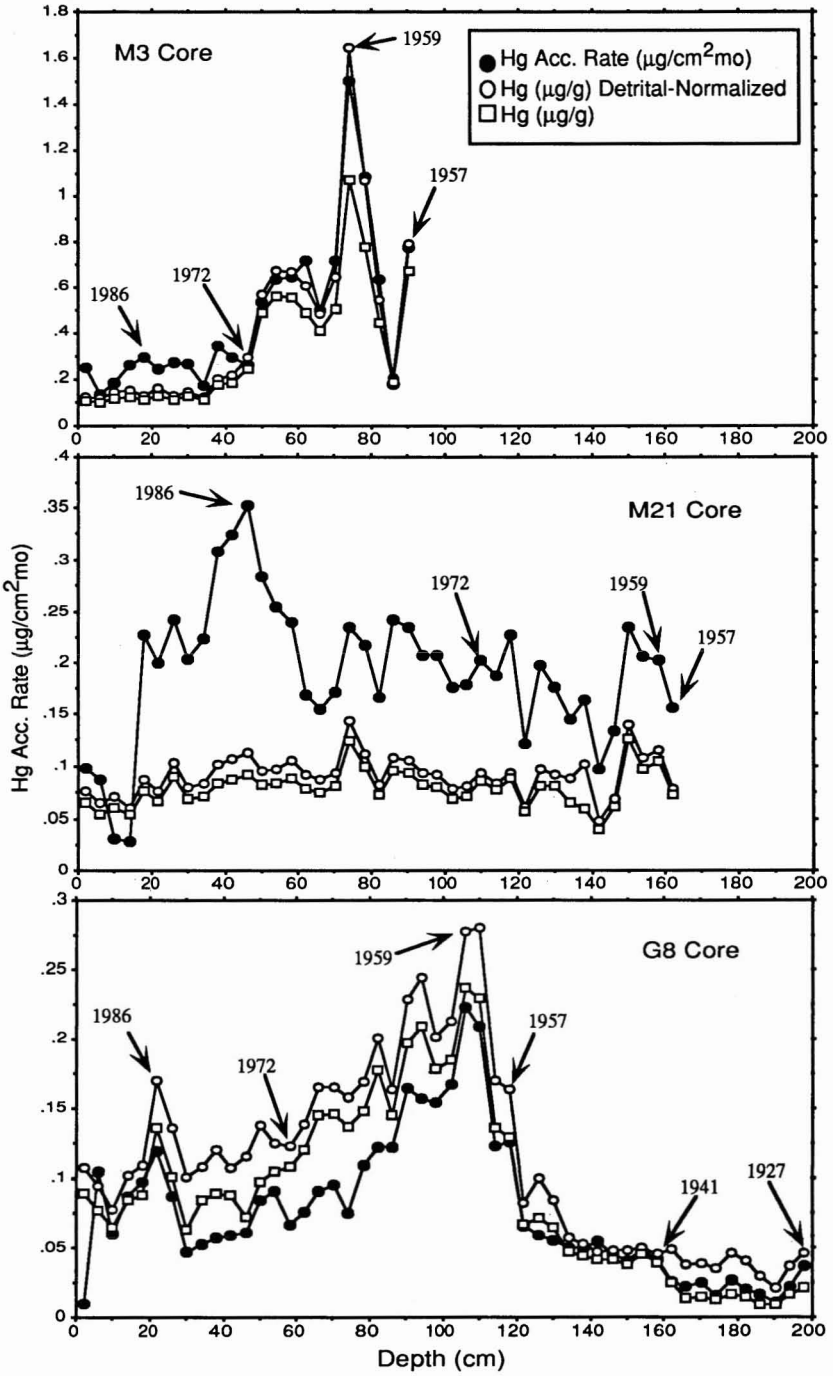

FIGURE 2. Accumulation rate, detritus fraction-normalized, and total mercury contents of Ala Wai Canal sediment cores M3, M21, and G8. The dating of the G8 core from 1957 to 1927 must be interpreted with care because an extrapolation of the average sedimentation rate was performed from 116 to 200 cm; therefore, dates preceding 1958 are only an approximation.

which the total mercury again rises in 1957 (0.670 μg/g). The core was unfortunately truncated at that point; therefore, it is not known if the mercury again peaks at the previous high level or levels off to preindustrial mercury levels as noted in other, deeper core samples (see following).

The mercury accumulation rate and detrital fraction-normalized mercury for the M3 core exhibit a distribution pattern similar to that of the total mercury (Figure 2). Mercury accumulation rates range from 0.134 to 1.501 (μg/cm^2 mo), whereas the detrital fraction-normalized concentrations range from 0.118 to 1.647 (μg/g) (Table 1).

The M21 core was taken from a section of the Ala Wai Canal that lies between the Mānoa-Pālolo Stream and the head of the canal (Figure 1). This core sample (total length = 162 cm) was determined by ^{137}Cs dating to have an average sedimentation rate of ca. 4.5 cm/yr. The M21 core exhibits several major sedimentation rate changes, with the more recent and older portions of the sediment accumulating more rapidly than the middle section of the core (McMurtry et al. 1995). The total mercury content of the core ranges from 0.039 to 0.127 μg/g (Table 1). Two peaks are shown in the data: one around 1979 (0.125 μg/g) and one at around 1962 (0.127 μg/g) (Figure 2).

The mercury accumulation rate for the M21 core exhibits a distribution pattern that is dissimilar to the total mercury concentrations (Figure 2). Mercury accumulation rates range from 0.029 to 0.353 (μg/cm^2 mo) (Table 1). The largest peak noted for the accumulation rate corresponds to 1986 (0.353 μg/cm^2 mo). The detrital fraction-normalized concentrations exhibit a distribution pattern similar to that of the total mercury, ranging from 0.048 to 0.145 (μg/g).

The G8 core was from a section of the Ala Wai Canal that lies closest to the head of the canal (Figure 1). This core was 200 cm long and was determined by ^{137}Cs dating to have an average sedimentation rate of ca. 2.5 cm/yr. The G8 core represents the most complete stratigraphic mercury profile of the Ala Wai Canal in this study. The total mercury content of the core ranges from 0.009 to 0.237 μg/g (Table 1, Figure 2). The mercury content in the G8 core samples increases steadily from the construction of the canal in 1927 and starts to rise around 1939. The highest mercury peak was deposited in about 1958 and was followed by four smaller peaks in 1959 (0.209 μg/g), 1962 (0.178 μg/g), 1964 (0.146 μg/g), and 1986 (0.136 μg/g). The total mercury of the core remains relatively stable after around 1978 but is still approximately two to three times greater than the mercury content noted in earlier sediments (1927–1951) (Figure 2).

The mercury accumulation rate for the G8 core exhibits a distribution pattern that is similar to the total mercury distribution (Figure 2). Mercury accumulation rates range from 0.010 to 0.223 (μg/cm^2 mo) (Table 1). The largest peak noted for the accumulation rate was in 1959 (0.223 μg/cm^2 mo). A smaller peak occurred in 1986 (0.119 μg/cm^2 mo) following a decreasing trend from the high mercury accumulation rate noted in 1959. The detrital fraction-normalized concentrations exhibit a distribution pattern that is generally similar to the total mercury concentrations, ranging from 0.048 to 0.145 (μg/g) (Table 1, Figure 2).

TABLE 2

TOTAL MERCURY CONTENT OF ALA WAI YACHT HARBOR SEDIMENT CORES B1 AND B3 (μg/g)

CORE	DEPTH (cm)	<63 μm	>63 μm
B1	0–3	0.507	0.347
	6–11	0.571	0.302
	16–21	0.284	0.236
	26–31	0.258	0.195
	36–41	0.283	0.232
	41–46		0.223
	46–53	0.275	0.241
B3	0–2	0.987	1.370
	4–6	1.371	1.159
	8–10	1.243	1.441
	15–20	1.664	1.600
	25–30	1.992	1.898
	35–40	2.813	2.740
	40–45		2.810
	45–50	1.551	1.346
	50–55	0.145	0.242
	55–60	0.166	0.054

TABLE 3

TOTAL MERCURY IN SOILS OF THE GREATER HONOLULU WATERSHED (μg/g)

DEPTH (cm)	SAMPLE SITE[a]													
	5	6	7	9	10	13	14	15	16	17	18	19	20	21
0–10	0.001	0.033	0.004	0.005	0.001	0.006	0.001	0.018	0.030	0.015	0.032	0.058	0.038	0.023
10–20	0.002	0.015	0.018	0.014	0.044	0.006	0.005	0.019	0.025	0.024	0.020	0.023	0.027	0.037
20–30	0.035	0.016	0.008	0.004	0.001	0.010	0.008	0.019	0.020	0.002	0.005	0.031	0.026	0.035
30–40	0.018	0.018	0.005	0.017	0.001	0.010	0.006	0.021	0.010	0.043	0.019	0.023	0.013	0.025
40–50	0.031	0.022	0.046	0.014	0.004	0.010	0.013	0.017	0.011	0.044	0.021	0.018	0.016	0.041
50–60						0.005					0.022			
60–70						0.007								
70–80						0.026								
80–90						0.022								
90–100						0.004								

[a] See Figure 1.

The B1 and B3 cores were taken from the Ala Wai Yacht Harbor (Figure 1). The total mercury content for these cores ranges from 0.054 to 2.810 μg/g (Table 2). ^{137}Cs dating of these cores was not attempted because of extensive dredging within the harbor. Therefore, the total mercury values found in these cores represent the presence of mercury in the Ala Wai Yacht Harbor and not its depositional history.

To determine potential sources for the mercury observed in the Ala Wai Canal core samples, 14 soil profiles and seven stream samples were taken from the surrounding watershed (Figure 1). The total mercury content of the soil sites ranges from 0.001 to 0.058 μg/g (Table 3, Figure 3*a*). The total mercury content of the stream sites ranges from 0.003 to 0.022 μg/g (Table 4, Figure 3*b*). The mercury concentrations of the stream sediments are comparable with those found in the soil profiles, indicating that soil erosion has contributed to the total mercury content found in stream sediments. There is generally more mercury in the fine fraction (<45 μm) than in the coarser fraction (45–1000 μm) of the stream sediments (Table 4, Figure 3*b*), suggesting surface adsorption of mercury. The soil samples taken from the watershed generally consist of brown, organic-rich soils with color changes noted at deeper levels that sometimes correlate with marked changes in mercury content (Figures 4 and 5). The stream samples consist of mostly gray-brown sandy gravel with clay and silt. The canal cores range from dusky yellowish brown to grayish black mud with either intercalated gray-white sediment at depths greater than 135 cm (M21) or gray carbonate-rich mud at depths greater than 162 cm (G8). The basin cores are similar in composition to the canal sediments. For more complete soil and stream sample descriptions of the Mānoa-Pālolo-Makiki Valleys watershed and Ala Wai Canal sediments, see McMurtry et al. (1995) and Glenn et al. (1995).

DISCUSSION

Mercury can be introduced into the environment through natural as well as anthropogenic deposition. A potential natural source of mercury found in the Ala Wai Canal core samples was evaluated by comparing the mercury distribution noted in the stratigraphic data with known volcanic eruptions of Mauna Loa and Kīlauea. A graphic representation of the frequency of these eruptions from 1924 to 1991 is presented in Figure 6. As can be readily noted in the eruptive history, a relatively quiescent period existed between 1924 and 1952, in which eruptions occurred rather infrequently and consisted of noncontinuous activity. During that period there were seven brief eruptions of Kīlauea

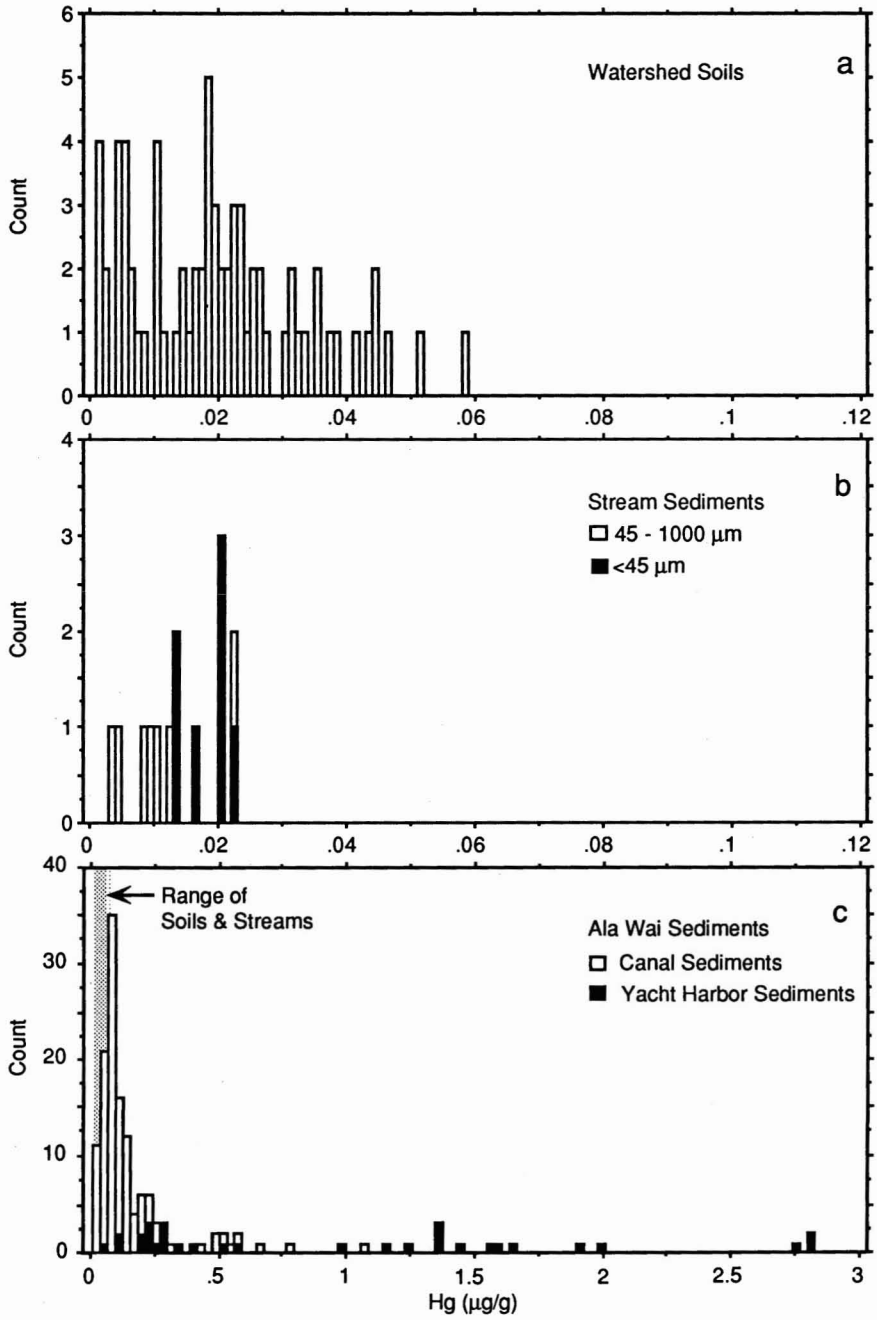

FIGURE 3. Frequency distributions of mercury in (*a*) soils and (*b*) stream sediments of the greater Honolulu watershed and in (*c*) Ala Wai Canal sediments.

TABLE 4

TOTAL MERCURY IN STREAM SEDIMENTS OF THE GREATER HONOLULU WATERSHED (μg/g)

PARTICLE SIZE	SAMPLE SITE[a]						
	1	2	3	4	8	11	12
<45 μm	0.004	0.013	0.016	0.020	0.022	0.020	0.020
45–1,000 μm	0.013	0.008	0.012	0.022	0.010	0.009	0.003

[a]See Figure 1.

(Halema'uma'u Crater) from 1924 to 1933, after which it did not erupt for the next 18 yr (Holcomb 1987). Mauna Loa erupted steadily once every 4 yr from 1832 to 1950; from 1950 to 1974 it exhibited a noneruptive quiescent period (Lockwood et al. 1987).

The total mercury peaks that were detected in the core samples do not in general correspond to the eruptive phases of the volcanoes (Figure 2). The total mercury content in the Ala Wai Canal G8 core starts to increase in about 1939 and peaks in 1959; however, both volcanoes were relatively quiet during that period, which limits volcanic atmospheric deposition of mercury in the Ala Wai Canal and its watershed. When the Kīlauea major eruptions (Kīlauea Iki, Mauna Ulu, and Pu'u 'Ō'ō) were compared with the canal core data there was no obvious relationship between eruption frequency and deposition of mercury. For example, with the possible exception of the 1986 mercury accumulation peak in these three cores, the continuous eruption of Pu'u 'Ō'ō from 1983 to 1991 does not appear to add substantially to the observed total mercury content of the core samples. The data do exhibit many smaller mercury peaks, especially in G8 and M21; however, with the possible exception of the 1986 peak in mercury accumulation, there is no obvious correlation with periods of intense volcanic activity.

The location of the Ala Wai Canal within a heavily urbanized portion of Honolulu suggests that much of the mercury concentrations found there, or in its watershed, could be anthropogenic in origin. Four possible anthropogenic sources for the total mercury found in the sediments are antifouling paints, illegal dumping (including batteries), agricultural fungicides, and mercury in percussion caps and fireworks.

Antifouling paints are used on marine craft to prevent the growth of marine organisms. The biotoxic characteristics of antifouling paints on the marine environment prompted the U.S. Environmental Protection Agency (EPA) to suspend the registration of 43 mercury-containing antifouling paints in 1972. Records pertaining to use of this paint in Hawai'i are difficult to obtain, but it can be postulated that the organomercurials found in antifouling paints, most noticeably during and after World War II, have contributed to the mercury increase noted in the Ala Wai Canal sediments. D'Itri (1972) and D'Itri and D'Itri (1977) noted that after 1940, the U.S. Navy had the hulls of its ships painted with organomercuric antifouling paints (formula number 142: a mixture of synthetic resins, salts of mercury, lead, and arsenic). Antifouling paint could have been available from the large stores at Pearl Harbor to nonmilitary sea vessels at approximately the same period. Nriagu (1979) presented information on the total quantity of mercury used in antifouling paints as annual consumption (in 76-lb [34.5-kg] flasks, a commercial measurement) for the United States. The total consumption of mercury for antifouling paints was 1661 flasks in 1945, peaked to 3133 flasks in 1950, and then fell off dramatically to 724 flasks in 1955. For each canal core, the total mercury drops and remains fairly constant from the early 1970s to the 1991 collection date, with most peak activity occurring in the 1950s. These data, when viewed in conjunction with the D'Itri data

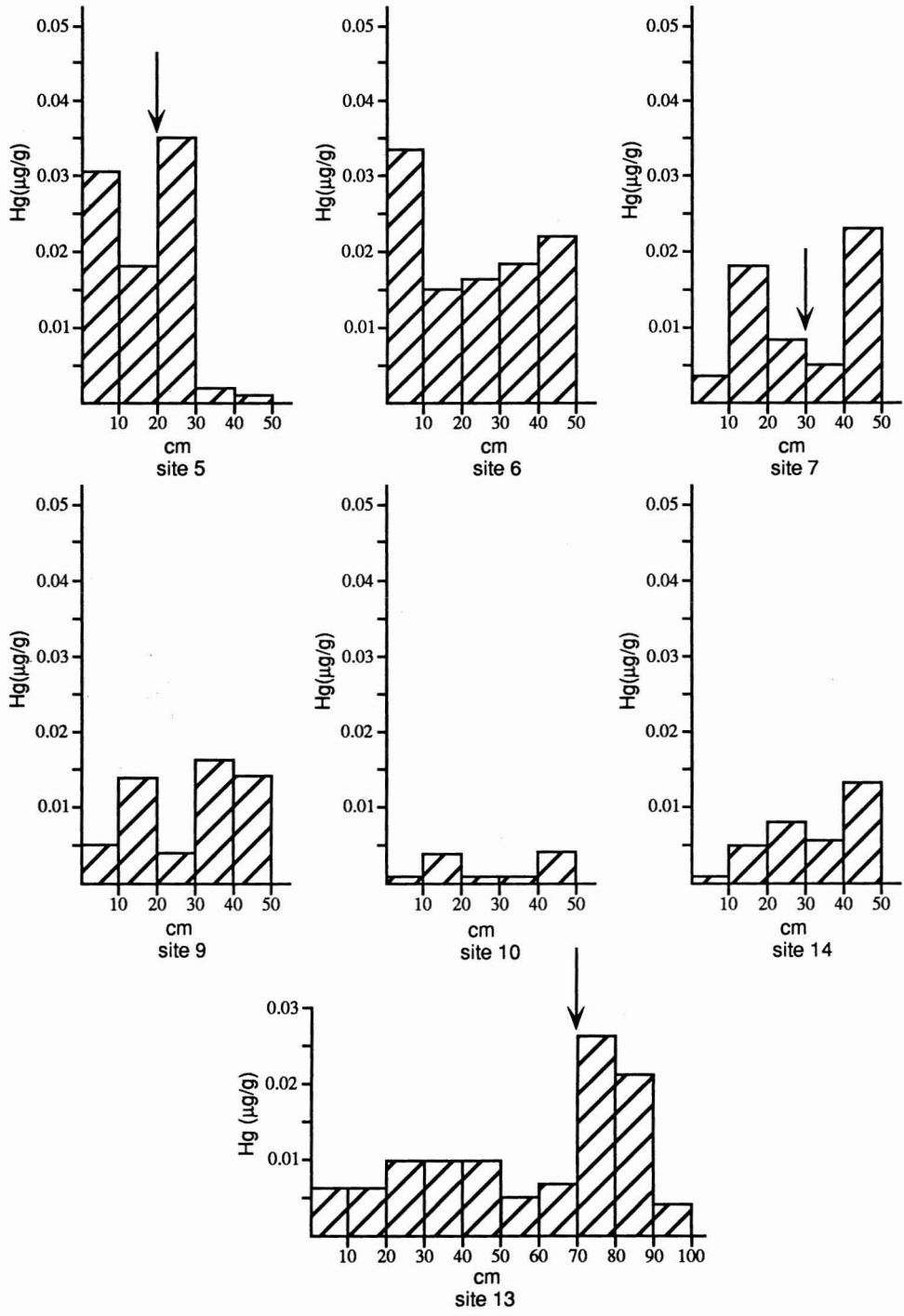

FIGURE 4. Depth profiles of mercury in soils of the greater Honolulu watershed. Arrows indicate color changes in soil horizons.

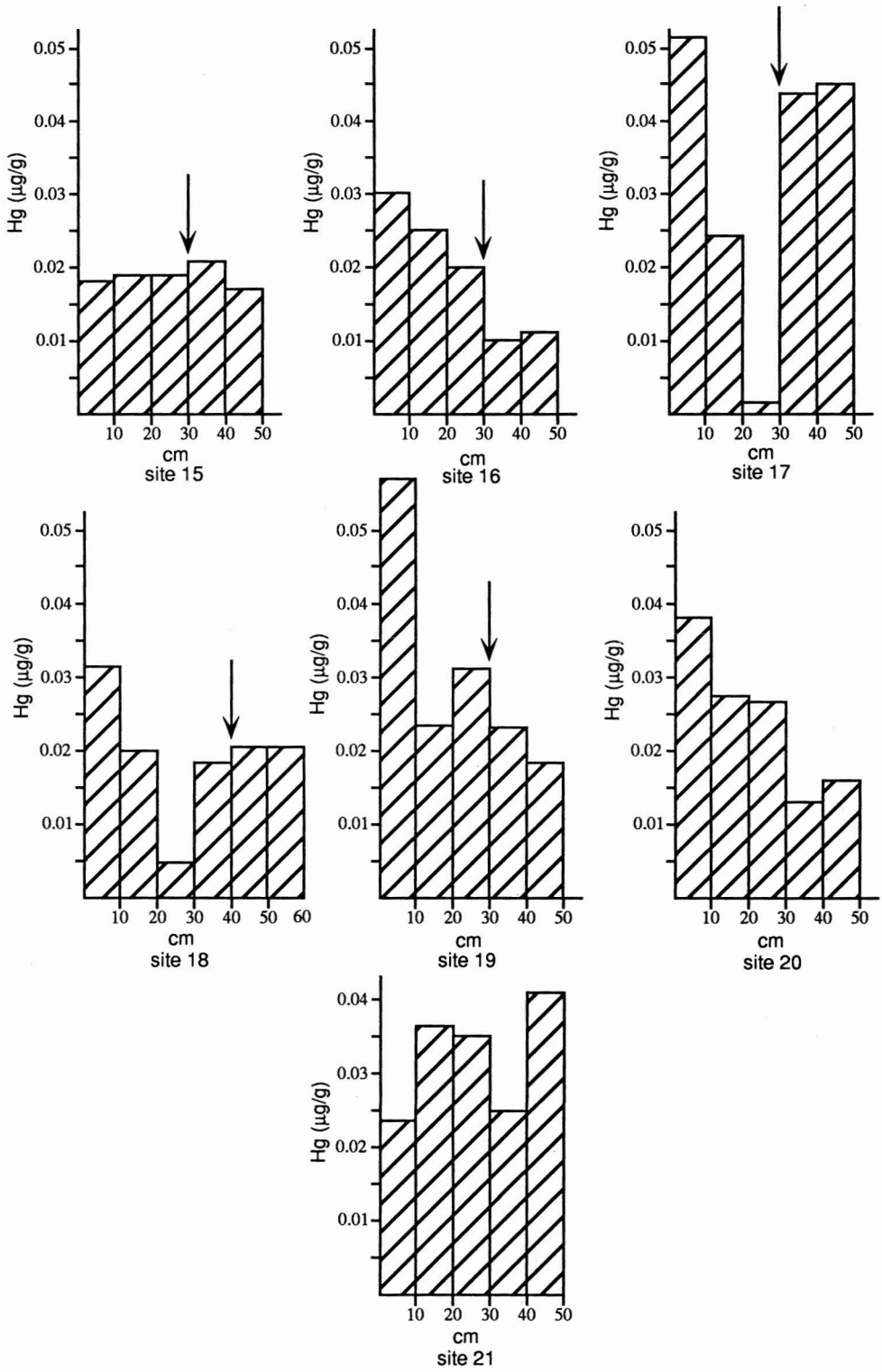

FIGURE 5. Depth profiles of mercury in soils of the greater Honolulu watershed. Arrows indicate color changes in soil horizons.

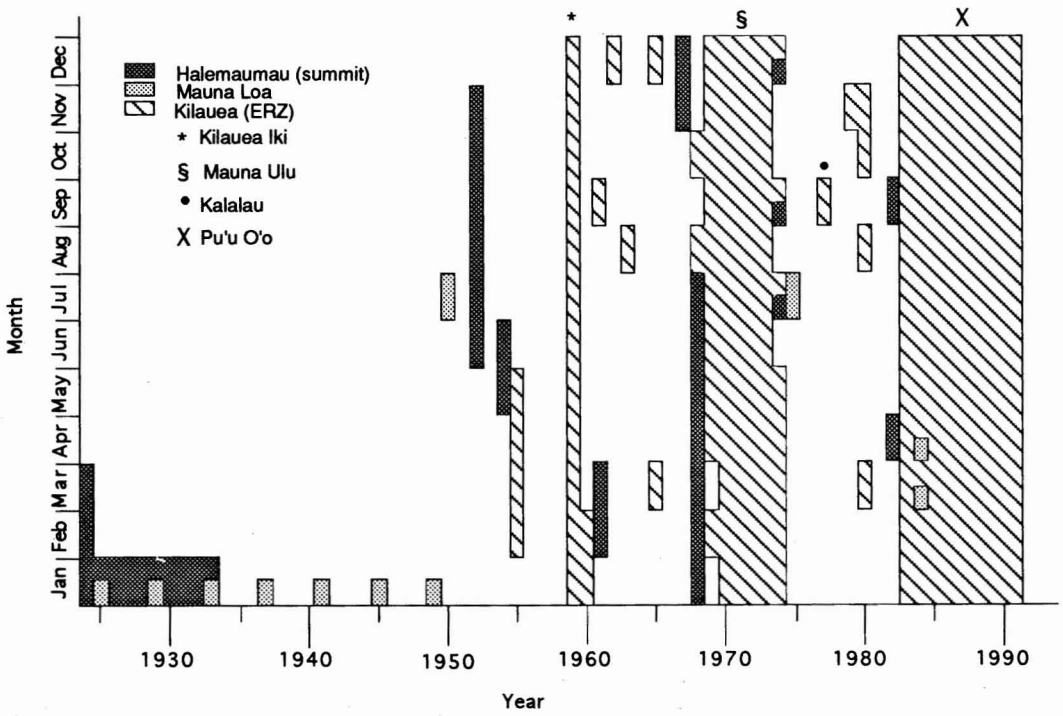

FIGURE 6. Recent eruptive histories of Mauna Loa and Kīlauea Volcanoes (after Holcomb 1987).

and Nriagu statistics on mercury-containing antifouling paints, must be interpreted with care. The Nriagu data represent total annual consumption of mercury-containing antifouling paints for the entire United States and may not reflect the distribution or utilization patterns that occurred in Hawai'i.

Mercury from organomercury compounds in antifouling paints diffuses into seawater continuously and could have become adsorbed onto the sediments in the Ala Wai Yacht Harbor. Degraded paint particles and dissolved mercury could also have been carried with the tides and deposited upstream in the sediments of the Ala Wai Canal. Eshleman (1973) noted that the mercury content of samples taken from surface sediments (0–5 cm) obtained from the Ala Wai Canal (midchannel) was highest at the Ala Wai Yacht Harbor (0.210–1.3 μg/g) and lowest at the head of the Ala Wai Canal (0.110–0.120 μg/g). Eshleman postulated that antifouling paints may present a continuous source of mercury in the harbor. Luoma (1974) sampled the top 5 mm of sediment taken from the landward end of the Ala Wai Canal and found that the mercury content ranged from 0.344 to 2.086 μg/g in 1973. This sediment contained much higher values than those of the nearby G8 core for that period.

The relative mercury accumulation pattern in the three cores analyzed in this study supports a tidal transport from the Ala Wai Yacht Harbor. When the mercury accumulation rates for M3, M21, and G8 cores are plotted against distance from the Ala Wai Yacht Harbor, there is a roughly exponential decrease in the mercury accumulation rate from the harbor toward the head of the canal (Figure 7). Sediment samples taken from the Ala Wai Yacht Harbor exhibited a total mercury content range of 0.054–2.813 μg/g, whereas samples taken from the most distal core (G8) ranged from 0.009 to 0.237 μg/g. Because the samples from the Ala Wai Yacht Harbor were freeze-dried, and because

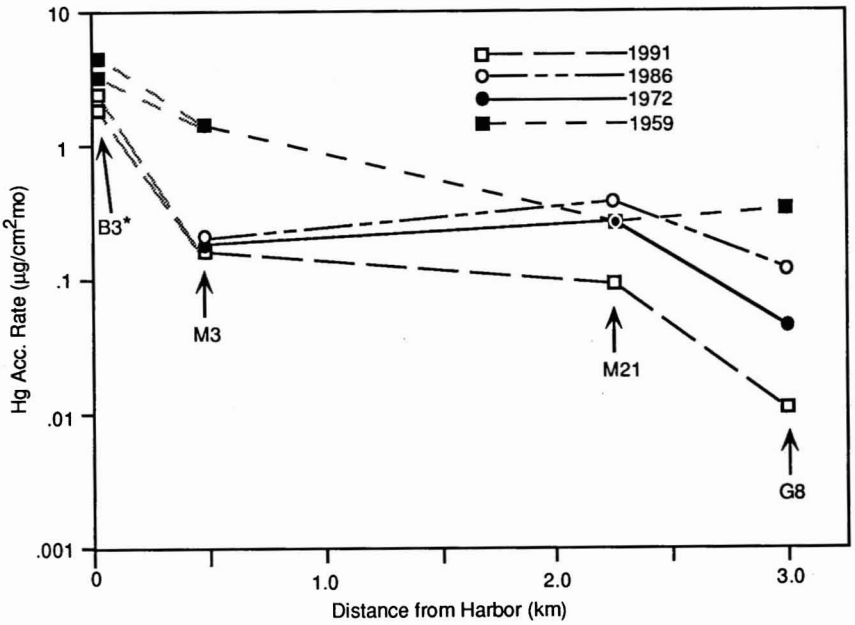

FIGURE 7. Profiles of selected mercury accumulation rates for the Ala Wai Canal and the Ala Wai Yacht Harbor at selected dates. *Denotes mercury accumulation rates for the Ala Wai Yacht Harbor calculated for 1991 and 1959 based on the assumption that the sedimentation rate and the dry-bulk densities for the B3 core are similar to those for the M3 core (the most proximal core). The B3 core displays the least disturbed and most complete stratigraphic profile of the two cores taken from the harbor (E. De Carlo, pers. comm., 1993). Two mercury accumulation rates for 1991 and 1959 were calculated from the lowest and highest total mercury concentrations from the fine and coarse fractions of the B3 core at the surface (ca. 1991) and at a depth immediately above a stratigraphic change from gray-black to gray carbonate-rich mud (ca. 1959). The mercury accumulation rates for the Ala Wai Yacht Harbor samples must be interpreted with caution because these cores were not dated by ^{137}Cs and are meant only to illustrate the possible tidal transport of mercury in the canal.

the vapor pressure of mercury is high (1.2×10^{-3} mm at 20°C), the mercury quantities may actually reflect lower values resulting from the process of volatilization.

By the early 1960s, tributyltin (TBT) as well as copper-based antifouling paints were beginning to replace mercury as the biocide of choice for prevention of damage to boats caused by marine organisms. The substitution of TBT and copper for mercury in antifouling paints could very well explain why mercury deposition dropped off in all Ala Wai Canal core samples by the 1960s and 1970s. The total mercury content in all of the relatively recent Ala Wai Canal samples has remained high when compared with values from when the canal was first constructed. This observation could be attributed to residual sources of mercury in the Ala Wai Yacht Harbor or from other natural or anthropogenic sources.

An agricultural contribution to the total mercury content in the Ala Wai Canal sediments must also be considered. The fungicide phenylmercuric acetate (PMA) was used to treat sugarcane seed pieces before they were planted in the ground to prevent fungal infection. Agricultural production throughout Hawai'i consisted of either small truck crops or sugarcane (Magistad and Frazier 1938). PMA could have leached from the soil into the streams and ultimately been deposited into the canal. Soil and stream samples taken from Mānoa, Makiki, and Pālolo Valleys suggest that the past and present impact of a widespread agricultural component contributing to the mercury levels found in the canal is quite minimal (Figure

3). However, these data do not preclude past agricultural contamination, because most of the soil sites are not within agricultural areas and the stream sediments likely reflect only recent deposition. The relatively low mercury levels present in the soil and stream sediments may result from inputs by continued agricultural, rock weathering, and volcanic and distal atmospheric deposition (e.g., from North America or Asia or both, depending on the altitude of transport) minus some component lost from direct degassing and biological cycling (Siegel and Siegel 1987).

Nevertheless, watershed soil mercury sources to the canal are minimal because the lowest quantity of mercury noted in the Ala Wai Yacht Harbor (0.054 μg/g) was quite close to or exceeded the maximum levels found in the soil (0.058 μg/g) and stream samples (0.022 μg/g) (Tables 2–4). The total quantity of mercury in the soils, stream, and Ala Wai sediment core samples was determined on a wet basis, except the Ala Wai Yacht Harbor samples, which were freeze-dried. Therefore, the amount of mercury found in the soils, stream, and the Ala Wai Canal samples probably underestimates the dry-weight mercury content of these samples, which is possibly a factor of two or three higher than the reported values. However, the relative concentration trends between the Ala Wai Yacht Harbor, canal, and Honolulu watershed stream sediments and soils are probably underestimated in the directions we have indicated.

The use of mercury fulminate in percussion caps of explosives and ammunition and mercurous chloride (calomel) in fireworks (Watkins et al. 1968) may also account for some of the mercury in the canal. The mercury content in the G8 core began to rise near 1941, which could possibly be correlated with the bombing of Pearl Harbor (Figure 2). Honolulu has extensive home fireworks displays as part of its cultural expression. These sources could contribute additional, albeit minimal, amounts of mercury to the canal, given the present and past soil concentrations as noted in their depth distributions (Table 3, Figures 4 and 5).

Illegal or unintentional dumping of mercury into the Ala Wai Canal could account for some of the mercury found in the canal. Research and clinical laboratories use metallic, inorganic, and organic mercury compounds and are located upstream from the Ala Wai Canal (e.g., the University of Hawai'i near the Mānoa Stream [Figure 1: sample site 3] and the Hawai'i Sugar Planters' Association Research Station (1896 to 1975) near the Makiki Stream (Figure 1). However, if dumping of mercury from these sources had occurred, it would likely have been deposited into the sanitary sewer system that vents subsea at the Sand Island Outfall, ca. 6 km west of the canal. Mercury contamination from these sources could have occurred if storms caused the sewers to overflow into the streams—a remote possibility. Other potential anthropogenic sources of mercury in the canal sediments are airborne and waterborne emissions from landfills, incineration of municipal solid waste, municipal sewage sludge, and fossil fuel power plants. However, O'ahu's landfills, incinerators, and power plant have been designed to take advantage of Hawai'i's prevailing trade wind patterns to minimize the impact on both the environment and heavily urbanized population centers.

CONCLUSIONS

Accumulation rate, detrital fraction-normalized, and total mercury analyses of sediment cores collected from the Ala Wai Canal and the Ala Wai Yacht Harbor suggest that mercury from the harbor has been transported by tides to the most distal portions of the canal. Of a variety of potential sources considered, it appears that mercury-containing antifouling paints are the probable source of the majority of mercury found in the canal sediment. Mercury concentrations of watershed soils and stream sediments suggest relatively minor widespread contamination from volcanic, agricultural, or industrial sources. A small peak in mercury accumulation was noted in each core in 1986, which coincides

with the last year of a 3-yr intense fire-fountaining period of the ongoing Pu'u 'Ō'ō eruption of Kīlauea Volcano.

ACKNOWLEDGMENTS

We thank Eric De Carlo for providing samples of the Ala Wai Yacht Harbor cores.

LITERATURE CITED

CLARK, R. B. 1992. Marine pollution, 3rd ed. Clarendon Press, Oxford.

D'ITRI, F. M. 1972. The environmental mercury problem. CRC Press, Cleveland.

D'ITRI, P. A., and F. M. D'ITRI. 1977. Mercury contamination: A human tragedy. John Wiley & Sons, New York.

ESHLEMAN, A. M. 1973. A preliminary survey of lead and mercury in the Hawaiian environment. Ph.D. diss., University of Hawai'i, Honolulu.

FRYER, P. 1995. The 1991–1992 NSF Young Scholars Program at the University of Hawai'i: Science and engineering studies of the Ala Wai Canal, an urban estuary in Honolulu. Pac. Sci. 49:319–331.

GERLACH, S. A. 1981. Marine pollution: Diagnosis and therapy. Springer-Verlag, New York.

GLENN, C. R., S. RAJAN, G. M. MCMURTRY, and J. BENAMAN. 1995. Geochemistry, mineralogy, and stable isotopic results from the Ala Wai estuarine sediments: Records of hypereutrophication and abiotic whitings. Pac. Sci. 49:367–399.

HOLCOMB, R. T. 1987. Eruptive history and long-term behavior of Kilauea volcano. Pages 261–350 *in* R. W. Decker, T. L. Wright, and P. H. Stauffer, eds. Volcanism in Hawaii. U.S. Geol Surv. Prof. Pap. 1350.

LOCKWOOD, J. P., J. J. DVORAK, T. T. ENGLISH, R. Y. KOYANAGI, A. T. OKAMURA, M. L. SUMMERS, and W. R. TANIGAWA. 1987. Mauna Loa 1974–1984: A decade of intrusive and extrusive activity. Pages 537–570 *in* R. W. Decker, T. L. Wright, and P. H. Stauffer, eds. Volcanism in Hawaii. U.S. Geol. Surv. Prof. Pap. 1350.

LUOMA, S. N. 1974. Mercury cycling in a small Hawaiian estuary. Technical Memorandum Report No. 42. Water Resources Research Center, University of Hawai'i, Honolulu.

MAGISTAD, O. C., and T. O. FRAZIER. 1938. Production and marketing of truck crops in the territory of Hawaii. Hawaii Agric. Exp. Stn. Bull. 78.

MCMURTRY, G. M., A. SNIDVONGS, and C. R. GLENN. 1995. Modeling sediment accumulation and soil erosion with ^{137}Cs and ^{210}Pb in the Ala Wai Canal and central Honolulu watershed, Hawai'i. Pac. Sci. 49:412–451.

NRIAGU, J. O. 1979. Topics in environmental health. Vol. 3. The biogeochemistry of mercury in the environment. Elsevier/North-Holland Biomedical Press, New York.

PICKARD, J. A., and J. T. MARTIN. 1960. Determination of mercury in plant material. J. Sci. Food Agric. 11:374–377.

SIEGEL, B. Z., and S. M. SIEGEL. 1978*a*. Mercury emission in Hawaii: Aerometric study of the Kalalua eruption of 1977. Environ. Sci. Technol. 12:1036–1039.

———. 1987. Hawaiian volcanoes and the biogeology of mercury. Pages 827–839 *in* R. W. Decker, T. L. Wright, and P. H. Stauffer, eds. Volcanism in Hawaii. U.S. Geol. Surv. Prof. Pap. 1350.

SIEGEL, S. M., and B. Z. SIEGEL. 1978*b*. Mercury fallout in Hawaii. Water Air Soil Pollut. 9:113–118.

SIEGEL, S. M., B. Z. SIEGEL, and G. M. MCMURTRY. 1980. Atmosphere-soil mercury distribution: The biotic factor. Water Air Soil Pollut. 13:109–112.

WATKINS, T. F., J. C. CACKETT, and R. G. HALL. 1968. Chemical warfare, pyrotechnics and the fireworks industry. Pergamon Press, New York.