

Records of Lead and Other Heavy Metal Inputs to Sediments of the Ala Wai Canal, O'ahu, Hawai'i¹

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ABSTRACT: In this paper we present depth profiles of selected transition metals and major constituents in four sediment cores recovered from the Ala Wai Canal, a small drainage estuary in Honolulu, Hawai'i. Our study documents the advent, increase in use, and subsequent phasing out of Pb-alkyl fuel additives in Honolulu over the past 60 yr. Sedimentary Pb concentrations increase from <10 ppm in the oldest (deepest) portions of the cores to a maximum of about 750 ppm in sediments corresponding to the mid-1970s; subsequently Pb contents decrease to a range of 100–300 ppm in the most recent deposits. Other metals, including Cd, Cu, and Zn, reveal patterns that are also consistent with an increasing flux of metals to the sediments attributable to anthropogenic inputs. However, unlike Pb, these metals do not exhibit clear maxima in sediments deposited during the mid-1970s. Rather, there appears to be a continued input of these metals from the watershed likely associated with ever-increasing anthropogenic activity in Honolulu. Approximately 25–75%, depending on the depth within the core, of the Cu and Zn contents of the sediments can be attributed to natural inputs of soils formed by weathering of the O'ahu volcanic edifices. Elements such as Co and Ni are found in concentration ranges consistent with the dominant mineralogy of the sediments and do not appear to exhibit an anthropogenic signal.

IN THIS PAPER we present results of a study of metal concentrations in sediments of the Ala Wai Canal, a small drainage estuary in Honolulu, Hawai'i (Figure 1). The Ala Wai Canal, which separates urban Honolulu from the resort area of Waikiki, was created in 1927 by the U.S. Corps of Engineers to provide drainage for runoff waters originating in residential valleys inland of Waikiki, to

provide (dredged) materials to fill wetlands, and to control mosquitoes through drainage and filling of the wetland.

The Ala Wai is an estuary subject to tidal flushing and exhibits a classical "type A" salt wedge structure. During the rising tide, a bottom current carries water from the sea and harbor area into the upper reaches of the canal (Hans Krock, pers. comm., 1992). Several streams (Makiki, Mānoa, and Pālolo) and numerous street drainage culverts run directly into the Ala Wai. Mānoa and Pālolo Streams are the major contributors of freshwater and join in a smaller drainage canal approximately 1.5 km above their confluence with the Ala Wai (Figure 1).

Since its opening in 1927, the Ala Wai Canal has been dredged periodically between the Mānoa-Pālolo input and the Kalākaua Avenue bridge to remove sediments that accumulate from the erosion of the Ko'olau range. Hence, some of the historical record has been removed from that portion of the

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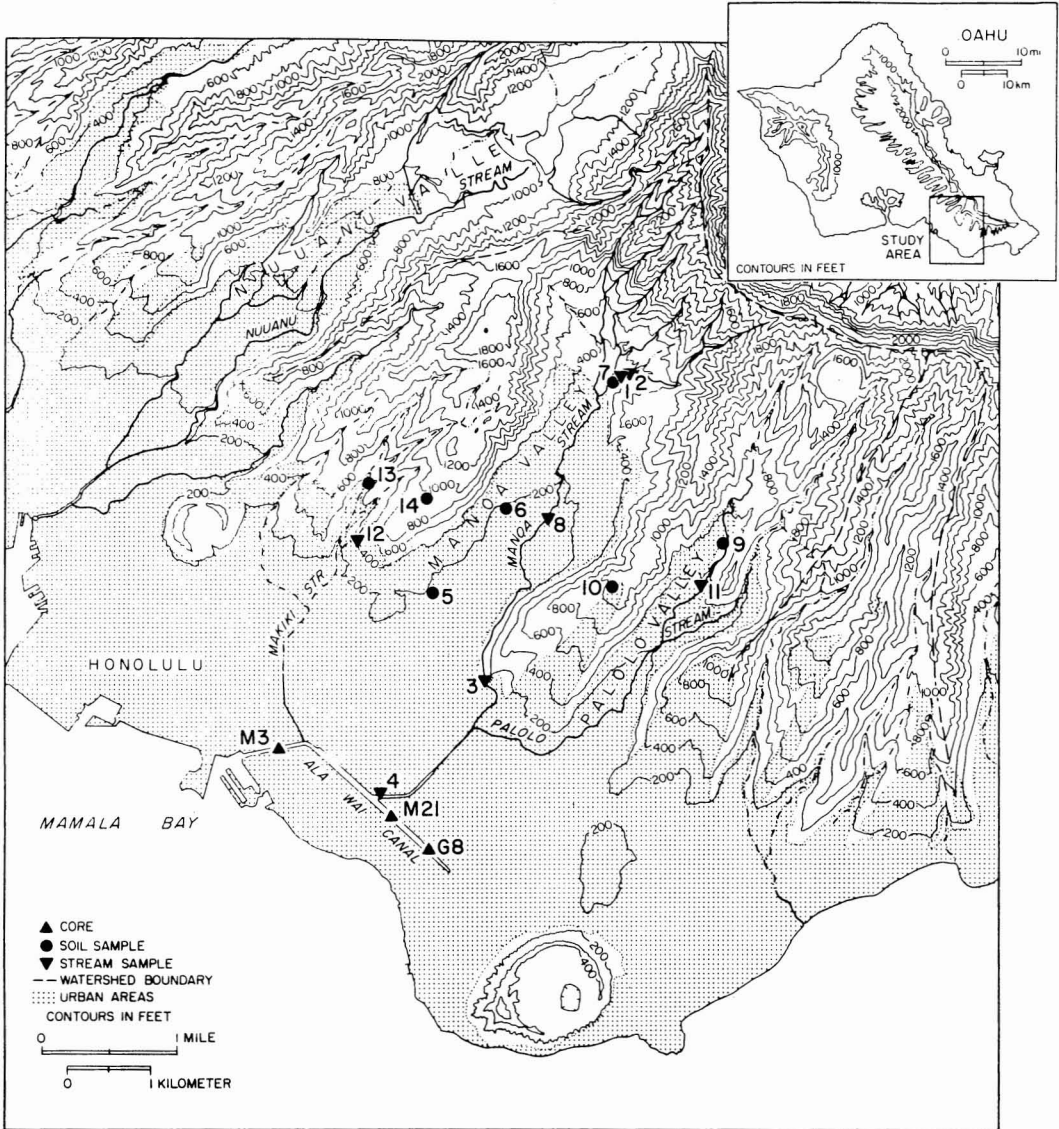


FIGURE 1. Site location map of Honolulu showing the Ala Wai Canal and its watershed, including Mānoa Valley, Pāloalo Valley, and Nu'uuanu Valley. Core collection sites and stream sediment sampling locations are also indicated.

canal. The last dredging of the canal occurred in 1978. A description of the Ala Wai was given by Laws et al. (1993).

Metals and the Environment

Industrialization and urbanization during the nineteenth and twentieth centuries have

led to major increases in fluxes of heavy metals to the environment that greatly exceed preindustrial natural inputs. Metal production and coal burning operations during the late nineteenth century and the early twentieth century composed two major sources of metal released to the atmosphere, rivers, and lakes. However, only a small contribution

from those latter sources reached Hawai'i by atmospheric transport of aerosols (Patterson and Settle 1987a).

Between 1940 and 1975 a major portion of anthropogenic Pb input to the atmosphere could be attributed to lead-alkyl fuel additives first introduced in 1923 (Chow and Earl 1972). For example, during 1971 approximately 450 metric tons of Pb were released to the Hawaiian environment from the use of leaded gasoline (Eshleman 1973). Although many industrialized nations are now phasing out leaded gasoline, it is still used extensively in developing nations. Lead is also released to the world's atmosphere from iron smelting (50,000 metric tons/yr); copper, zinc, and lead smelting (50,000 metric tons/yr); and from burning of coal (15,000 metric tons/yr) (Patterson and Settle 1987a).

A wide variety of potential pollutants are retained strongly by metal oxides because of their high particle reactivity (e.g., Santschi et al. 1984). The rate and extent of sorption onto solid phases has been evaluated in laboratory and field studies of metals such as Pb (Hayes and Leckie 1986, Erel et al. 1990); Cd, Cr, and Hg (Amacher et al. 1986, 1988, 1990, Selim et al. 1989); and the rare earth elements (Koeppenkastrop and De Carlo 1992, 1993). However, low pH conditions or the presence of alternative ligands can lead to a subsequent release of the metals to solution.

It would be expected that concentrations of heavy metals in sediments and soils could be used to evaluate temporal variations in metal fluxes from adjoining land areas. However, because sorption processes typically concentrate metals within the upper few centimeters of soils, the resulting integrated contaminant flux cannot be resolved chronologically and is difficult to interpret (Erel et al. 1990). In contrast, when freshwater runoff reaches saline waters in estuaries, colloidal matter flocculates and begins to settle along with its adsorbed metal load. Flocculation of colloidal organic matter with increased salinity further enhances metal removal (e.g., Sholkovitz 1976). Thus species scavenged by suspended particles that accumulate sequentially in aquatic sediments, such as those of the Ala Wai Canal, can provide potentially

resolvable records of metal inputs not available from soil horizons.

The extremely rapid removal of metals by suspended matter upon entering estuarine waters has been documented recently by Bricker (1992), who showed that metal concentrations in upper Narragansett Bay sediments are highest close to the primary point sources of contamination. It should be borne in mind, however, that particle dynamics lead to multiple episodes of resuspension and gravity settling before elements scavenged by particles are finally immobilized within the sediments (Olsen et al. 1982).

Because of high orographic rainfall and extensive land use, sedimentation in the Ala Wai is rapid and ranges between 1 and 4 cm/yr (Laws et al. 1993, McMurtry et al. 1995). Elevated accumulation rates often lead to anoxic conditions that minimize mixing by bioturbation and, hence, enhance preservation of the chronology of the sediments. In the highly sedimented Ala Wai the anoxic and unbioturbated sediments provide a historical record of metal pollution in urban Honolulu.

MATERIALS AND METHODS

To obtain the best possible stratigraphic records, cores were collected from sites we believed not to have been subject to major sedimentary disturbances, such as dredging or bioturbation. Cores were obtained by manually driving 5-cm-diameter, 7-m-long, plastic core-liners (as used by the Ocean Drilling Program) into the sediments from a small boat. The top of the core barrel was capped to create a vacuum before the core was pulled from the sediment. The bottom of the core-liner was capped immediately before the core was lifted out of the water. Excess water trapped in the core-liner was drained through precut drainage holes located a few centimeters above the sediment-water interface, excess liner was removed, and the core was sealed. Cores were transported upright and refrigerated until processed. The cores were sawed longitudinally to expose the

entire stratigraphic sequence and to allow examination and sediment description.

Sediment samples were taken every 2–4 cm downcore from four cores, labeled G8, G8B, M21, and M3 (Figure 1), paying particular attention not to collect matter in contact with the core-liner or the saw blade. Samples were homogenized, sieved, and freeze-dried. Subsequent sample handling was conducted in Class-100 clean benches to minimize contamination.

Approximately 400-mg subsamples were weighed to the nearest 0.1 mg and placed in Teflon digestion vessels. Decomposition was achieved by digestion in a microwave oven using 15 ml aqua regia (2 : 1 HNO₃ : HCl) (core G8) or a mixture of 15 ml aqua regia and 3 ml HF (cores G8B, M21, M3). Duplicate digestions were performed approximately every eighth sample. Acid/procedural blanks were processed in an analogous fashion. NIST (NBS-1645 river sediment) and NRC Canada (MESS-1 marine estuarine sediment) standard reference materials (SRM)

were carried through all analytical procedures to assess metal recovery during the digestion procedure and to provide quality control and assurance during analysis. Analysis of the SRM samples indicated that complete digestion of the sediments was achieved and recovery of analytes of interest was effected to better than 5% relative except for Al, Ca, Co, Ni, and Si (better than 10% relative).

Elemental analyses were performed by inductively coupled plasma optical emission spectroscopy (ICP/OES) on a Leeman Labs Plasma Spec I and by graphite furnace atomic absorption spectroscopy (GFAAS) on a Perkin-Elmer Model Z-5100PC for Cd and low abundance Pb samples. The accuracy of low-level Pb concentrations was verified by analysis of several samples on a VG sector mass spectrometer by isotope dilution (Spencer et al. 1995). Duplicates of three sediment samples collected in Mānoa Stream were also carried through all the above procedures.

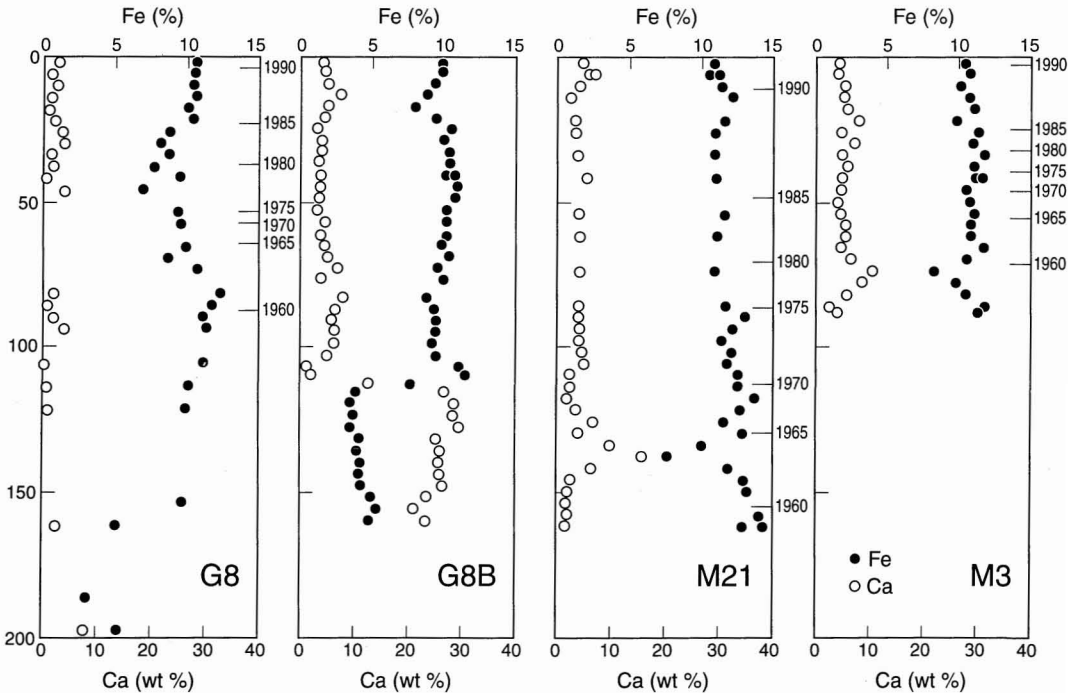


FIGURE 2. Plot of Fe and Ca concentrations on a percentage dry weight basis in Ala Wai sediment cores.

RESULTS

Four cores were analyzed in this study. Core G8 (200 cm) (Figure 1) and another collected close by (G8B, 160 cm) are believed to have penetrated the earliest canal sediments as evidenced by the occurrence of a zone of abundant CaCO_3 , believed to be of authigenic origin (Glenn et al. 1995), admixed with clay minerals in the bottom sections. The other two cores (M21 [164 cm] and M3 [95 cm]) did not sample the entire stratigraphic history of the canal but did penetrate sediments sufficiently to confirm several observations made on the first two cores.

Profiles of two major constituents (Ca and Fe) are presented in Figure 2, and elemental concentrations are given in Tables 1–4. These data complement mineralogical analyses of

the cores (Fan et al. 1995) that indicate that the sediments are composed largely of detrital volcanic minerals and their weathering products. Sediments contain various amounts of Al- and Fe-oxides, some Fe-sulfides, clay minerals, and other aluminosilicates of volcanic origin as well as (authigenic) CaCO_3 . The relative proportions of the various minerals are influenced by factors such as extent of orographic rainfall (transport of eroded soils during rainstorms) and the occurrence of plankton blooms within the canal (CaCO_3) (Glenn et al. 1995).

Differentiating between the natural and anthropogenic sources of trace metals can often be complicated by the large natural variability of trace metal concentrations in sediments arising from differences in lithology, mineralogy, grain size, and organic

TABLE 1
ELEMENTAL DATA FOR CORE G8, ALA WAI CANAL, O'AHU, HAWAII

DEPTH (cm)	Al	Fe	Si	Ca	Mg	Mn	Pb	Zn	Cu	Co	Ni
2	3.28	10.61	19.82	2.14	2,894	1,604	315	381	241	53.7	180
6	1.55	10.51	21.01	0.93	990	1,596	319	394	240	55.5	183
10	3.84	10.39	22.60	2.31	4,867	1,608	372	393	234	56.3	187
14	2.01	10.60	19.98	1.23	903	1,842	417	375	229	53.9	186
18	1.13	10.02	21.27	0.73	1,334	2,103	468	361	216	52.0	183
22	1.66	10.35	23.75	1.69	3,016	2,026	496	363	211	51.4	175
26	0.96	8.79	11.94	3.22	498	1,758	534	332	176	47.6	162
30	0.76	8.08	14.16	3.86	857	1,850	494	286	161	45.4	166
34	0.72	8.72	19.09	1.53	1,932	1,571	759	376	181	53.8	179
38	0.86	7.75	17.99	1.81	577	1,248	507	298	161	53.1	171
42	0.73	9.53	21.52	0.47	407	1,621	609	326	166	55.0	182
46	0.91	6.91	13.26	3.85	566	1,347	335	239	129	42.9	151
54	6.20	9.43					651	405	139	80.6	195
58	7.09	9.60					623	384	137	84.0	231
66	6.95	9.98					475	319	120	71.5	184
70	5.99	8.70					350	276	142	60.0	154
74	7.28	10.76					374	313	109	85.8	220
82	4.53	12.38	26.22	1.96	4,798	1,715	291	290	162	69.7	210
86	2.26	11.85	25.83	0.75	936	1,396	285	336	182	69.3	234
90	3.07	11.16					273	262	84	63.9	171
90	3.12	11.16	22.05	1.94	5,224	1,475	230	256	84	56.5	193
94	6.90	11.41	29.64	3.73	7,465	1,368	227	251	179	73.0	207
106	0.89	11.23	21.89	0.20	669	1,012	146	252	158	49.4	193
114	0.95	10.20	21.10	0.66	1,577	1,048	137	275	162	52.8	197
122	0.62	10.01	13.33	0.96	322	1,151	125	252	126	57.5	209
154	6.98	9.84					115	119		45.2	115
162	0.25	5.28	15.17	2.52	1,186	837	16	87	76	32.0	114
186	0.28	3.20					16	43		21.9	47
198	0.54	5.36	20.61	7.92	4,090	584	14	70	77	33.1	113

TABLE 2
ELEMENTAL DATA FOR CORE G8B, ALA WAI CANAL, O'AHU, HAWAII

DEPTH (cm)	Al	Fe	Si	Ca	Mg	Mn	Pb	Zn	Cd	Cu	Co	Ni
2	8.13	9.72	13.98	3.90	1.62	1,214	243	330	1.21	227	97	194
5	7.93	9.74	13.93	4.27	1.66	1,237	270	354	1.09	231	105	206
9	7.65	9.26	13.39	4.89	1.65	1,506	265	327	1.24	211	102	191
13	7.33	8.69	13.07	7.27	1.70	1,504	343	300	1.03	183	95	181
17	6.05	7.90	11.60	4.97	1.89	1,665	325	222	0.99	127	93	191
21	7.57	9.29	13.30	4.33	2.13	2,667	441	316	1.36	141	109	220
25	7.94	10.37	14.18	2.97	2.31	2,061	571	400	2.02	158	116	241
29	9.02	9.85	14.95	3.57	1.79	2,319	369	290	1.36	145	108	222
33	8.90	10.23	15.40	3.50	2.04	1,841	403	319	1.64	153	112	238
37	9.25	10.38	15.27	3.15	1.74	2,115	205	252	1.16	155	117	239
41	7.93	10.74	15.24	3.67	2.51	1,692	183	264	0.87	136	120	274
45	8.71	10.76	15.94	3.65	2.31	1,774	236	280	1.04	146	113	251
49	9.20	10.72	16.55	3.46	2.18	1,440	181	272	1.08	144	109	234
53	8.37	10.09	14.04	3.24	2.54	1,088	226	309	1.27	147	113	262
57	8.52	10.07	15.84	4.44	1.92	1,429	121	236	0.96	147	103	212
62	8.33	10.09	15.32	3.85	1.95	1,197	102	236	0.86	145	107	222
65	8.25	9.81	14.89	4.15	1.85	1,034	94	235	0.90	149	109	215
69	8.63	10.31	15.65	4.91	2.07	1,037	98	233	0.85	146	105	211
73	7.96	9.43	14.97	6.78	2.28	1,196	64	195	0.72	127	93	184
77	7.23	9.85	16.94	3.80	3.41	1,010	83	216	0.87	106	109	249
83	7.51	8.79	13.51	7.86	1.73	1,671	43	150	0.48	114	94	171
87	8.47	9.28	14.33	6.54	1.54	878	25	133	0.38	132	102	188
91	8.86	9.38	14.59	5.79	1.44	747	30	133	0.29	135	99	189
95	9.01	9.35	14.35	6.16	1.41	633	22	129	0.28	130	103	185
99	9.05	9.22	15.31	6.20	1.43	736	26	129	0.29	125	96	180
103	8.79	9.44	14.69	5.16	1.32	531	19	121	0.19	116	94	176
107	11.13	11.01	17.75	1.32	1.04	433	15	132	0.26	148	120	216
110	10.05	11.36	16.34	1.83	0.96	410	14	111	0.3	138	110	211
110	10.36	11.50	16.64	1.73	0.94	445	14	122	0.32	138	116	220
113	6.79	7.73	11.90	12.78	1.55	895						
116	3.87	3.91	6.11	26.64	2.15	564	4	43	0.15	51	37	70
116							7	46		53	37	72
120	3.59	3.57	6.05	28.55	2.08	525	4	39	0.12	51	37	65
124	3.73	3.69	5.94	28.34	2.01	440	3	40	0.09	55	39	71
128	3.68	3.58	5.65	29.51	2.04	410	3	37	0.10	53	37	67
132	4.07	4.14	6.48	25.30	2.08	526	5	45	0.10	63	46	80
136	3.99	4.04	6.19	25.91	2.05	535	6	44	0.10	62	46	81
140	4.09	4.19	6.19	25.70	2.05	570	5	47	0.08	63	49	87
144	4.00	4.14	6.08	25.98	2.06	566	3	35	0.08	56	47	83
144							4	48		63	43	88
148	4.24	4.29	6.39	26.44	2.13	639	1	37	0.14	58	49	84
148							3	48		64	44	87
152	4.74	4.96	7.48	23.49	1.96	536	4	59	0.17	73	52	106
156	5.16	5.34	8.31	21.15	1.97	542	5	62	0.15	76	54	115
160	4.68	4.92	7.53	23.32	2.01	498	7	61	0.15	71	52	109
160	4.68	4.86	7.43	23.38	2.03	505	8	61	0.19	72	52	107

matter content. Carbonate sediments, for example, are well known to exhibit lower trace metal contents than Fe- and clay-rich sediments (Turekian and Wedepohl 1961).

Such differences in composition owing to lithological (and mineralogical) control arise in the Ala Wai where CaCO₃-rich zones within the sediments (Figure 2) typically are

TABLE 3
ELEMENTAL DATA FOR CORE M21, ALA WAI CANAL, O'AHU, HAWAII

DEPTH (cm)	Al	Fe	Si	Ca	Mg	Mn	Pb	Zn	Cd	Cu	Co	Ni
2	9.03	10.97	14.64	4.55	1.76	933	116	279	1.39	202	108	188
6	8.77	10.81	13.01	5.81	1.85	959	124	265	1.02	201	106	177
6	8.87	11.37	13.41	6.07	1.92	934	118	269	1.09	202	100	175
10	9.28	11.37	14.03	3.94	1.81	995	145	295	0.83	213	114	204
14	9.95	12.09	15.05	2.44	1.75	566	119	260	1.04		99	164
22	9.95	11.93	15.25	3.04	1.87	740	227	333	1.50	227	107	193
26	9.49	11.32	14.54	3.40	1.83	723	270	348	1.98	235	104	184
34	9.23	11.32	14.33	3.88	1.87	686	235	312	1.89	217	82	161
42	9.03	11.37	12.65	5.36	1.99	804	326	353	1.69	213	105	184
42	9.03	11.37	12.65	5.36	1.99	791	324	354		208	81	181
54	9.23	12.04	14.54	4.09	2.03	808	410	356	1.71	201	113	195
54	9.23	12.04	14.54	4.09	2.03	859	426	362		214	114	218
54						838	420	359		204	95	208
62	9.28	11.53	14.64	4.25	1.86	997	458	354	1.26	204	114	214
62	9.28	11.53	14.64	4.25	1.86	973	439	338		198	110	203
74	9.18	10.86	14.69	4.06	1.80	1,070	427	313	1.30	188	113	198
86	9.95	11.83	15.05	4.05	1.73	1,100	242	238	1.44	179	119	199
86	9.95	11.83	15.05	4.05	1.73	1,150	263	274		172	117	203
90	10.66	13.77	16.22	3.76	1.75	1,090	208	260	0.94	168	126	222
94	10.25	12.19	15.56	4.20	1.71	1,020	148	206	0.82	165	132	221
94	10.25	12.19	15.56	4.20	1.71	1,050	158	222		163	131	225
98	9.95	11.68	15.15	4.36	1.60	1,220	196	245	1.07	154	118	203
102	10.40	12.19	16.01	4.34	1.68	1,340	202	245	0.97	173	131	225
106	10.10	12.04	15.71	4.98	1.78	1,600	172	236	0.94	176	133	223
106	10.00	11.93	15.30	4.89	1.75	1,560	168	233	0.75	176	131	221
110	11.32	12.75	16.32	2.46	1.40	1,030	111	199	0.67	153	129	232
110	11.22	12.65	16.12	2.45	1.38	924	107	194	0.71	133	116	210
114	11.37	12.60	16.58	2.63	2.87	1,410	143	212	0.76	174	133	240
118	11.32	13.92	15.71	1.92	1.36	1,110	98	196	0.66	168	141	248
122	11.02	13.06	15.20	3.45	1.35	1,080	105	189	0.65	164	127	235
126	10.25	11.73	13.97	6.58	1.49	1,300	99	172	0.50	151	117	208
130	11.12	13.06	14.69	4.00	1.39	1,040	131	186	0.72	167	130	234
134	9.13	10.20	12.75	9.64	1.54	1,120	96	151	0.56	129	103	182
138	6.78	7.85	9.95	16.63	1.82	861	68	124	0.41	105	81	140
138	6.83	8.06	9.84	16.63	1.85	844	67	121	0.40	105	82	138
142	9.89	11.99	13.67	6.53	1.56	1,090	56	169	0.42	154	129	222
146	11.22	13.21	16.12	2.61	1.36	1,180	200	149	0.89	176	141	243
150	11.48	13.41	16.27	2.03	1.37	1,270	134	223	0.69	165	103	248
154	12.60	17.54	18.41	1.80	1.55	1,060	136	226	1.15	162	104	255
158	12.39	14.33	17.08	2.07	1.42	1,580	91	216	0.18	177	113	277
162	11.07	13.16	15.30	1.72	1.26	1,420	80	202	0.59	157	103	264
162	12.29	14.69	16.93	1.90	1.40	1,330	82	205	0.60	140	106	251

characterized by lower concentrations of Pb, Zn, Cd, and Cu (Tables 1–4).

Elucidation of sources contributing to the metal contents of sediments often requires normalization to a reference element such as Al (Schropp et al. 1990). This can be particularly useful when comparing sediments on a regional basis or those exhibiting substantial

mineralogical variations, and thus assessing whether metal concentrations result from anthropogenic or natural causes. Because samples from core G8 were digested only in HCl:HNO₃, the amount of refractory aluminosilicates that were solubilized varied. Hence, normalization of the trace metal data to Al could not be performed for this core.

TABLE 4
ELEMENTAL DATA FOR CORE M3, ALA WAI CANAL, O'AHU, HAWAII

DEPTH (cm)	Al	Fe	Si	Ca	Mg	Mn	Pb	Zn	Cu	Co	Ni
2	7.63	10.43	11.99	3.75	2.00	382	173	421	230	119	216
6	8.06	10.79	12.47	3.95	2.11	704	174	415	247	118	214
10	7.24	10.15	11.33	5.22	2.14	661	176	383	222	112	206
14	6.91	10.65	11.39	4.98	2.97	725	244	412	216	115	234
14	6.96	10.74	11.47	5.06	3.13	734	228	405	214	117	238
18	6.96	11.06	12.11	5.46	3.60	735	288	395	200	115	250
22	6.20	9.84	10.73	7.61	3.62	725	336	398	154	112	244
26	7.77	11.37	13.16	4.49	3.46	717	204	311	157	138	311
30	7.29	11.01	12.11	6.88	3.79	719	189	267	140	126	308
34	7.72	11.82	13.17	4.65	3.82	684	188	276	149	136	340
38	7.39	11.10	11.58	5.50	3.76	678	443	327	142	128	301
42	8.34	11.64	13.16	4.78	3.07	718	514	325	150	134	281
42	7.63	11.19	12.43	4.78	3.57	733	538	305	150	130	293
46	8.39	10.56	12.35	4.41	1.95	661	267	305	155	128	246
50	9.25	10.83	12.84	3.83	1.60	593	247	333	190	132	249
54	9.15	11.10	12.41	4.41	1.72	607	195	306	182	130	246
58	9.10	10.88	12.02	5.34	1.76	602	171	295	191	125	232
62	8.34	10.88	11.91	5.30	1.87	576	179	314	169	122	230
66	9.01	11.78	13.20	4.45	1.90	575	157	279	162	128	237
70	7.48	10.61	11.55	6.40	2.17	608	231	341	154	110	201
74	6.43	8.21	9.56	10.48	0.64	552	116	253	143	94	175
78	6.91	9.84	10.49	8.46	2.38	575	159	273	129	107	213
78	7.29	9.84	10.68	8.38	2.36	584	110	272	123	107	226
82	8.77	10.52	12.21	5.38	1.78	501	74	233	152	115	224
86	10.01	11.78	13.88	2.23	1.40	506	53	226	163	131	251
88	8.58	11.37	12.84	3.63	1.86	599	125	318	166	122	221
88	8.58	11.37	12.72	3.66	1.85	598	132	311	166	118	219

For the sake of uniformity we chose, instead, to normalize to the Fe content of all cores. This process smooths out equally well the variations caused by the mineralogical changes reflected in the Ca and Fe data in Figure 2. Because it could be argued that normalization to Fe might not be valid owing to potential remobilization or other transformations that might affect the Fe content of the sediments, we show in Figure 3 a plot of Fe versus Al for all samples from the three cores subjected to total dissolution. The good linear relationship ($R^2 = 0.84$, $n = 107$) suggests that Fe can indeed be used as a proxy for Al, and hence as a normalizing element. Fe in the Hawaiian environment is primarily converted to rather immobile clay minerals and Fe oxides upon weathering of the primary volcanic minerals and soil formation. The close relationship between Fe and Al

also indicates that sediments of the Ala Wai Canal consist primarily of eroded soils.

Trace element profiles for Pb, Zn, Cd, Cu, and Mn are shown in Figures 4–8. Trace metal concentrations were normalized to Fe except for Mn. Each core generally exhibits increased metal abundances in the upper (younger) sediments relative to deeper (older) sediments. Cobalt (Figure 9) does not display strong temporal trends (except an artificial trend in core G8 resulting from a variable extent of dissolution of aluminosilicates), suggesting that there has been little systematic change in its flux to the canal over time. Nickel profiles (Figure 10) are also generally devoid of trends except in Core M3. The chronology of three of the Ala Wai sediment cores, based on ^{210}Pb and ^{137}Cs chronology (McMurtry et al. 1995), is superimposed on the metal profiles shown in Figures 4–10.

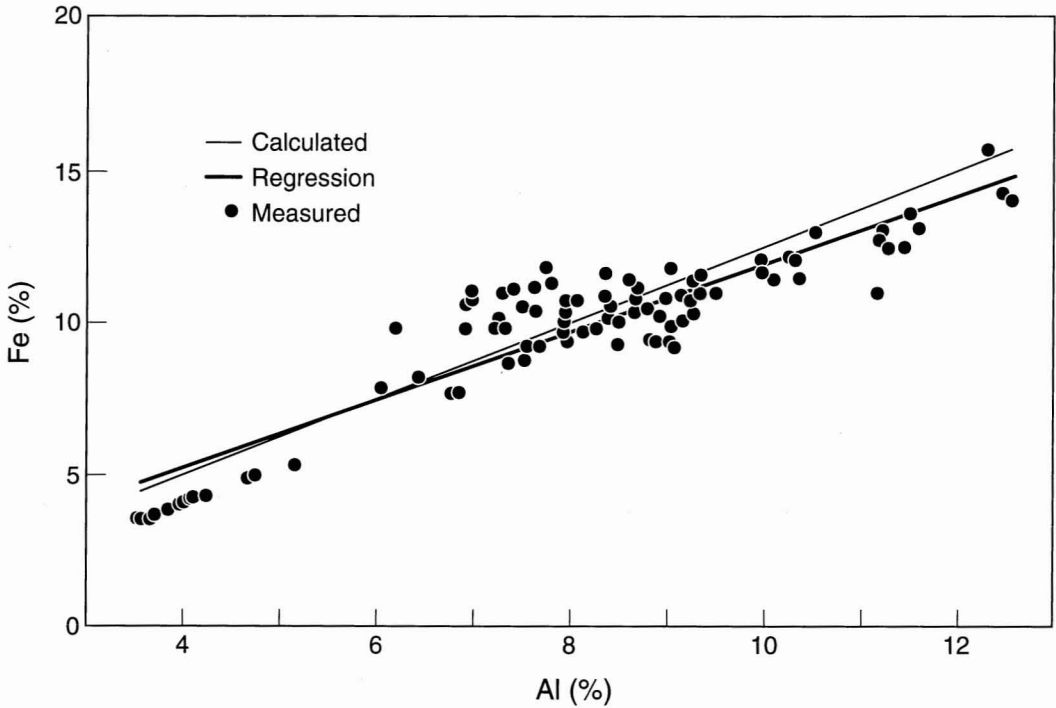


FIGURE 3. Plot of Fe (wt %) versus Al (wt %) for cores G8B, M21, and M3 ($n = 107$). The calculated line represents Fe concentrations calculated from measured Al data and assuming an Fe/Al ratio from tholeiitic basalt. $R^2 = 0.84$ for the regression line of the experimental data.

Elemental abundances for sediment samples collected in Mānoa Stream are given in Table 5.

DISCUSSION

Concentrations of metals in rapidly depositing sediments have been used previously to evaluate temporal variations in metal fluxes to both fresh and saline waters (Bruland et al. 1974, Goldberg et al. 1977, 1978, 1979, McCaffrey and Thomson 1980, Evans and Dillon 1982, Elbaz-Poulichet et al. 1984, Windom et al. 1984, Trefry et al. 1985, Stoffers et al. 1986, Schropp et al. 1990, Bricker 1992). Metal contamination of inland waters and estuarine and coastal sediments generally results either from anthropogenic activity in the immediately adjacent areas and in watersheds feeding these areas or from deposition of contaminated aerosols trans-

ported over long distances (Patterson and Settle 1987b). In remote island environments, far from major industrial sources, the latter is deemed to be more important and contributes to elevated metal baselines.

The island of O'ahu, Hawai'i, has experienced extensive growth since the 1950s that has significantly impacted the local environment. The other islands of Hawai'i have not been the foci of such accelerated development. Jernigan (1969) conducted a study of Pb pollution in Hawaiian aerosols, and Eshleman (1973) subsequently surveyed Pb and Hg and, to a lesser extent, Cu and Zn in the Hawaiian environment. Extreme Pb contamination has also been observed in Kāne'ohe Bay behind the U.S. Marine Corps Air Station firing range, where large quantities of Pb pellets rest on the reef (A. Lincoff, U.S. EPA, pers. comm., 1990).

Among the various studies that have documented historical heavy metal contamination

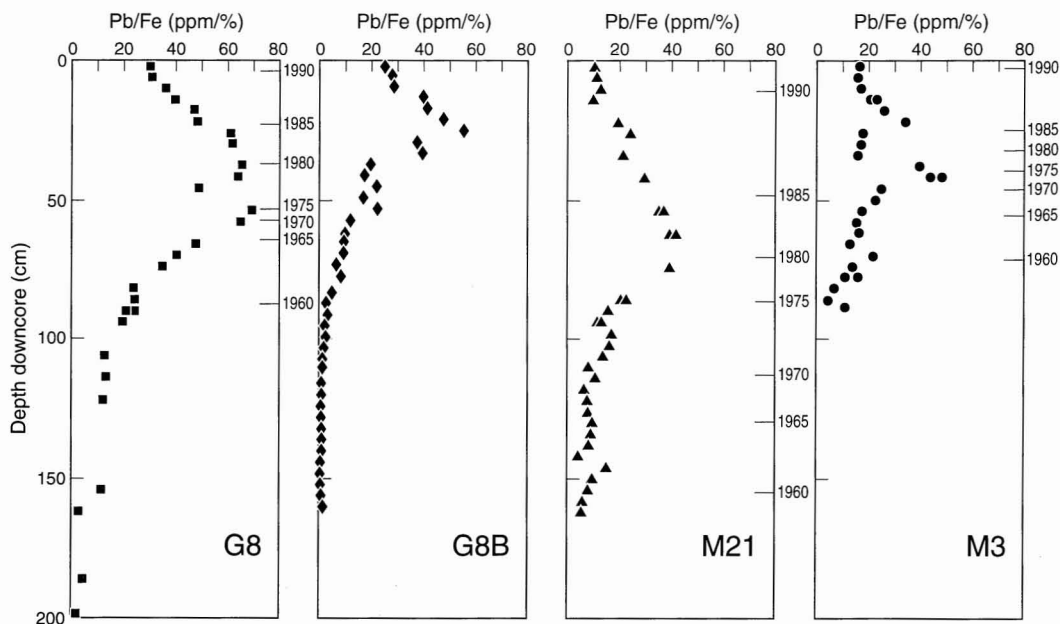


FIGURE 4. Plot of Pb/Fe ratio on a dry weight basis in Ala Wai sediment cores. Radioisotope chronology from McMurtry et al. (1995).

of aquatic sediments, those conducted since 1980 indicate that environmental awareness over the past two decades and ensuing legislation have led to measurable reductions in anthropogenic metal emissions. Indeed, Pb profiles shown in Figure 4 clearly demonstrate the beneficial effect of national legislation on metal inputs to the Hawaiian environment. A Pb background of 5–10 ppm is evident in pre-canal sediments (bottoms of cores G8 and G8B) followed by a small increase in Pb during the 1950s. This is followed by a dramatic rise in the 1960s to a maximum of ~750 ppm (in core G8) in late 1970s to early 1980s sediments. Subsequently, Pb concentrations decrease by up to a factor of three in the most recently deposited sediments (top of cores). Each of the Ala Wai cores exhibits similar trends although absolute concentrations vary in part because of differences in accumulation rates. In core M3 the maximum appears to occur during the early rather than late 1970s, but this may be an artifact resulting from a large pulse of (relatively Pb-free) aluminosilicate-rich sedi-

ment around 1979–1981 (see discussion on Ni below). We are thus able to correlate sedimentary Pb profiles in the Ala Wai with the advent, increased use (owing to increased traffic density resulting from growth), and subsequent phasing out of leaded alkyl fuel additives in Hawai'i.

In our study of the Ala Wai Canal sediments, it has been possible to differentiate between natural and anthropogenic Pb contributions on the basis of concentrations because natural abundances in Hawai'i rarely exceed 25–40 ppm and are much lower in most cases. For example, in a baseline study of metal concentrations conducted in relatively uncontaminated soils of the island of Hawai'i, Halbig et al. (1985) observed a range of 1.5–17.5 ppm Pb (the highest values were observed in urban Hilo) that was easily removed by treatment with 0.5 N HCl. The fraction of soils solubilized by this treatment is limited primarily to carbonates and Al- and Fe-oxides, but the latter constituents likely contain the majority of the Pb bound to soils. However, the differences that exist

between soils and sediments and the fact that the island of Hawai'i has generally been less weathered than O'ahu can significantly alter the baseline Pb concentrations to be expected in sediments.

Stable isotopic signatures of Nd, Pb, and Sr, discussed elsewhere (Spencer et al. 1995), further constrain the sources of Pb and suggest that the overwhelming majority of the Pb in Ala Wai cores can be attributed to anthropogenic activity, likely automotive use. That Pb concentration profiles (Figure 4) are consistent with automotive sources is evidenced by a temporal correlation with the use of lead-alkyls in gasoline. Growth of auto traffic in Honolulu from 1950 to 1975 led to an increase in the Pb abundance from under 100 ppm to approximately 750 ppm. The 1975 legislation phasing out leaded fuels is then reflected in a decrease in concentration to 100–300 ppm Pb near the sediment-water interface. The notable failure to return to preanthropogenic levels of Pb in current-day sediments can be attributed partly to a continued input of Pb from previously contaminated soils that are mobilized during land excavation and development. Remobilized roadside soils, which contain up to several thousand ppm Pb (Eshleman 1973), are likely an important source of current-day Pb fluxes to the canal sediments.

The stream sediment data shown in Table 5 further attest to a continued input of anthropogenic Pb to the canal. Lead concentrations increase from 14 ppm at the head of Mānoa Valley to 32 ppm within the residential area in the middle of the valley and reach 231 ppm in sediments collected near the University of Hawai'i (U.H.). Continued Pb contamination from Mānoa Valley in the form of transported contaminated soils probably contributes to this progressive Pb increase downstream, but culverts draining highly traveled Dole Street near the U.H. are more likely responsible for transporting a large proportion of (automotive) Pb bound to roadside soils.

Peak Pb concentrations in sediments from the Ala Wai Canal (Table 6) are similar to those in Biscayne Bay (Schropp et al. 1990) and upper Narragansett Bay (Bricker

TABLE 5
COMPOSITION OF MĀNOA STREAM SEDIMENTS

SAMPLE	92-2		92-8		92-3	
	AVG.	SD	AVG.	SD	AVG.	SD
Al ^a	10.35	0.19	12.67	0.08	10.28	0.22
Si	10.23	0.25	15.06	0.11	15.66	0.71
Fe	12.00	0.20	13.81	0.00	11.87	0.32
Ca	0.740	0.028	0.84	0.00	2.04	0.06
Mg	0.972	0.018	0.620	0.004	1.72	0.04
Mn ^b	601	4.2	1,740	71	1,785	71
Sr	1,510	57	1,990	15	4,540	113
Pb ^c	14		32		231	2
Zn	228	4	262	14	454	6
Cu	146	2	186	5	298	4
Co	153	2	156	7	150	0
Ni	337	3	342	8	286	2

^aMajor element concentrations expressed in dry weight percentage.

^bTrace element concentrations expressed in mg/kg (ppm).

^cLead data for samples 92-2 and 92-8 obtained by solid source mass spectrometry (SSMS); Pb data for sample 92-3 are average of inductively coupled plasma/optical emission spectroscopy (ICP/OES) and SSMS.

1992), but are approximately one order of magnitude greater than in Mississippi delta sediments (Trefry et al. 1985). The lower concentrations observed by Trefry et al. likely result from the higher sediment loads of the Mississippi River and its more extensive drainage of agricultural rather than urbanized land. Concentrations of Pb in the Ala Wai cores are also an order of magnitude greater than observed by Goldberg et al. (1978) in Chesapeake Bay. No distinct Pb peak was observed in the latter study because it preceded the 1975 legislation controlling lead-alkyl use. Other contaminated sediments such as those from the Houston ship channel (Trefry and Presley 1976) and areas of Wellington Harbour near point sources of contamination (Table 6) contain similar and up to an order of magnitude greater concentrations of Pb, respectively. To the best of our knowledge, there currently are no data from tropical island environments. However, relatively uncontaminated sediments from the Gulf of Thailand (Table 6), another subtropical environment, provide some basis for comparison (Windom et al. 1984).

Another element likely to exhibit an an-

TABLE 6
COMPARISON OF SELECTED HEAVY METAL CONCENTRATIONS IN ESTUARINE WATERS

AREA OR CORE		RANGE OF CONCENTRATIONS (ppm)					
		Pb	Zn	Cd	Cu	Co	Ni
G8	Range	3.6-759	43-405	—	77-210	22-85	47-234
	Sediment surface	315	381	—	210	54	180
	Depth of max ^a	34	54	—	2	74	86
G8B	Range	3.5-571	35-400	0.08-2.2	51-231	37-120	65-274
	Sediment surface	243	330	1.2	227	97	194
	Depth of max	25	25	25	5	41	41
M21	Range	56-458	121-362	0.18-2.0	105-235	81-133	138-277
	Sediment surface	116	279	1.4	202	108	188
	Depth of max	62	54	26	26	106	158
M3	Range	53-514	226-421	—	123-230	94-138	175-340
	Sediment surface	173	421	—	230	119	216
	Depth of max	42	2	—	2	26	34
Narragansett Bay ^b							
	Sediments	585	160	—	506	—	—
	Suspended matter	446	—	—	655	—	—
Miami River and Biscayne Bay ^c		500-600	500	3.5	300	—	10
Galveston Bay ^d		5-50	9.8-141	0.2-4.9	4-96	—	0.6-58
Houston ship channel ^d		30-268	74-622	0.1-10.7	17-157	—	15-63
Gulf of Thailand ^e		8.6	—	0.025	31	15	38
Wellington Harbour ^f							
	Pencarrow Sewer Outfall	47-6,740	105-2,270	—	15-216	—	13-82
	Harbour basin	44-232	120-165	—	19-22	—	17-22

^aDepth (in cm) downcore at which maximum metal concentration occurs.

^bMetal values in cores are quoted for top 1 cm of sediments (Bricker 1992).

^cSchropp et al. (1990); maximum metal values approximated from figures.

^dTrefry and Presley (1976); range of acid leachable metal concentrations.

^eWindom et al. (1984); metal values in essentially uncontaminated sediments.

^fStoffers et al. (1986); ranges of metal values are given for cores from the most contaminated area and from the central harbor basin, away from point sources.

thropogenic signal related to automotive use is Zn. The most probable source of this metal is through wear of automobile tires, because Zn is widely used in the vulcanization of rubber. Batteries, galvanized pipes, garbage cans, and air-conditioning ducts could all contribute to the flux of anthropogenic Zn, but these materials are much less prone to the extensive wear typical of tires and, hence, should release proportionally less Zn to the environment.

Concentrations of Zn typically reach a maximum of about 300-400 ppm near the sediment-water interface of the cores (Tables 1-4) except in core M21. This core experienced coring disturbances during collection that may have affected the top 15-20 cm of the sediment. We hypothesize that a significant fraction of the Zn in Ala Wai sedi-

ments is of anthropogenic origin and originates from road runoff. The low baseline concentrations (about 50 ppm in CaCO₃-rich sediments and about 100 ppm in Fe- and Al-rich sediments) near the bottom of the cores, which presumably are representative of relatively uncontaminated material, are consistent with this hypothesis. Furthermore, the large increases in Zn contents occur in post-1950 sediments in all cores and generally coincide with those of Pb. However, unlike Pb, Zn concentrations do not decrease after 1975.

Examination of the Mānoa Stream sediment data (Table 5) also reveals an increase in the Zn content of the sediments from near 230 ppm at the head of the valley to 460 ppm at the mouth of the valley. Halbig et al. (1985) reported a range of 80-200 ppm Zn

in Big Island soils, with one sample, possibly an alkalic rock matrix, containing 380 ppm Zn. Kabata-Pendias and Pendias (1984) reported a range of only 30–110 ppm in soils over volcanic rocks, but their data may reflect a dilutionary effect from organic matter. Roden et al. (1984) reported approximately 100 and 200 ppm Zn in Ko'olau tholeiites and Honolulu volcanics, respectively. Based on these data it appears that at least 50% and up to 75% of the peak Zn concentrations may result from anthropogenic activity. A lack of a significant difference between the G8 sediment samples, which were digested only with aqua regia, and samples from the other three cores suggests that more of the Zn in Ala Wai Canal sediments is associated with carbonates and Fe- and Al-oxides than is mineralogically bound to refractory aluminosilicates.

Because of generally low Cd abundances of 0.1–0.3 ppm in the natural (uncontaminated) environment (Kabata-Pendias and Pendias 1984), this element can be difficult to determine even in sediments exhibiting 5- to

10-fold excess anthropogenic contributions. Cd was analyzed only in cores G8B and M21 using GFAAS. Results revealed that Ala Wai sediments are also contaminated with Cd (Figure 6) although not extensively. Within the bottom CaCO_3 -rich sediments, Cd contents are in the 0.1–0.2 ppm range (Table 2) and approximately 0.3 ppm in the bottom-most Fe- and Al-rich sediments (Tables 2 and 3). Concentrations then increase to a peak of 2 ppm and return to a range between 1 and 1.5 ppm in the near-surface sediments. Although histosols and other organic-rich soils can contain as much as 1.2 ppm Cd (Kabata-Pendias and Pendias 1984), we believe that the Cd peaks observed here, which are coincident with the Pb (Figure 4) and Zn (Figure 5) peaks in core G8B, but occur in slightly more recent sediments in core M21, represent anthropogenic inputs. The peak coincidence between these three elements in core G8B suggests an association of Cd with automobile traffic, although the Cd enrichment may simply reflect overall development in Hawai'i accompanied by increased auto-

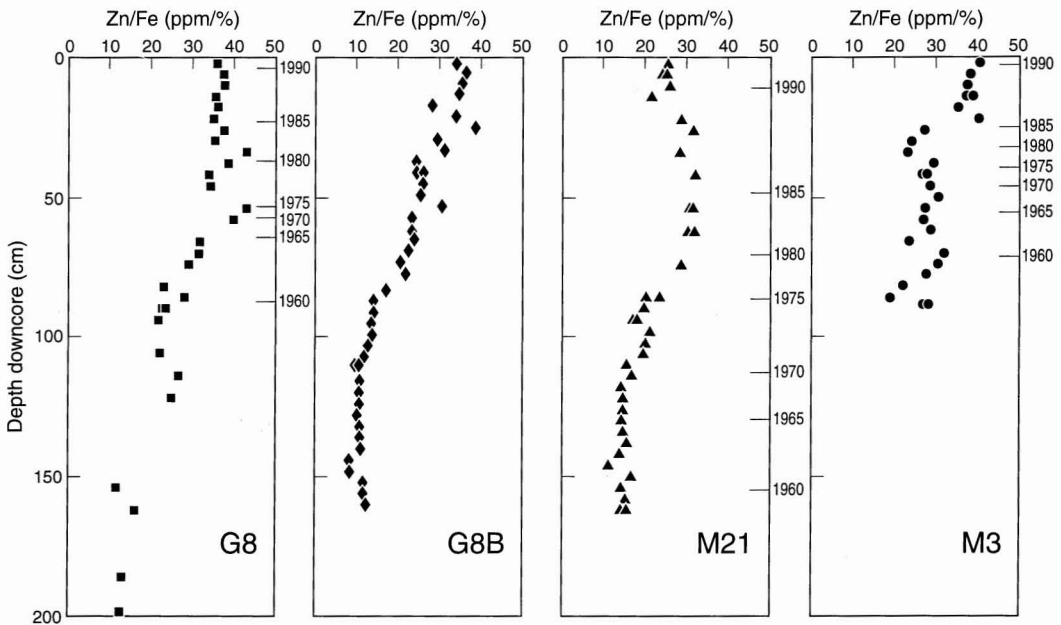


FIGURE 5. Plot of Zn/Fe ratio on a dry weight basis in Ala Wai sediment cores. Radioisotope chronology from McMurtry et al. (1995).

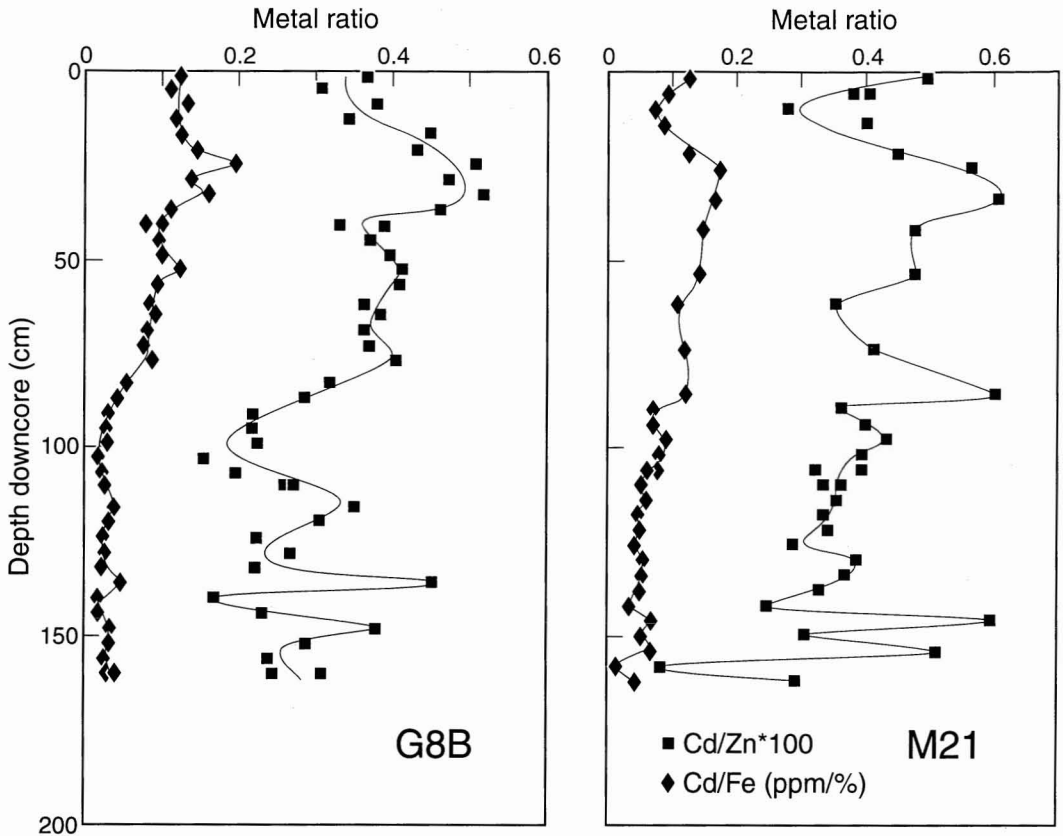


FIGURE 6. Plot of Cd/Fe and the Cd/Zn ratios on a dry weight basis in Ala Wai sediment cores G8B and M21.

mobile traffic. A plot of the Cd/Zn ratio for both cores, also shown in Figure 6, reveals significant fluctuations (a 5-fold change between minimum and maximum values). A slight increase in the Cd/Zn ratio is noted from the bottom of the Fe-rich zone through the top of core G8B, whereas in core M21 this trend is not as pronounced. Because of the well-known association of Cd with Zn-rich matter, we propose that a portion of the Cd input to the canal is derived from automobile tire wear. However, significant variations in the Cd/Zn ratio in both cores (particularly in CaCO_3 -rich zones) suggest that other uncorrelated sources of these elements also contributed to the observed elemental abundances. This is particularly evident in sections of the cores believed to represent

pre-World War II sediments, and the sources of Cd and Zn therein remain uncertain.

Copper concentrations (Figure 7) generally are similar in all cores, typically reaching a maximum of ~ 250 ppm near the sediment-water interface. An exception is core M21, where the maximum occurs approximately 20 cm below the surface, the level to which this core may have experienced coring disturbance. Sedimentary Cu levels appear to have increased mostly during the past 10 yr, although a gradual increase is evident in sediments deposited between 1960 and 1980. Because of extensive pleasure boat traffic in the Ala Wai Yacht Harbor, located at the mouth of the canal, and because antifoulants used to paint hulls of boats can contain up to 70% CuO by weight, we had expected to find

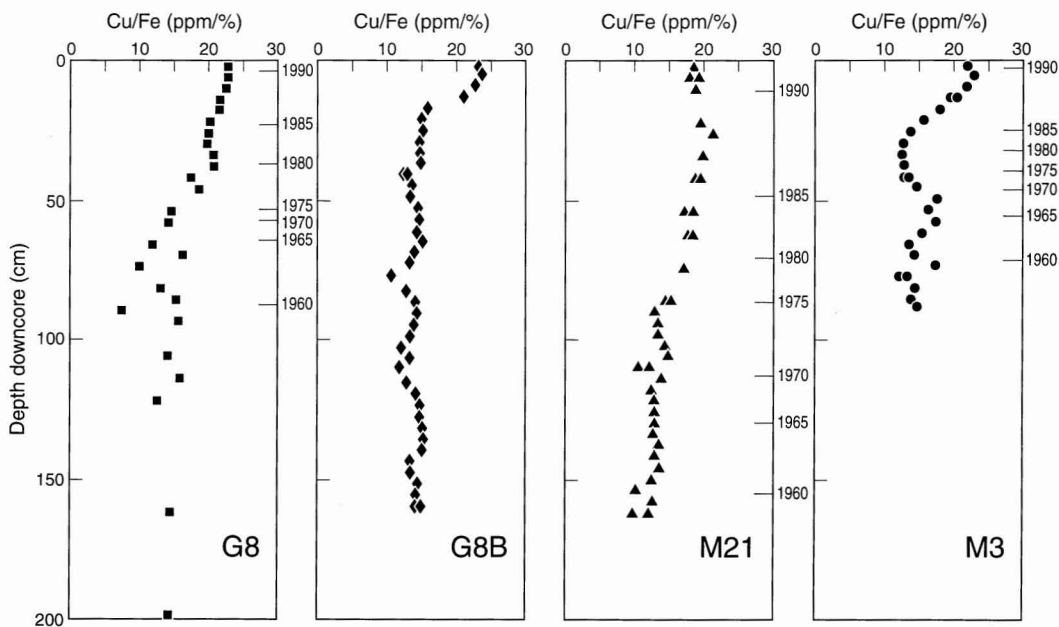


FIGURE 7. Plot of Cu/Fe ratio on a dry weight basis in Ala Wai sediment cores. Radioisotope chronology from McMurtry et al. (1995).

greater Cu concentrations in sediments from the lower reaches of the Ala Wai Canal relative to those at the head of the canal. The occurrence of a relatively uniform distribution of Cu from core to core throughout the canal, however, suggests that antifoulants may not be the primary source of Cu to the sediments.

Halbig et al. (1985) reported that Big Island soils contain from 20 to 200 ppm Cu, with the higher end of this range often observed near developed areas likely affected by anthropogenic inputs. Kabata-Pendias and Pendias (1984) reported a range of 60–120 ppm Cu in basalts. Hence, we suggest that approximately half of the Cu in Ala Wai sediments results from anthropogenic activity, whereas the other half is likely mineralogically bound. Data from the Mānoa Stream sediment samples (Table 5), which exhibit Cu concentrations that increase from 150 to 300 ppm downstream, are consistent with this hypothesis. The approximately 300 ppm Cu in the downstream sediments (near the U.H.) suggest that anthropogenic Cu is being trans-

ported out of the watershed and into the canal. Perhaps an increased use of Cu pipes in plumbing and other commercial products may be an important source of this metal. U.S. Bureau of Mines data indicate that, although quite variable, Cu consumption in the United States increased by approximately 50% between 1975 and 1987 (Lauenstein et al. 1990). This increase correlates well temporally with the large increases in Cu abundances noted in each core.

Elevated concentrations of Cu (about 300 mg/kg), Zn (about 500 mg/kg), and Cd (about 3 mg/kg) were reported by Schropp et al. (1990) in sediments from Biscayne Bay, Florida, whereas Ni showed no significant enrichment over natural levels. Their results are comparable with those observed here (Table 6) and suggest that development in the cities of Honolulu and Miami has followed a similar course and has resulted in substantial contamination of natural sediments. Even higher enrichments of Cu (500–1000 mg/kg) and Zn (400–800 mg/kg) were reported by Bricker (1992) in Narragansett Bay, Rhode

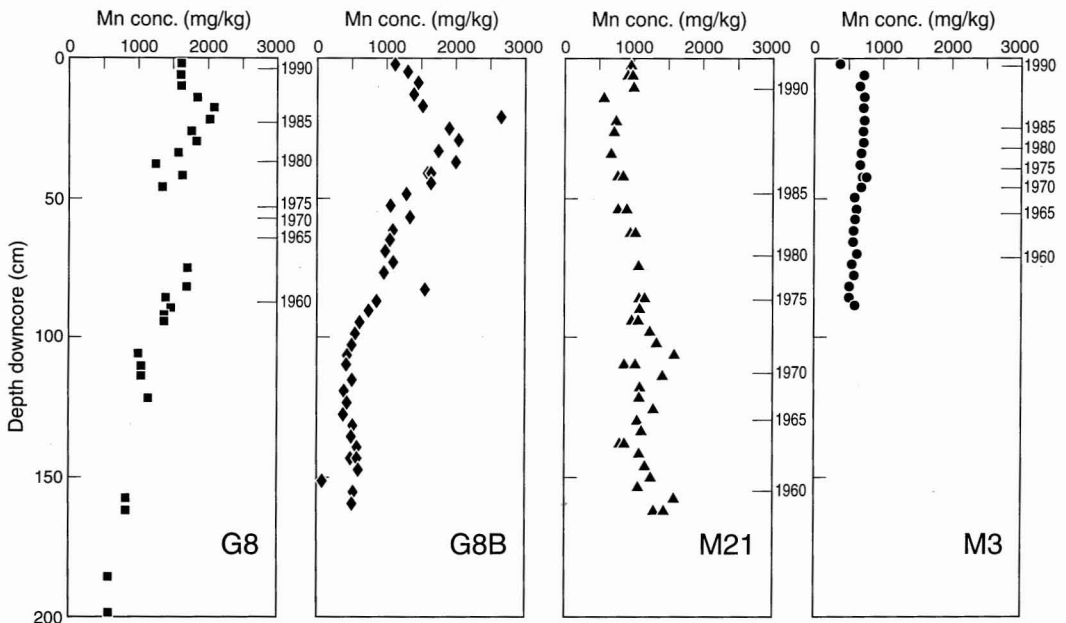


FIGURE 8. Plot of Mn (ppm) concentrations on a dry weight basis in Ala Wai sediment cores. Radioisotope chronology from McMurtry et al. (1995).

Island, where the sediments reflect the much more extensive pollution in the northeastern United States, with respect to these elements, than in either Miami or Honolulu.

The Mn profiles shown in Figure 8 are more difficult to interpret, likely because of the well-known diagenetic behavior of this element in sediments. Two cores (G8, G8B) display a generally increasing trend from approximately 500 ppm Mn in the bottom of the cores to between 2000 and 2700 ppm near about 20–30 cm downcore. Closer to the sediment-water interface, concentrations decrease significantly to 1600 ppm in core G8 and to 1200 ppm in core G8B. However, cores M21 and M3 do not exhibit such a trend. On the contrary, the Mn content of core M21 decreases from the bottom to the top, whereas little or no significant variation is observed throughout core M3 except at the sediment-water interface. The lower concentrations in cores collected closer to the mouth of the Ala Wai likely reflect an increasing abundance of coarse-grained material near

the harbor mouth. More elevated Mn contents in the (most anoxic) core collected nearest the golf course suggest that drainage through organic matter-rich soils accompanied by sedimentary diagenesis strongly influences Mn concentrations. Actual sources of Mn, however, remain unclear.

A mineralogical control over metal concentrations appears most likely for Co and Ni (Tables 1–4) because, based upon the relatively constant Fe-normalized profiles of these elements (Figures 9–10), their abundances do not appear to have been influenced significantly by anthropogenic inputs. Within the Fe-rich sediments of the cores, Co concentrations range between 100 and 140 ppm (e.g., cores G8B, M21, and M3); however, concentrations drop dramatically to near 50 ppm in the CaCO_3 -rich zone of core G8B. In other cores, differences are less dramatic because of generally lower CaCO_3 abundances compared with the lower sections of core G8B.

Because samples from core G8 were di-

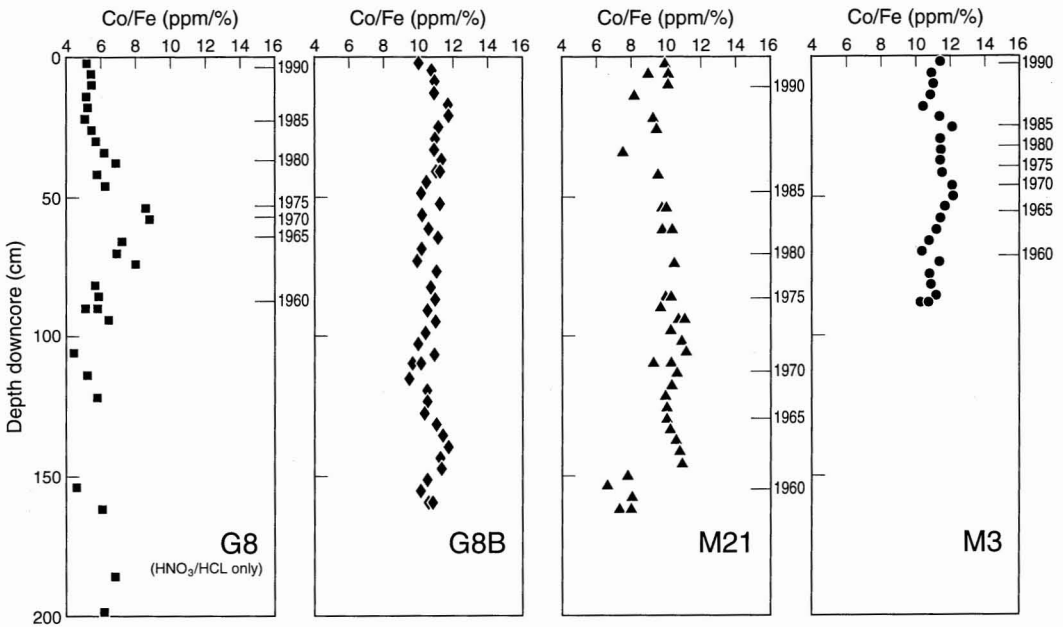


FIGURE 9. Plot of Co/Fe ratio on a dry weight basis in Ala Wai sediment cores. Radioisotope chronology from McMurtry et al. (1995).

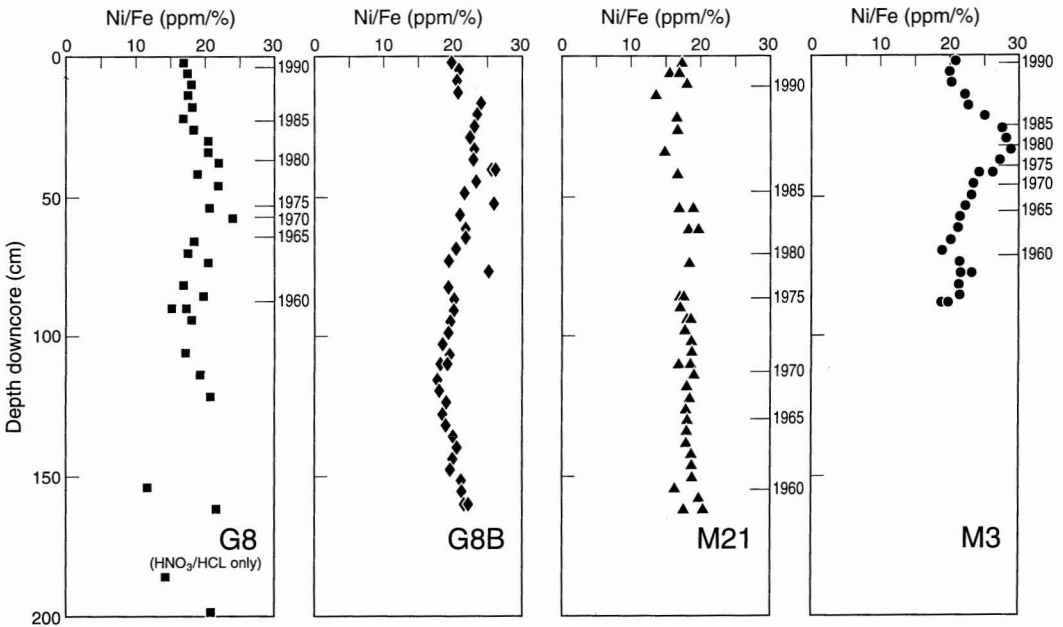


FIGURE 10. Plot of Ni/Fe on a dry weight basis in Ala Wai sediment cores. Radioisotope chronology from McMurtry et al. (1995).

gested using HNO_3 and HCl , which do not effectively attack refractory aluminosilicates, measured Co concentrations between 50 and 80 ppm may be representative of the amount of natural Co associated primarily with the readily solubilized mineral assemblage of the sediments. These data are consistent with Co concentrations of 20–80 ppm measured in uncontaminated soils by Halbig et al. (1985) and indicate that about 50 ppm Co resides within the refractory aluminosilicates, assuming that the total Co content of sediments in core G8 is similar to that in the other cores. A 50 ppm Co concentration is consistent with the amount of Co in basalts (Kabata-Pendias and Pendias 1984). The somewhat higher Co contents near 150 ppm in Mānoa Stream sediments (Table 5) may be attributed to selective pyroxene enrichment in these sediments (Fan et al. 1995). Pyroxenes are typically enriched in Co by a factor of three to four over the basaltic groundmass in which they are included.

Based on the lack of significant variations in the Ni/Fe ratio throughout most of the cores (Figure 10), mineralogical control can likely be invoked to account for Ni abundances (60–100 ppm in CaCO_3 -rich zones of core G8B and 180–250 elsewhere) in the Ala Wai sediments and in the Mānoa Stream samples (150–300 ppm). A peak in Ni abundances is observed between 24 and 40 cm depth within core M3 where Ni concentrations reach a maximum of 340 ppm. Considering the lack of other metals with anthropogenic inputs at this depth, it is possible that this peak represents natural Ni. Indeed, even these elevated Ni contents are well within the range of 150–800 ppm Ni found in soils by Halbig et al. (1985) and of 130–2000 ppm reported by Kabata-Pendias and Pendias (1984) for mafic and ultramafic rocks. Only three samples (collected along a gully) analyzed by Halbig et al. (1985) displayed values above 500 ppm Ni, and in each of these less than 40 ppm was extractable with HCl . Hence, it is possible that these three high Ni samples reflect a pulse of pyroxene- or olivine-rich matter to the Ala Wai. The absence of such a peak in the other three cores suggests that the pulse pyroxene or olivine

input to the Ala Wai occurred downstream of cores G8, G8B, and M21.

CONCLUSIONS

This study has assessed the influence of selected human activities on metal concentrations in sediments within the Ala Wai Canal. Indirectly, our results are also indicative of the quality of waters feeding the Ala Wai Canal and provide both a measure of the retention of selected metallic species within sediments and historic trends of metal inputs. Our work has shown that, as observed in other regions such as Narragansett Bay (Rhode Island), Wellington Harbour (New Zealand), and subtropical environments such as southern Florida, large quantities of heavy metals are transported through stream and street runoff and are subsequently strongly retained in the sediments when they enter estuarine water. Furthermore, there is evidence of a contribution from local and distal atmospheric fallout sources that may be resolvable by use of stable isotope techniques (Spencer et al. 1995).

Profiles of Pb in sediment cores provide historical records of lead-alkyl fuel additives in automobiles and clearly show the decreased flux of this element on O'ahu since the implementation in 1975 of legislation restricting its use. Based upon concentrations and stable isotope data (Spencer et al. 1995), it appears that most of the Pb in post-World War II sediments is derived from automotive use and enters the canal through street runoff. Stream sediment data are consistent with this conclusion.

The Zn and Cd concentrations in the sediments also reflect increased automotive traffic in Honolulu since the creation of the Ala Wai Canal, but particularly since 1960. The Zn/Cd ratios within the Ala Wai sediments suggest an association between these two elements, although variations in the ratios indicate that other unrelated sources of Cd exist, possibly such as high Cd-containing superphosphate fertilizers. These two elements, which enter streams and the canal primarily via street runoff, are likely derived

in large part from the wear of tires on road surfaces. Approximately one-half to two-thirds of the Zn is of anthropogenic origin, whereas for Cd the value may exceed 90%.

Sedimentary profiles document an increase in the flux of Cu since the early 1960s but particularly during the past 10 yr. Unlike Pb, Zn, and Cd, whose increased fluxes over time largely can be attributed to automobile traffic, Cu appears to be derived from various other uses of this metal such as plumbing, gutters, and so forth. Increasing concentrations of Cu downstream within Mānoa Stream sediment are consistent with greater residential and commercial sources of Cu than CuO-containing antifoulant paints used on boats within the harbor. Nonetheless, approximately 50% of the Cu in near-surface sediments is still of natural origin.

Manganese profiles suggest either that different areas of the Ala Wai Canal are subject to variable inputs of this element or that diagenetic reactions in the upper reaches of the canal are more extensive than nearer the mouth of the Ala Wai.

Two elements, Ni and Co, do not display trends indicative of large anthropogenic contribution to the sediments, although the Fe-normalized Ni profile of core M3 indicates an additional significant input of Ni around 1980. Overall, mineralogical control can be invoked to account for Ni and Co concentrations and most of their variability.

Anthropogenically derived fractions of the metals appear to be surface-bound to the sediments and are easily released by digestion with aqua regia. The proportion of anthropogenic to natural contributions increases in the order $Co \sim Ni < Cu < Zn \ll Cd \sim Pb$.

The Ala Wai Canal study has provided a historical record of inputs of heavy metals resulting from anthropogenic activity in urban Honolulu. Because we obtained complete sedimentary records, including what we believe are relatively uncontaminated sediments in the bottom of two cores, results of our study can be used as a comparative basis to evaluate the effect of anthropogenic activity on streams and estuaries in Hawai'i and in other subtropical volcanic island environments.

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