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Retrospective Analysis of Anthropogenic Inputs of Lead and Other Heavy Metals to the Hawaiian Sedimentary Environment*

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In this paper we present and discuss heavy-metal concentrations in sediment cores from the Ala Wai Canal, a small urban drainage estuary in Honolulu, Hawaii (Oahu Island), and from selected soils and sediments collected in less impacted areas of Hawaii. We focus on lead and its isotope ratios to document the introduction, proliferation and subsequent phasing-out of alkyl-lead fuel additives in Honolulu over the past 60 years. Sedimentary lead increases from <10 ppm in the oldest (deepest) unimpacted portions of the cores to ~ 750 ppm in sediments from the mid-1970s; lead contents then decrease to a range of 100–300 ppm in the most recent deposits.

Lead concentrations in the canal sediments closely track the consumption of alkyl-lead fuel additives used on Oahu in the middle of this century. More than 90% of the lead in certain core intervals is of anthropogenic origin. Stable lead isotope ratios reflect changes in the estuary's sources of lead and show that this lead has an isotopic signature distinct from natural samples. Undisturbed layers of sediments in the Ala Wai canal track the average composition of anthropogenic lead used in its Honolulu watershed through time.

The distinctive pattern of lead isotopes measured in Ala Wai Canal sediments can be used to distinguish anthropogenic from natural lead in Hawaiian rural locations. Soils located away from point-sources of contamination have isotopic compositions defined by mixtures of locally erupted volcanic rock, atmospheric dust and components similar to Ala Wai Canal anthropogenic lead. Natural lead concentrations in Hawaii are in the range of a few to a few tens of parts per million, with the high-concentration end-member occurring in a few selected intramountain basins where soils contain a significant component of continental dust fines scavenged by rainfall and concentrated by local geological conditions. Rural watershed material exhibits small but discernible elevations in lead concentrations due to anthropogenic effects.

Other metals (cadmium, copper and zinc) in the Ala Wai Canal sediments also display patterns consistent with increased fluxes of metals attributable to anthropogenic activity. Unlike lead, no clear maxima are observed in sediments deposited during the mid 1970s. Rather, a continued input of these metals is attributed to expanding anthropogenic activity in the Ala Wai Canal watershed. **© 1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

The Ala Wai Canal, a small drainage estuary in Honolulu, Hawaii (Fig. 1), separates urban Honolulu from the resort area of Waikiki. It was completed in 1927 by the US Corps of Engineers as drainage for runoff originating in valleys inland of Waikiki to provide materials to fill wetlands, and for mosquito control.

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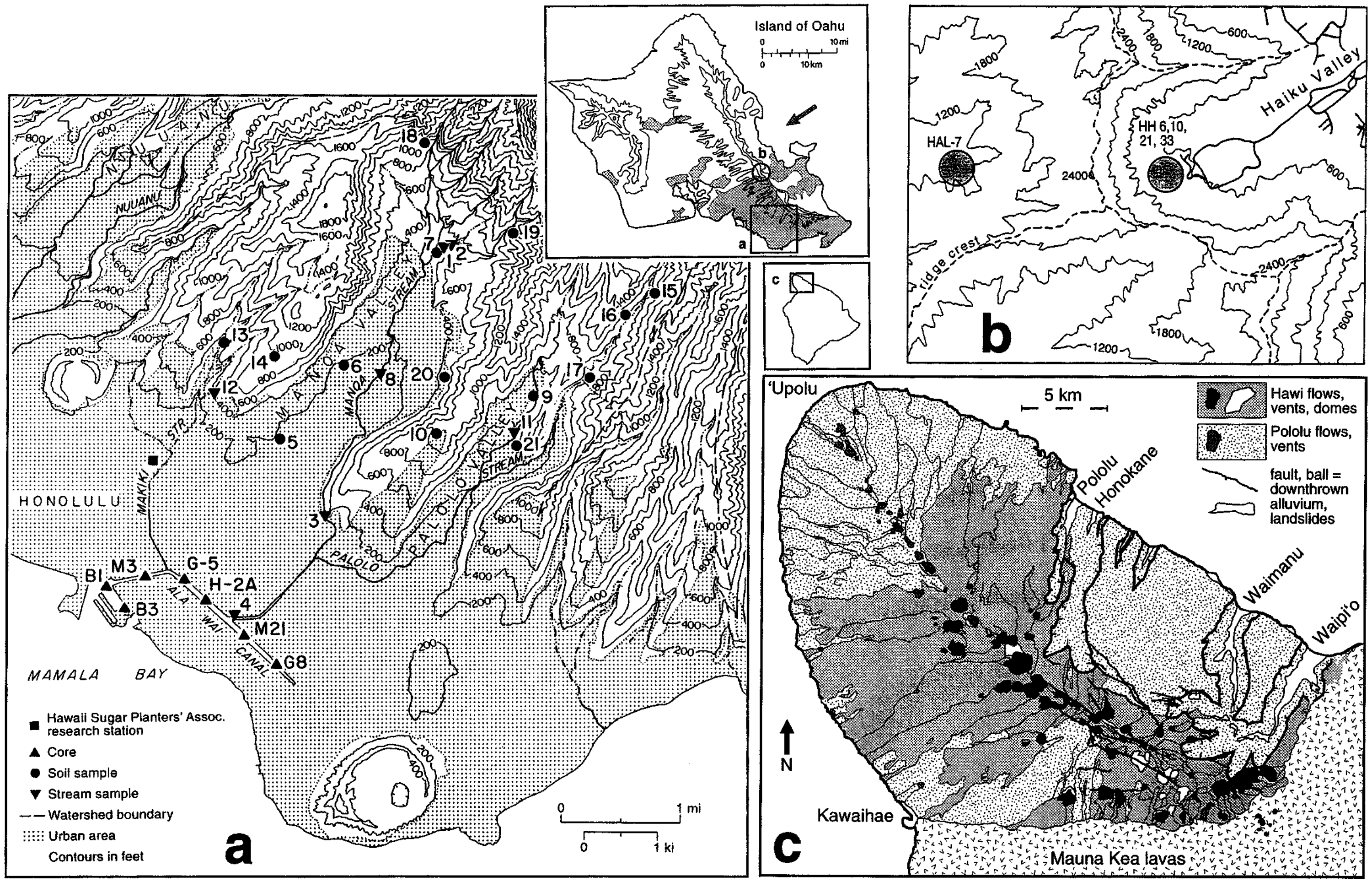

Figure 1 Site location map of sample locations on Oahu and Hawaii islands. The small insert map shows the island of Oahu; the black arrow indicates the direction of the prevailing winds. Small circles **a** and **b** correspond to enlargements (a) and (b). (a) The Alai Wai Canal and its watershed including Manoa Valley, Palolo Valley and Makiki. Core collection sites and stream sediment sampling locations are also indicated. (b) A portion of the Koolau Mountain ridge crest dividing the western portion of Haiku Valley and the eastern portion of Halawa Valley. A fuller description of these two localities is given in Ref. 24. Location map (c) shows the Kohala peninsula on the island of Hawaii, where Pololu Valley is located.

The Ala Wai exhibits a salt-wedge structure typical of an estuary subject to tidal flushing. Several streams (Maikiki, Manoa and Palolo; Fig. 1) and numerous urban storm drains discharge into the Ala Wai. The Manoa and Palolo Streams are major contributors of freshwater and join in a smaller drainage canal approximately 1.5 km above the Ala Wai. The Ala Wai Canal was dredged in 1966, and again in 1978, to remove accumulated sediments resulting from erosion of the Koolau range and watershed soils. Only the section between the Manoa–Palolo input and the Kalakaua Avenue bridge (Fig. 1) was dredged. A comprehensive description of the Ala Wai Canal is given by Laws *et al.*[1]

High orographic rainfall in the Koolau range and the associated erosion, combined with urban runoff in Honolulu, causes rapid sedimentation of the Ala Wai (1–4 cm/yr^{-1}).[1,2] The elevated accumulation rates, accompanied by high productivity in the Ala Wai, often result in anoxia that minimizes bioturbation and enhances preservation of sedimentary layering. The Ala Wai Canal sediments generally provide a well-preserved record of metal pollution in urban Honolulu.

In the case of lead, the high concentrations found in undisturbed, datable Ala Wai Canal sediment layers have enabled us to identify the isotopic signature of pollutant lead through time and test for its presence elsewhere in less impacted areas of Hawaii. We can therefore test whether small-scale variations in lead concentrations in rural (relatively unimpacted) Hawaiian soils and sediments are due to natural or anthropogenic processes. We have examined soils collected in the Haiku Valley in windward Oahu and sediments from the Pololu Valley, on the Kohala peninsula of Hawaii, to examine the dispersal of anthropogenic lead into the rural Hawaiian environment. These locations are shown in Fig. 1.

METALS AND THE ENVIRONMENT

Fluxes of heavy metals to the environment have increased greatly over the past century as a result of industrialization and urbanization. Metal production and coal-burning operations during the late 19th and early 20th centuries were two major sources of metal release to the atmosphere, rivers and lakes. Most probably, only a small contribution from these sources reaches Hawaii through atmospheric transport of aerosols.[3] A major portion of anthropogenic lead input to the atmosphere between 1940 and 1975 consisted of alkyl-lead fuel additives first introduced in 1923.[4] In Hawaii alone, nearly 450 tons of lead were released in 1971 from the use of leaded gasoline;[5] alkyl-leads were not entirely eliminated in Hawaii until 1989, according to the State of Hawaii Dept of Business and Economic Development records. Although most industrialized nations are phasing-out alkyl-leads they are still used widely in developing nations. Other sources of lead in the world's atmosphere include the smelting of iron, copper, zinc and lead, and the burning of coal. Each of these releases tens of thousands of tons of metals to the environment.[6]

Owing to their high particle reactivity, many dissolved metallic species are retained strongly by metal oxides (e.g. Ref. 7). Hence, the heavy-metal contents of sediments and soils should reflect fluxes from adjoining land areas.[8] Because sorption processes concentrate metals within the upper few centimeters of soils, the resulting integrated contaminant fluxes are difficult to interpret and cannot be resolved chronologically.[9] In contrast, when runoff reaches saline waters in estuaries, colloidal matter flocculates and settles along with its adsorbed metal load. Thus, species scavenged by suspended particles accumulate sequentially in aquatic sediments, such as those of the Ala Wai Canal, and provide potentially resolvable records of metal inputs not available from examination of soils.

In the case of lead, isotopic studies can distinguish natural variations from contamination. However, to make use of isotopes to elucidate the sources of anthropogenic and natural lead present in an area, the various input signals must be characterized and compared. The volcanic units in Hawaii, which decompose to form residual soils, have been analyzed for some or all of their lead, neodymium and strontium isotopes.[10–19]

The atmospherically transported silicate dust component in Hawaiian soils is isotopically distinct from Hawaiian lavas. Dymond *et al.*[20] and Jackson *et al.*[21] identified strontium isotope ratios in mineral separates collected from soils on Oahu having $^{87}Sr/^{86}Sr \simeq 0.722$, too high to evolve from Hawaiian igneous rocks ($\sim$0.7033–0.7045) and requiring an old continental source. North Pacific pelagic sediments, proxies for atmospheric dust (data from Refs 22 and 23) and D. G. Waggoner, unpublished results), and Hawaiian soils contain continentally derived source material.[24,25] These soils and sediments are characterized by ^{207}Pb/^{204}Pb ratios higher than Hawaiian rocks for a given ^{206}Pb/^{204}Pb, and by higher ^{87}Sr/^{86}Sr ratios.

Anthropogenic lead is derived from ore bodies and most often has an isotopic composition distinct from natural rocks or soils because this lead has been isolated from its parent uranium and thorium since the ore formed. Thus, its lead isotopic composition remains frozen in time, while that of the unsegregated lead in rocks and minerals continues to evolve as its radioactive parents decay. Erel and Patterson[26] have shown that, to a first approximation, most of the industrial (anthropogenic) lead used in the USA can be thought of as a mixture of low ^{206}Pb/^{204}Pb lead such as is found in deposits from New York (Balmat) and high-^{206}Pb/^{204}Pb lead from the mines around Joplin, Missouri, commonly referred to as ‘J-lead’ (for examples see Fig. 2). By contrast, some Pacific nations use a predominance of low-^{206}Pb/^{204}Pb ores mined in Australia.[27] These isotopic compositions are distinct from the isotopic compositions seen in Hawaiian rocks or North Pacific pelagic sediments, proxies for continental dust.[24]

When anthropogenic lead emissions of different times are mixed and integrated along with the natural lead in soils and sediments, the mixed signals can produce a confusing picture, possibly mimicking naturally occurring lead.[28] Nonetheless, lead isotopes have clearly documented the concentrations and sources of anthropogenic lead in atmospheric aerosols[3,27,29–32], nearshore ocean basins,[33] lakes,[34–36] rivers, estuaries, and streams,[37–39] deep-water sediments,[40,41] and freshwater sediments.[28]

METHODS

Sediment cores were collected from sites free of major sedimentary disturbances (e.g. dredging or bioturbation). Cores were collected by manually driving plastic core-liners into the sediments, either from a small boat or by wading. Cores were sealed and stored upright in a refrigerated core locker until processed. They were cut longitudinally to expose the entire stratigraphic sequence and allow sediment description.

Sediments were sampled every few centimeters in each core. Particular attention was paid to avoid material that contacted the core-liner or the saw blade. Individual samples were homogenized, sieved and freeze-dried. Subsequent handling was conducted on clean benches. Details of sampling and analytical procedures are given in Refs 24 and 42. Only a brief summary is provided here.

Soils were collected using clean plastic disposable trowels and stored in precleaned glass containers. The samples were grossly sorted to remove large rock chunks and organic debris, after which they were ground to powders in precleaned alumina crucibles. A minimum of grinding was done in each case to avoid contamination.

Core samples were digested in Teflon vessels using aqua regia (core G8) or a mixture of aqua

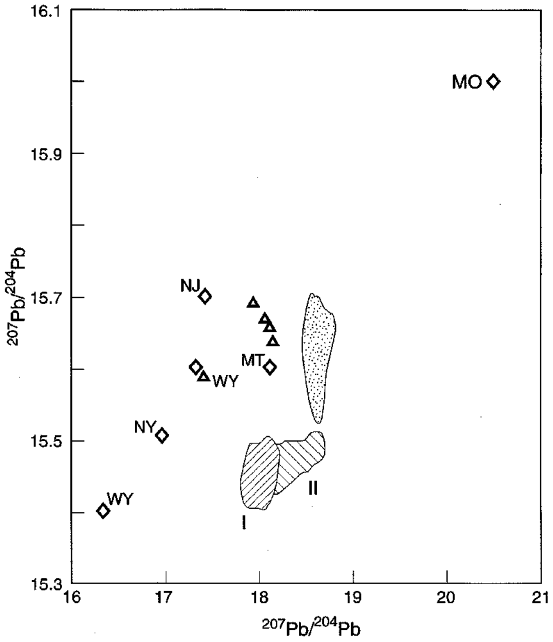

Figure 2 ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb data for rocks, sediments and ores relevant to this study. Hawaiian volcanic rocks are indicated by diagonally striped fields; field I encloses lead isotopic analyses on Oahu volcanic rocks while field II encloses analyses on island of Hawaii volcanic rocks. Field II continues under field I for most of its length. North Pacific pelagic sediments (proxies for continental dust) are represented by a stippled field. See text for these data sources. The diamonds are lead-ore isotopic compositions from US mines in the following states: New Jersey (NJ), New York (NY), Wyoming (WY) and Missouri (MO)[64] and the open triangles are isotopic compositions on alkyl-leads from mid-1960s leaded gasolines sold in Southern California, USA.[58]

regia and HF (Ala Wai cores G8B, M21, M3; Pololu Valley core; and soils). Replicate digestions were performed approximately every eighth sample. Procedural blanks were processed in an analogous fashion. Standard reference materials (SRM) (NBS-1645 river sediment, MESS-1 marine estaurine sediment) were carried through procedures to assess metal recovery during digestion and for quality control and assurance during elemental analysis. Recovery of elements was within 5% of the SRM reference values, except for aluminium, calcium, cobalt, nickel and silicon (within 10% or better).

Elemental analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP–OES) and by graphite furnace atomic absorption spectroscopy (GFAAS) for cadmium and low-abundance lead samples. Selected samples from the Manoa Stream (Fig. 1) and soils from other locations are also carried through these procedures.

Selected samples were analyzed by thermal ionization mass spectrometry (TIMS) to determine their lead isotopic compositions (ICMS) with some lead concentrations determined by isotope dilution (IDMS). For ICMS and IDMS measurements, samples were processed following clean protocols developed in the SOEST isotope geochemistry laboratory.[24,43] Samples were subjected to sequential attacks by HF/HNO_3 and hot HCl/HNO_3 in order to decompose organic matter and silicates.

Leaching experiments for lead isotopes were carried out using 1 M HCl and solutions of ammonium acetate and hydroxylamine–HCl buffered to pH 3 with acetic acid. Water and HCl were prepared by quartz-subboiling distillation to achieve a lead blank of <1 pg/g^{-1}. The hydroxylamine–HCl and ammonium acetate solutions were purified by column-cleaning using Chelex-100 resin, reducing their lead blank to 15–20 pg/cm^{-3}, an acceptable level for our purposes.

The 1 M HCl leach was carried out for 1 h at room temperature in a sonic bath. The hydroxylamine–HCl and ammonium acetate leaching experiments were carried out for about 3–5 h each in a sonic bath at 40–50°C. Samples were then centrifuged to separate the liquid and solid phases. A small amount of liquid was always left covering the solid interface to avoid pipetting residual solids into the leaching solutions. Thus, the amount of leached lead in a sample is always underestimated by a few per cent.

Samples analyzed by isotope dilution were spiked with a ^{206}Pb tracer. Because of additional sample handling and regents, our IDMS measurements are less accurate than the 1% value reported by Mahoney *et al.*[43] for other geological samples. Total lead blanks for this study are aproximately twice the 20–40 pg blanks reported in previous work.[24,43] In any case, a doubling of the silicate blank is not likely to be a significant source of error in our ICMS measurements. Samples were analyzed using the single-rhenium filament, silica gel–phosphoric acid technique. Mass spectrometric procedures used in the SOEST Isotope Geochemistry laboratory have been described elsewhere.[24,43]

RESULTS

Cores G8 (200 cm) and G8B (160 cm) (Fig. 1) are believed to have penetrated the earliest canal sediments, as evidenced by a zone of abundant $CaCO_3$ admixed with clay minerals near the bottom of the cores. Cores M21 (164 cm) and M3 (95 cm) only partially sampled the stratigraphic record of the canal.

Ala Wai Canal sediments are composed primarily of detrital volcanic minerals and their weathering products. They contain varying amounts of aluminium and iron oxides, clay minerals and primary alumino silicates, as well as $CaCO_3$ and some iron sulfides. Relative proportions of individual minerals are influenced by various factors, including the extent of orographic rainfall (transport of eroded soils during rainstorms) and abiotic whitings within the canal.[44] Profiles of calcium and iron are presented in Fig. 3; elemental concentrations are given in Tables 1–4.

Differentiating between natural and anthropogenic sources of metals is complicated by the natural variability of trace-metal concentrations in sediments owing to differences in mineralogy, grain size and organic matter content. For example, carbonates are known to exhibit much lower trace-metal contents than iron and clay-rich sediments,[45] and, in the Ala Wai cores, $CaCO_3$-rich zones (Fig. 3) contain low concentrations of lead, zinc, cadmium and copper (Tables 1–4). Therefore, it is necessary to normalize metal concentrations to a reference element such as aluminium or iron in order to discriminate between sources or physical charac-

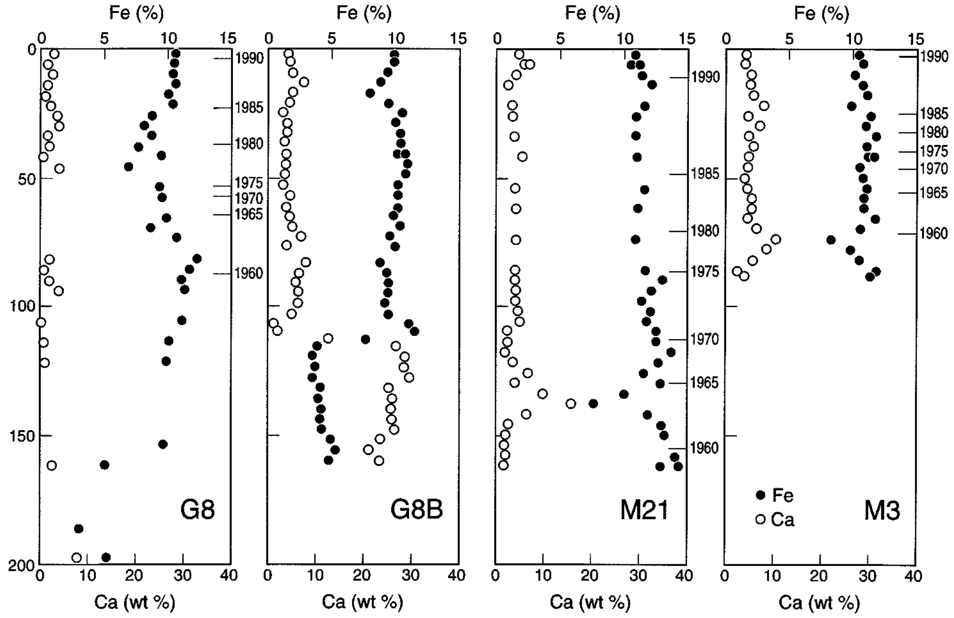

Figure 3 Plot of iron and calcium concentrations on a percentage dry weight basis in Ala Wai sediment cores. Open symbols cadmium; closed symbols, iron.

teristics contributing to variations in the metal contents of sediments.[45]

Because samples from core G8 were digested in HCl/HNO_3 and refractory aluminosilicates were incompletely solubilized, normalization of the trace-metal data to aluminium was not possible. We chose, instead, to normalize to the iron content of all cores. This approach also eliminates variations caused by the mineralogical changes that are reflected in the calcium and iron profiles (Fig. 3). Because diagenetic processes can affect the iron content of sediments and might invalidate the use of normalization to iron, we show in Fig. 4 a plot of iron versus aluminium for samples subjected to total dissolution. The strong correlation ($r^2=0.84$, $n=107$) suggests that iron is a valid proxy for detrital aluminium and can be used as a normalizing element. During weathering of volcanic edifices and soil formation in tropical environments, iron in igneous minerals is transformed primarily into clay minerals and iron oxides. The close relationship between iron and aluminium observed here is consistent with sediments of the Ala Wai being composed primarily of eroded soils.

Profiles for lead, zinc and copper normalized to iron are presented in Fig. 5. Ratios of Cd/Zn and Cd/Fe are shown in Fig. 6. Each core exhibits generally elevated metal abundances in recent relative to older sediments. The chronology of three of the four cores, based on ^{210}Pb and ^{137}Cs,[2] is superimposed on the metal profiles (Figs 5 and 6). Cobalt and nickel do not display strong temporal trends, suggesting there has been little systematic change in their flux to the canal over time. Elemental abundances for surface sediments collected along the Manoa Stream are given in Table 5.

The isotopic compositions of newly analyzed Ala Wai Canal sediments from the Gonzales-8 core, along with lead and strontium analyses on Pololu Valley samples and leaching experiments conducted on selected Haiku Valley and Pololu Valley samples, are shown in Table 6.

DISCUSSION

Urban sediments

Concentrations of metals in rapidly depositing sediments have often been used to evaluate temporal variations in metal fluxes to fresh and saline waters.[8,37,42,46–55] However, studies conducted since 1980 reveal that environmental legislation enacted in the 1970s has led to reductions in some anthropogenic metal emissions. Indeed, our lead profiles (Fig. 4) clearly demonstrate the beneficial effect of phasing-out alkyl-lead fuel additives on inputs to the Hawaiian environment. A lead background of 5–10 ppm in pre-canal sediments (the bottoms of cores G8 and G8B) was followed by a small increase during the 1950s. A dramatic rise occurred in the 1960s, reaching a maximum of ~750 ppm lead (in core G8) in sediments of the late 1970s to early 1980s. Concentrations of lead decrease significantly in more recently deposited sediments (the tops of cores).

Each of the Ala Wai cores exhibits the same trends although absolute concentrations vary owing in part to differences in accumulation rates. In core M3 the maximum appears to occur during the early rather than the late 1970s but this may be an artifact resulting from a large pulse of (relatively lead-free) aluminosilicate-rich sediment *ca* 1979–1981 (see the discussion of nickel, below). Based on our results, and State of Hawaii leaded-gasoline consumption records (State of Hawaii, Department of Business, Economic Development, and Tourism, personal communication; see also Ref. 56), we are thus able to correlate the lead profiles in Ala Wai sediments with the advent, proliferation (owing to increased traffic density associated with growth) and subsequent phasing-out of alkyl-lead fuel additives in Hawaii (Fig. 7).

In our study of the Ala Wai canal sediments, it has been possible to differentiate between natural and anthropogenic lead contributions simply on the basis of concentrations because ‘natural’ abundances (e.g. in soils not thought to be polluted) in Hawaii rarely exceed 25–40 ppm and are significantly lower in most cases. In a baseline study of metal concentrations in relatively uncontaminated soils of Hawaii, Halbig *et al.*[57] observed a range of 1.5–17.5 ppm lead solubilized with 0.5 MHCl. The fraction of soils

Table 1 Elemental data for core G8, Ala Wai Canal, Oahu, Hawaii

Depth (cm)	Concentration (ppm) Al	Fe	Si	Ca	Mg	Mn	Pb	Zn	Cu	Co	Ni
2	3.28	10.61	19.82	2.14	2894	1604	315	381	241	53.7	180
6	1.55	10.51	21.01	0.93	990	1596	319	394	240	55.5	183
10	3.84	10.39	22.60	2.31	4867	1608	372	393	234	56.3	187
14	2.01	10.60	19.98	1.23	903	1842	417	375	229	53.9	186
18	1.13	10.02	21.27	0.73	1334	2103	468	361	216	52.0	183
22	1.66	10.35	23.75	1.69	3016	2026	496	363	211	51.4	175
26	0.96	8.79	11.94	3.22	498	1758	534	332	176	47.6	162
30	0.76	8.08	14.16	3.86	857	1850	494	286	161	45.4	166
34	0.72	8.72	19.09	1.53	1932	1571	759	376	181	53.8	179
38	0.86	7.75	17.99	1.81	577	1248	507	298	161	53.1	171
42	0.73	9.53	21.52	0.47	407	1621	609	326	166	55.0	182
46	0.91	6.91	13.26	3.85	566	1347	335	239	129	42.9	151
54	6.20	9.43	—[a]	—[a]	—[a]	—[a]	651	405	139	80.6	195
58	7.09	9.60	—[a]	—[a]	—[a]	—[a]	623	384	137	84.0	231
66	6.95	9.98	—[a]	—[a]	—[a]	—[a]	475	319	120	71.5	184
70	5.99	8.70	—[a]	—[a]	—[a]	—[a]	350	276	142	60.0	154
74	7.28	10.76	—[a]	—[a]	—[a]	—[a]	374	313	109	85.8	220
82	4.53	12.38	26.22	1.96	4798	1715	291	290	162	69.7	210
86	2.26	11.85	25.83	0.75	936	1396	285	336	182	69.3	234
90	3.07	11.16	—[a]	—[a]	—[a]	—[a]	273	262	84	63.9	171
90	3.12	11.16	22.05	1.94	5224	1475	230	256	84	56.5	193
94	6.90	11.41	29.64	3.73	7465	1368	227	251	179	73.0	207
106	0.89	11.23	21.89	0.20	669	1012	146	252	158	49.4	193
114	0.95	10.20	21.10	0.66	1577	1048	137	275	162	52.8	197
122	0.62	10.01	13.33	0.96	322	1151	125	252	126	57.5	209
154	6.98	9.84	—[a]	—[a]	—[a]	—[a]	115	119	—[a]	45.2	115
162	0.25	5.28	15.17	2.52	1186	837	16	87	76	32.0	114
186	0.28	3.20	—[a]	—[a]	—[a]	—[a]	16	43	—[a]	21.9	47
198	0.54	5.36	20.61	7.92	4090	584	14	70	77	33.1	113

[a] —, not determined.

dissolved by this treatment is limited to carbonates, and aluminium and iron oxides. The latter probably contain a large part of the lead bound to soils. However, differences between soils and sediments and the fact that the island of Hawaii has generally been less weathered than Oahu

Table 2 Elemental data for core G8B, Ala Wai Canal, Oahu, Hawaii

Depth	Concentration (ppm)											
(cm)	Al	Fe	Si	Ca	Mg	Mn	Pb	Zn	Cd	Cu	Co	Ni
2	8.13	9.72	13.98	3.90	1.62	1214	243	330	1.21	227	97	194
5	7.93	9.74	13.93	4.27	1.66	1237	270	354	1.09	231	105	206
9	7.65	9.26	13.39	4.89	1.65	1506	265	327	1.24	211	102	191
13	7.33	8.69	13.07	7.27	1.70	1504	343	300	1.03	183	95	181
17	6.05	7.90	11.60	4.97	1.89	1665	325	222	0.99	127	93	191
21	7.57	9.29	13.30	4.33	2.13	2667	441	316	1.36	141	109	220
25	7.94	10.37	14.18	2.97	2.31	2061	571	400	2.02	158	116	241
29	9.02	9.85	14.95	3.57	1.79	2319	369	290	1.36	145	108	222
33	8.90	10.23	15.40	3.50	2.04	1841	403	319	1.64	153	112	238
37	9.25	10.38	15.27	3.15	1.74	2115	205	252	1.16	155	117	239
41	7.93	10.74	15.24	3.67	2.51	1692	183	264	0.87	136	120	274
41	7.92	10.11	14.92	3.62	2.44	1608	182	262	1.02	132	111	266
45	8.71	10.76	15.94	3.65	2.31	1774	236	280	1.04	146	113	251
49	9.20	10.72	16.55	3.46	2.18	1440	181	272	1.08	144	109	234
53	8.37	10.09	14.04	3.24	2.54	1088	226	309	1.27	147	113	262
57	8.52	10.07	15.84	4.44	1.92	1429	121	236	0.96	147	103	212
62	8.33	10.09	15.32	3.85	1.95	1197	102	236	0.86	145	107	222
65	8.25	9.81	14.89	4.15	1.85	1034	94	235	0.90	149	109	215
69	8.63	10.31	15.65	4.91	2.07	1037	98	233	0.85	146	105	211
73	7.96	9.43	14.97	6.78	2.28	1196	64	195	0.72	127	93	184
77	7.23	9.85	16.94	3.80	3.41	1010	83	216	0.87	106	109	249
83	7.51	8.79	13.51	7.86	1.73	1671	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	6	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	0.30	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	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
116	3.87	3.91	6.11	26.64	2.15	564	4	43	0.15	51	37	70
116	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	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	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	4	48	—[a]	63	43	88
148	4.24	4.29	6.39	26.44	2.13	639	1	37	0.14	58	49	84
148	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	3	48	—[a]	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

[a] —, not determined.

could significantly alter baseline concentrations expected in sediments.

The lead isotope data for Ala Wai samples clearly fall outside the field of natural samples found in Hawaii. Variation in the $^{206}Pb/^{204}Pb$ ratio in this lead (Fig. 8) is broadly similar to US industrial lead as compiled by Erel and Patterson,[26] but in detail our measurements are different in several respects. The first $^{206}Pb/^{207}Pb$ maximum for US emissions is ~1940, while it is ~1960 in the Gonzales-8 core, or 20 years later. The first minimum in $^{206}Pb/^{207}Pb$ for the US occurs during the 1960s, and for Gonzales-8 samples it is ~1970, or *ca* eight years later. The depth vs age relationships for the Ala Wai samples during the last 30–40 years is well

Table 3 Elemental data for core M21, Ala Wai Canal, Oahu, Hawaii

Depth	Concentration (ppm)											
(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	—[a]	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	—[a]	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	—[a]	214	114	218
54	—[a]	—[a]	—[a]	—[a]	—[a]	838	420	359	—[a]	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	—[a]	198	110	203
74	9.95	11.83	15.05	4.05	1.73	1100	242	238	1.44	179	119	199
86	9.95	11.83	15.05	4.05	1.73	1150	263	274	—[a]	172	117	203
90	10.66	13.77	16.22	3.76	1.75	1090	208	260	0.94	168	126	222
94	10.25	12.19	15.56	4.20	1.71	1020	148	206	0.82	165	132	221
94	10.25	12.19	15.56	4.20	1.71	1050	158	222	—[a]	163	131	225
98	9.95	11.68	15.15	4.36	1.60	1220	196	245	1.07	154	118	203
102	10.40	12.19	16.01	4.34	1.68	1340	202	245	0.97	173	131	225
106	10.10	12.04	15.71	4.98	1.78	1600	172	236	0.94	176	133	223
106	10.00	11.93	15.30	4.89	1.75	1560	168	233	0.75	176	131	221
110	11.32	12.75	16.32	2.46	1.40	1030	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	1410	143	212	0.76	174	133	240
118	11.32	13.92	15.71	1.92	1.36	1110	98	196	0.66	168	141	248
122	11.02	13.06	15.20	3.45	1.35	1080	105	189	0.65	164	127	235
126	10.25	11.73	13.97	6.58	1.49	1300	99	172	0.50	151	117	208
130	11.12	13.06	14.69	4.00	1.39	1040	131	186	0.72	167	130	234
134	9.13	10.20	12.75	9.64	1.54	1120	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	1090	56	169	0.42	154	129	222
146	11.22	13.21	16.12	2.61	1.36	1180	200	149	0.89	176	141	243
150	11.48	13.41	16.27	2.03	1.37	1270	134	223	0.69	165	103	248
154	12.60	17.54	18.41	1.80	1.55	1060	136	226	1.15	162	104	255
158	12.39	14.33	17.08	2.07	1.42	1580	91	216	0.18	177	113	277
162	11.07	13.16	15.30	1.72	1.26	1420	80	202	0.59	157	103	264
162	12.29	14.69	16.93	1.90	1.40	1330	82	205	0.60	140	106	251

[a] —, not determined.

constrained by ^{137}Cs data,[2] so it is difficult to ‘align’ the US and Hawaii data using different sedimentation rates.

More importantly, the first Gonzales-8 maximum has a much higher ^{206}Pb/^{207}Pb isotopic signature, which requires a greater proportion of high ^{206}Pb/^{207}Pb, or J-like, lead than the US average during the 1940s through to the 1960s. The peak ^{206}Pb/^{207}Pb value of 1.184 in the Gonzales-8 core is higher than values measured in 1960s gasoline[4,58] but lower than a value of 1.204 measured for 1947 tetraethyl-lead referenced by Chow and Johnson.[58]

The anthropogenic lead measured in the Gonzales-8 core may differ in isotopic composition because the mix of emissions in Hawaii differs from the mix in the continental USA. Neither heavy industrial (i.e. smelting or coal oil burning ‘smokestack’ industries) nor home-heating emissions contribute to lead pollution in Hawaii, so the major sources of lead are most likely to be leaded-paint residues and alkyl-lead combustion products. The increase in ^{206}Pb/^{207}Pb seen in Hawaii in more recent years parallels that seen in the continental USA, but the Hawaii curve does not increase as dramatically in ^{206}Pb/^{207}Pb. This could perhaps be explained if lead used in gasoline refined in Hawaii contained some Australian ore with a lower ^{206}Pb/^{207}Pb composition (e.g. Fig. 2).

A second explanation for the lower ^{206}Pb/^{207}Pb composition seen in recent years is that lead deposited earlier in the 20th century is being eroded and mixed with recently deposited lead and they are then deposited in the canal together. During the early part of 20th century the Makiki–Palolo–Manoa watershed had few roads and more agricultural land. Much of the lead combusted in automotive use or chipped off houses in the form of leaded paint (a second source of pre-1960s lead in Hawaii, when up to 50% of some paint ingredients was litharge (PbO; State of Hawaii Department of Health, personal communication) could have remained bound to soils

Table 4 Elemental data for core M3, Ala Wai Canal, Oahu, Hawaii

Depth (cm)	Concentration (ppm)										
	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

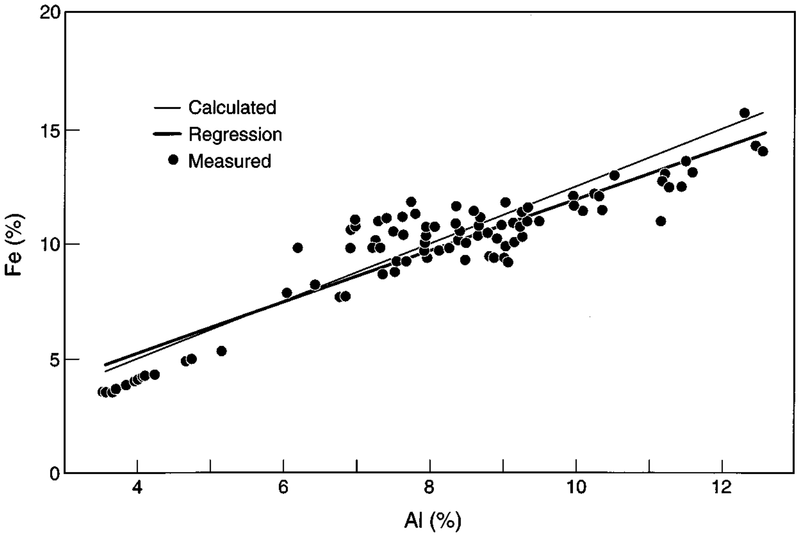

Figure 4 Plot of iron (% wt) versus aluminium (% wt) for cores G8B, M21 and M3 ($n = 107$). The calculated line represents iron concentrations calculated from measured aluminium data and assuming an Fe/Al ratio from tholeiitic basalt. $r^2 = 0.84$ for the regression line of the experimental data.

or dirt along unimproved roadways. Since the 1960s, the massive development in urban Honolulu has brought with it a greater number and density of roads, homes and driveways (especially near the more steeply sloped backs of residential valleys), more channelized stream beds, and more soil erosion as new sites are excavated. More recently deposited lead-rich aerosols and paint chips would be directly deposited on or near hardened surfaces and subsequently washed into drainage at the first opportune rainstorm, thereby mixing with older anthropogenic lead being eroded with soils from the watershed.

The lead concentration profiles correlate temporally with the use of alkyl-leads in gasoline (Fig. 7). Growth of automobile traffic in Honolulu from 1950 to 1975 led to an increase in the lead abundance from under 100 ppm to ~750 ppm. Legislation (in 1975) for the phasing-out of leaded fuels, which were competely eliminated in Hawaii by 1989, is reflected in a decrease in concentration, to 100–300 ppm lead near the sediment–water interface. The failure to return to 'pre-anthropogenic' levels of lead in very recent sediments can be attributed partly to a continued input of lead from previously contaminated soils, mobilized as described above. Furthermore, leaded gasoline was available on Oahu as late as 1989, during which year over 20 million US gallons of leaded fuel was sold in Hawaii. Remobilized roadside soils, which contain up to several thousand parts per million of lead,[5] are probably the primary source of current-day lead fluxes to the canal sediments, although some contribution from lead derived from household paints is still possible in the older residential valleys of Honolulu.

The stream sediment data (Table 5) further attest to a continued input of anthropogenic lead to the canal. Lead concentrations increase from 16.6 ppm at the head of Manoa Valley to 37.1 ppm within the residential area in the middle of the valley and reach 284 ppm in sediments collected near the University of Hawaii at Manoa (UHM). The isotopic composition of these samples, especially sample 3, containing 284 ppm Pb, is similar (Fig. 8) to that measured in canal sediments and suggests that continued lead contamination from Manoa Valley, in the form of transported soils, probably contributes to the progressive lead increase downstream. However, culverts draining the highly traveled streets near UHM are more likely to be responsible for transporting a large portion of alkyl-lead-derived lead bound to roadside soils.

Peak sedimentary lead concentrations in the Ala Wai Canal are similar to those in Biscayne Bay and upper Narragansett Bay[55] and approximately one order of magnitude greater than in Mississippi delta sediments.[8] Lower concentrations in the Mississippi probably result from higher sediment loads and extensive drainage of agricultural land. Other contaminated areas, including the Houston ship channel[59] and Wellington Harbour,[56] particularly near point sources of contamination, exhibit concentrations of lead that are similar and up to an order of magnitude greater respectively. Data are sparse for subtropical island environments; however, uncontaminated sediments from the Gulf of Thailand, also a subtropical environment, provide some basis for comparison[53] and are shown in Table 7.

Several other elements display anthropogenic signals. Among these, an automotive source can also be invoked for zinc, a metal widely used in the vulcanization of rubber. Other sources, such as batteries, galvanized pipes and air-conditioning ducts, can contribute to the anthropogenic flux of zinc, but these materials are more wear-resistant than tires and are more prone to be affected by point-source contamination. Zinc concentrations reach ~300–400 ppm near the sediment water–interface (Tables 1–4), except in core M21 where coring disturbances may have affected the top 15–20 cm of the sediment. The baseline of ~50 ppm in $CaCO_3$-rich sediments and ~100 ppm in iron and aluminium-rich

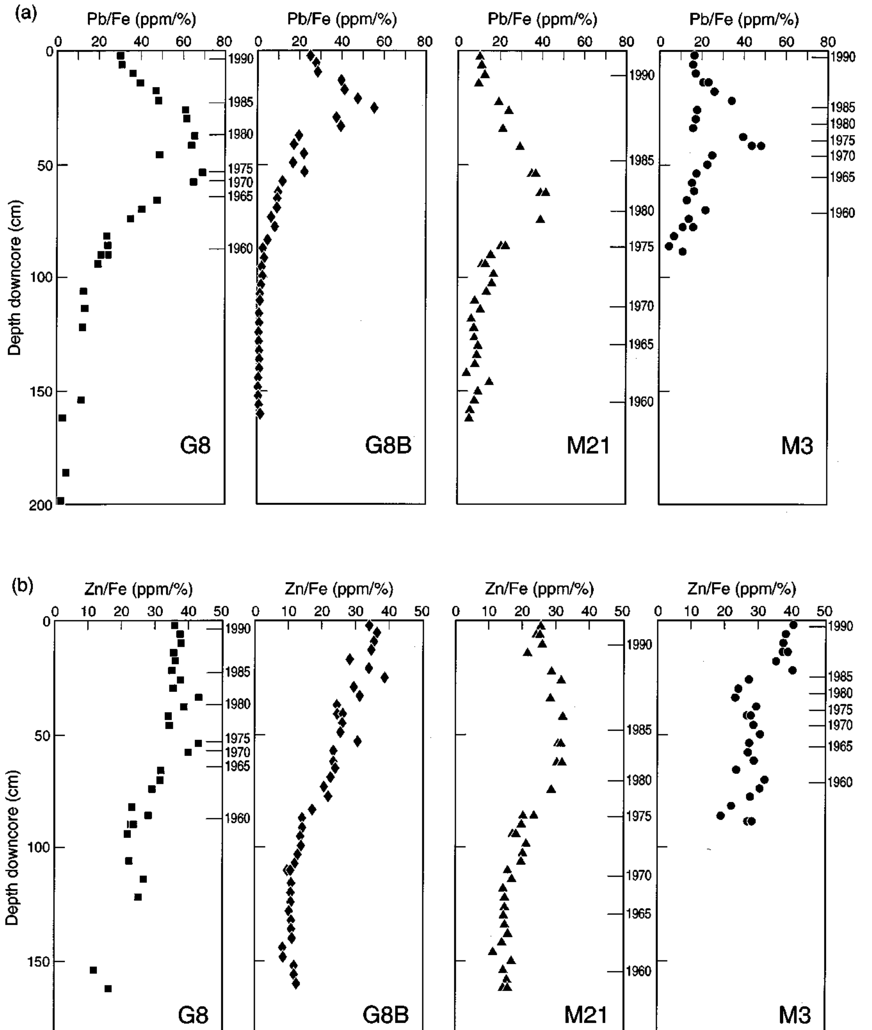

Figure 5 Plots of heavy-metal concentration ratios on a dry weight basis on Ala Wai sediment cores. Radioisotope chronology from Ref. 2: (a) Pb/Fe; (b) Zn/Fe; (c) Cu/Fe.

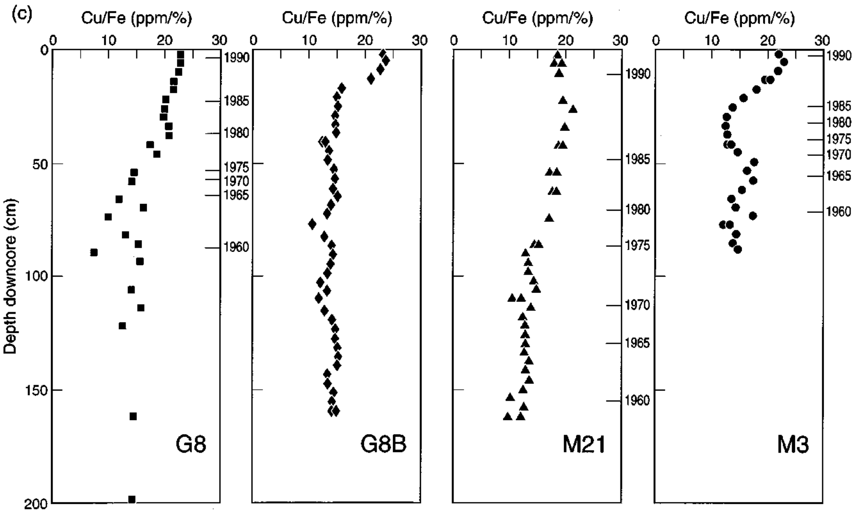

Figure 5 Continued.

sediments near the bottom of the cores, presumably representative of relatively uncontaminated material, is consistent with the hypothesis that a large fraction of the zinc in Ala Wai sediments is of anthropogenic origin. Large increases in zinc are observed in post-1950 sediments in all cores and generally coincide with those of lead, consistently with an automotive source. However, unlike lead, zinc concentrations have not decreased after 1975.

Sediments from the Manoa Stream (Table 5) show an increase in the zinc content from near 230 ppm at the head of the valley to 460 ppm at the mouth of the valley. Big Island (Hawaii) soils[57] range between 80 and 200 ppm zinc, and Koolau tholeiites and Honolulu volcanics contain 100–200 ppm zinc.[11] Thus, sediments from the head of the valley appear to contain a slight anthropogenic component, whereas at least 50% and possibly up to 75% of the peak zinc concentrations throughout the Ala Wai watershed result from anthropogenic activity. A lack of

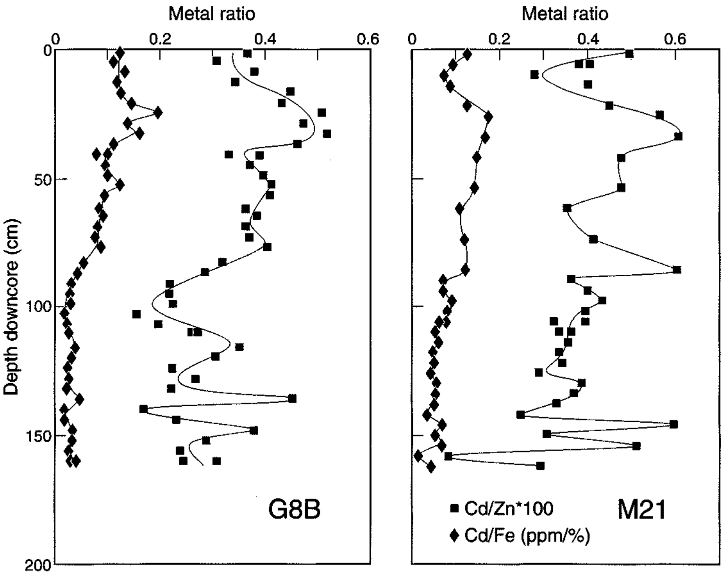

Figure 6 Plots of Cd/Fe and Cd/Zn ratios on a dry weight basis in Ala Wai sediment cores G8B and M21. ◆ Cd/Zn; ■ Cd/Fe (ppm/%).

Table 5 Composition of Manoa Stream sediments

	Sample					
	92–2		92–8		92–3	
	Ave.	SD	Ave.	SD	Ave.	SD
Al[a]	10.35	0.19	12.67	0.08	10.28	0.22
Si[a]	10.23	0.25	15.06	0.11	15.66	0.71
Fe[a]	12.00	0.20	13.81	0.00	11.87	0.32
Ca[a]	0.740	0.028	0.84	0.00	2.04	0.06
Mg[a]	0.972	0.018	0.620	0.004	1.72	0.04
Mn[b]	601	4.2	1740	71	1785	71
Sr[b]	1510	57	1990	15	4540	113
Pb[b,c]	16.6	0.3	37.1	0.8	284	6
Zn[b]	228	4	262	14	454	6
Cu[b]	146	2	186	5	298	4
Co[b]	153	2	156	7	150	0
Ni[b]	337	3	342	8	286	2

[a] Major element concentrations expressed in % dry weight.

[b] Trace element concentrations expressed in $\mathrm{mg/kg^{-1}}$ (ppm).

[c] Lead data for samples 92–2 and 92–8 obtained by solid-source mass spectrometry (SSMS); lead value for sample 92–3 is average of ICP/OES and SSMS.

significant difference between the G8 sediments digested with aqua regia and those from other cores suggests that zinc in Ala Wai sediments is primarily associated with easily leached phases rather than bound in refractory aluminosilicates.

Typically, cadmium displays abundances of 0.1–0.3 ppm in the natural (uncontaminated) environment.[60] Results for cores G8B and M21 (Fig. 6) reveal some contamination of the sediments. Within the $CaCO_3$-rich sediments cadmium is in the 0.1–0.2 ppm range (Table 2) increasing to approximately 0.3 ppm in the bottom-most iron- and aluminium-rich sediments (Tables 2, 3). Concentrations peak near 2 ppm, and return to between 1 and 1.5 ppm in near-surface sediments. Although histosols and other organic-rich soils may contain up to 1.2 ppm cadmium,[60] we believe that peak cadmium concentrations, which coincide with elevated lead and zinc concentrations in core G8B but which occur in more recent sediments in core M21, also reflect anthropogenic inputs. The correlation between cadmium, lead and zinc in core G8B suggests an association with automotive traffic. The similarity of the Cd/Fe and Cd/Zn depth profiles (Fig. 6) of both cores may reflect diagenetic processes (involving sulfide) since these cores exhibit significantly different accumulation rates. However, the Cd/Zn ratio increases more from bottom to top in core G8B than in core M21, although larger relative variations are observed in the latter. Fluctuations in the Cd/Zn ratio may result from multiple sources of these elements. However, the common association of cadmium with zinc in the environment suggests that some of the cadmium input to the canal should also be derived from automobile tire wear.

Copper trends (Fig. 5c) are generally similar in all cores; concentrations reach a maximum of ~250 ppm near the sediment–water interface. In core M21, the maximum occurs approximately 20 cm below the surface, the level to which this core may have experienced coring disturbance. Sedimentary copper levels appear to have increased substantially during the past 10 years, although a gradual increase is also evident in earlier sediments. Because many boats in the marina at the mouth of the canal have their hulls painted with antifoulants containing up to 70% CuO by weight, we expected greater copper concentrations in sediments recovered nearest the marina. However, the relatively uniform spatial distribution of copper throughout surface (i.e. very recently deposited) sediments of the Ala Wai Canal suggests antifoulants may not be the principal source of copper in these sediments.

Table 6 Isotopic results[a]

(a) Pololu Stream

Core interval (cm)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	Pb concen. (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
1	18.443	15.575	38.316	4.11[b]	
3	18.487	15.592	38.457	8.0[c]	0.705867[d]
19	18.337	15.579	38.263	14[c]	0.705850
25	18.3	15.547	38.156	5.0[c]	0.706938
31	18.371	15.574	38.283	5.5[c]	

(b) Leaching experiments	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	Pb concn. (% of total)	$^{87}\text{Sr}/^{86}\text{Sr}$
Haiku Valley soils					
HH-6					
NaAc, pH 5	18.388	15.626	38.392	.034[b]	
HyHCl, pH 5	18.395	15.629	38.396	.045[b]	
HyHCl, pH 3	18.372	15.609	38.325	.73[b]	
(bulk leach)	18.448	15.603	38.419	1.4[b]	
(whole rock)[a]	18.422	15.605	38.387	48.8 ppm[b]	0.709341 ul[d]
Pololu core					
Po 19					
HyHCl, pH 3	18.243	15.575	38.155	4.6[b]	
AmAc, pH 5	18.261	15.584	38.137	0.08[b]	
(bulk pH 3 leach)	18.342	15.579	38.268	95.4[c]	
Po 17					
HyHCl, pH 3 leach	18.319	15.576	38.247	3.3[b]	
HCl	18.298	15.574	38.223	28.8[b]	0.707487
HF res	18.419	15.566	38.349	70.8[b]	0.705863
Calc. 'bulk'	18.381	15.569	38.309	12.1 ppm[b]	
Gonzales-8 core, Ala Wai Canal					
120–124 cm	18.185	15.567	37.933		
152–156 cm	17.966	15.564	37.817		

[a] The Sr isotopic fractionation factor is $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Standard value for SRM 987 is $^{87}\text{Sr}/^{86}\text{Sr} = 0.710237 +/- 0.000022$ (2-σ). Pb isotopes are corrected for fractionation using the values of Todt (W. Todd, R. A. Cliff, A. Hanser and A. W. Hoffman. $^{202}\text{Pb} + ^{205}\text{Pb}$ double-spike for lead isotope analysis. *Terra Cognita* **4**, 209 (1984)) and the total ranges measured on NBS 981 are +/−0.008 for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.008 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 0.030 for $^{208}\text{Pb}/^{204}\text{Pb}$. Errors on samples measured with an ion-counting Daly are approximately twice these amounts. Errors for individual samples are less than the stated uncertainties on standards. Total proceedural blanks are <60 pg for Pb, <120 pg for Sr. Sr abundances measured by isotope dilution are known to better than 0.4%. Pb abundance uncertainties may be greater than 1% because of problems splitting samples for ID/IC when organic residues were present.

[b] From IDMS.

[c] from GFAAS.

[d] Abbreviation: ul = unleached, bulk sample.

[e] From Ref. 24.

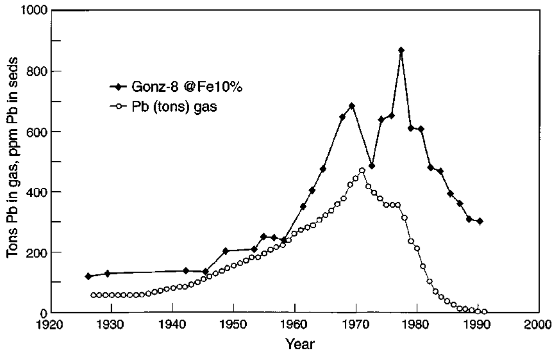

Figure 7 Plot of lead concentrations in sediments from core Gonzales-8 versus leaded gasoline sold on Oahu since the early 1950s. See text for data sources.

Halbig *et al.*[57] report 20–200 ppm Cu in Big Island (Hawaii) soils, with the higher values often near developed areas, whereas Kabata-Pendias and Pendias[60] report a range of 60–120 ppm copper in basalts. Thus, roughly half of the copper in Ala Wai sediments can be attributed to anthropogenic sources with the rest mineralogically controlled. Manoa Stream sediment samples (Table 5), which exhibit copper levels that increase from 150 to 300 ppm downstream, are consistent with this hypothesis as well as with a substantial mid-to-upper watershed source of this metal. Perhaps increased use of copper in plumbing and other commercial products provides a significant source of this metal. Although quite variable, copper consumption in the USA increased approximately 50% between 1975 and 1987.[61] This increase correlates temporally with the increased copper abundances noted in each core.

Elevated concentrations of copper ($\sim$300 mg/kg^{-1}), zinc ($\sim$500 mg/kg^{-1}) and cadmium ($\sim$3 mg/kg^{-1}) were reported by Schropp *et al.*[46] in sediments from Biscayne Bay, Florida, whereas nickel showed no statistically valid enrichment over natural levels. These results are comparable with ours (Table 7) and suggest that development in Honolulu and Miami has followed a similar course and resulted in contamination of natural sediments. Higher enrichments of copper (500–1000 mg/kg^{-1}) and zinc (400–800 mg/kg^{-1}) reported by Bricker[55] in sediments from Narragansett Bay, Rhode Island, reflect the more extensive industrialization of the north-east United States.

Concentrations of cobalt and nickel (Tables 1–4) appear mineralogically controlled. Relatively constant iron-normalized values (not shown) suggest that these elements have not been influenced significantly by anthropogenic inputs.Within iron-rich sediments of the cores, cobalt ranges between 100 and 140 ppm (e.g. cores G8B, M21 and M3) but drops to *ca* 50 ppm

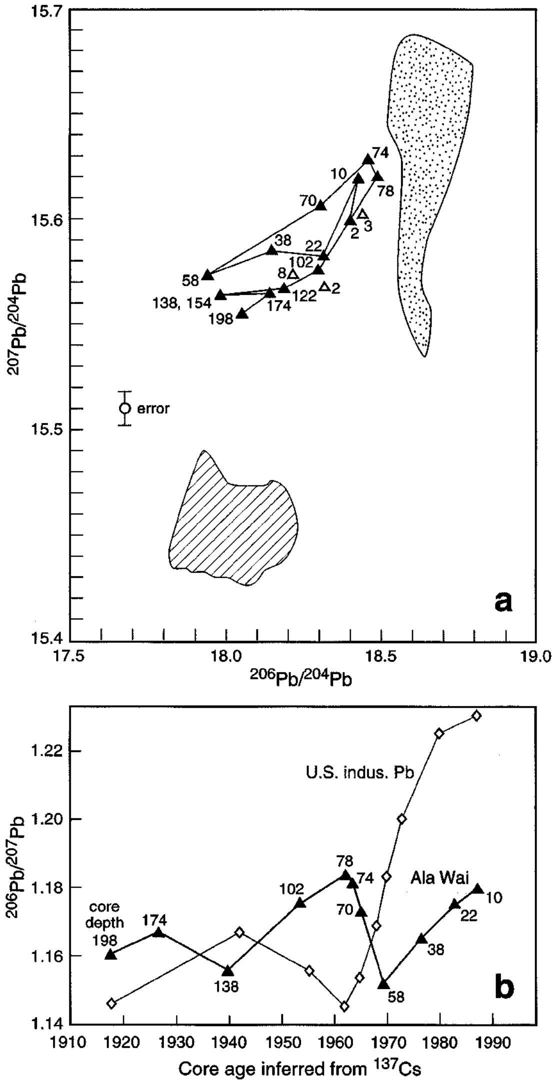

Figure 8 (a) ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb data for Gonzales-8 (closed triangles) and Manoa Stream samples (open triangles). Data are from this work and from Ref. 24. Labels on Gonzales-8 data, linked by lines, are core depths (cm). The diagonally striped field encloses isotopic analyses on Oahu volcanic rocks while the stippled field encloses analyses on North Pacific pelagic sediments (see references in the text). (b) ^{206}Pb/^{207}Pb vs time for Gonzales-8 core samples and average US industrial emissions.[26] Ages for Gonzales-8 core samples are estimated using an average accumulation rate of 2.5 cm/y^{-1}.[2]

in the $CaCO_3$-rich zone of core G8B. In other cores less dramatic differences are observed because of lower $CaCO_3$ abundances compared with core G8B.

Samples from core G8 were digested with aqua regia, which does not completely solubilize refractory aluminosilicates. Hence, the observed cobalt concentrations of 50–80 ppm may represent natural cobalt associated with the readily solubilized mineral assemblage of the sediments. These data are consistent with the 20–80 ppm cobalt reported by Halbig *et al.*[57] in uncontaminated soils. We estimate that approximately 50 ppm cobalt resides within refractory aluminosilicates, assuming the total cobalt content of sediments in core G8 is similar to that in the other cores. Concentrations near 50 ppm are also consistent with the amount of cobalt in basalts.[60] Somewhat higher values in Manoa Stream sediments (150 ppm; Table 5) may result from the presence of pyroxene in these sediments.[25] Pyroxenes typically contain three to four times more cobalt than the basaltic groundmass in which they are included.

Mineralogy probably controls nickel concentrations in the Ala Wai and its watershed. This is illustrated by a near-300 ppm nickel concentration maximum at between 24 and 40 cm depth in core M3. Other metals display local minima at this depth downcore, and thus the peak may represent nickel associated with specific minerals. Concentrations of nickel in this interval are within the wide ranges reported by Halbig *et al.*[57] for soils (150–800 ppm) and by Kabata-Pendias and Pendias[60] for mafic and ultramafic rocks (130–2000 ppm). The absence of a nickel peak in the 'upstream' cores suggests that the hypothesized pulse of pyroxene or olivine may have issued from the Manoa–Palolo drainage under higher flow conditions and that these relatively heavy mineral particles settled preferentially to finer-grained (and anthropogenic metal-enriched) particles. This hypothesis is supported by Fan *et al.*[25] who report an abundance of

Table 7 Comparison of selected heavy-metal concentrations (ppm) in estuarine waters

Area or core		Pb	Zn	Cd	Cu	Co	Ni
G8	Range	3.6–759	43–405	—	77–210	22–85	47–234
	Sediment surface	315	381	—	210	5	180
	Depth of max. concn.[a]	34 cm	54 cm	—	2 cm	74 cm	86 cm
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. concn.	25 cm	25 cm	25 cm	5 cm	41 cm	41 cm
M21	Range	56–458	121–362	—	105–235	81–133	138–277
	Sediment surface	116	279	—	202	108	188
	Depth of max. concn.	62 cm	54 cm	—	26 cm	106 cm	158 cm
M3	Range	53–514	226–421	—	123–230	94–138	175–340
	Sediment surface	173	421	—	230	119	216
	Depth of max. concn.	42 cm	2 cm	—	2 cm	26 cm	34 cm
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		47–6740	105–2270	—	15–216	—	13–82
Harbor basin		44–232	120–165	—	19–22	—	17–22

[a] Depth downcore at which maximum metal concentration occurs.

[b] From Ref. 55; metal values in cores are quoted for top 1 cm of sediments.

[c] From Ref. 46; maximum metal values approximated from figures.

[d] From Ref. 59; range of acid-leachable metal concentrations.

[e] From Ref. 53; metal values in essentially uncontaminated sediments.

[f] From Ref. 54; ranges of metal values are given for cores from the most contaminated area and from the central harbor basin, away from point sources.

pyroxene and olivine in Manoa and Palolo Valley materials and also show a greater abundance of primary minerals 35–37 cm downcore in M3 sediments relative to other cores.

Lead concentrations in rural and semi-rural soils and sediments in Hawaii

Soils in Hawaii contain variable mixtures of anthropogenic, dust and volcanic-derived lead. Soils in watershed areas receiving heavy orographic rainfall most probably contain a greater fraction of atmospherically transported dust and anthropogenic fines than dry areas, while urban soils would contain more locally derived pollutants than rural soils. The three Manoa Stream samples collected from the headwater, middle and mouth of the Manoa Valley illustrate this conceptual framework. These samples, collected from locations increasingly impacted by urban development, contain increasing lead concentrations and isotopic compositions similar to sediments in the Ala Wai Canal. By contrast, as seen in Fig. 9, soils collected in intermountain valleys often contain isotopic evidence of a lead and strontium provenance from older continental crust.[24] In order to deconvolve these signals, we conducted leaching experiments on soils from rural locations.

Soils collected from the upper reaches of Haiku and North Halawa Valleys, close to the spine of the Koolau range on Oahu (Fig. 1), have been exposed to intense orographic rainfall that can introduce lead sequestered on natural dust and on industrial aerosols generated elsewhere. Lead-rich aerosols could have been introduced from automotive emissions generated upwind of the site in the town of Kaneohe during tradewind (prevailing easterlies) conditions, or generated in Honolulu and transported to the area during southerly ('Kona') or south-westerly wind conditions. The Haiku Valley site, on the windward side of the Koolau range, was developed as a US Navy base during World War II, was turned over to the US Coast Guard in 1973, and is currently near the site of a major freeway construction project. One location on the site was contaminated (>400 ppm lead) as a result of human activity, but its isotopic composition (i.e. ^{206}Pb/^{204}Pb$>$19) is distinct from the Ala Wai Canal lead. The Halawa soil was collected nearby but to the west, on the leeward side of the Koolau ridge.

The Haiku and Halawa soils have been shown to be mixtures of volcanic weathering products and eolian dust.[24] Lead concentrations range from about 7 to 49 ppm in samples not obviously contaminated. The Halawa sample has low lead concentrations (10 ppm) but almost all of the lead is of probable anthropogenic origin, as indicated by lead–neodymium–strontium isotopic analyses.[24]

A leaching experiment was carried out on HH-6, which contains 49 ppm lead and a ^{87}Sr/^{86}Sr signature (0.70934 ± 0.00002) indicating a partial continental provenance. The results are shown in Fig. 10. The high lead concentration in this sample is suggestive of contamination but can also be explained by mixtures of natural components.[24] Leaching could test whether any of the lead in this sample has been contributed by the

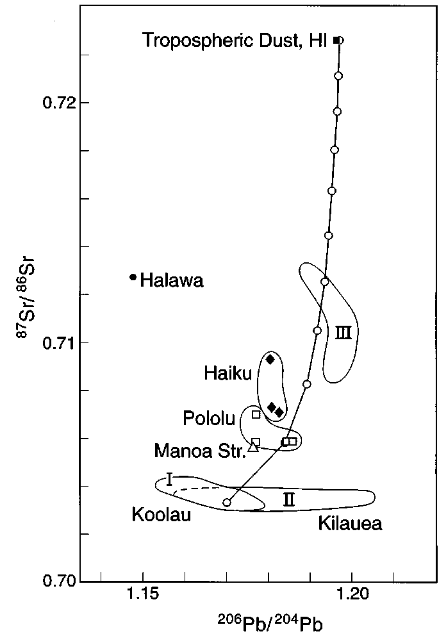

Figure 9 87Sr/^{86}Sr vs ^{206}Pb/^{204}Pb data for Hawaiian soils. The Oahu samples were collected in Manoa, North Halawa and Haiku Valleys. The Hawaii samples were collected north-east of Hilo, Hawaii ('Tropospheric Dust, HI' collected near Papaikou; data from Ref. 24), and from Pololu Valley, Hawaii (this study). Data fields are shown for Hawaiian rocks. Field I shows Oahu and field II shows Hawaii isotopic compositions. Here we have labeled the low-^{206}Pb/^{204}Pb 'Koolau' and high-^{206}Pb/^{204}Pb 'Kilauea' ends of the data fields. North Pacific pelagic sediments are shown in field III. The lead in the Halawa sample is nearly all anthropogenic,[24] while the Haiku and Pololu samples have Sr–Pb systematics consistent with mixtures of locally derived rock and 'pelagic sediment' lead and strontium.

contaminant that is present in soil sample HH-21 (429 ppm lead, ^{206}Pb/^{204}Pb = 19.09[24]) or by other anthropogenic lead.

A hydroxylamine–HCl leach buffered at pH 3 removed 34% of the total lead in the sample. The isotopic composition of the leachable lead has a lower ^{206}Pb/^{204}Pb ratio than the bulk sample. This is not suggestive of contamination by lead with the high ^{206}Pb/^{204}Pb ratio seen in sample HH-21. Since the leachable lead is close to the composition of anthropogenic lead seen in the Ala Wai Canal, the simplest explanation for this sample is that it was contaminated locally by lead-rich aerosols.

The wide variation in soil lead concentrations measured at Haiku (7–49 ppm) does not suggest contamination from a distant source, however, as such contamination would probably affect all of the soils more evenly, because they are within tens of meters of each other and experience virtually identical weather conditions. The higher concentration of presumed anthropogenic lead in

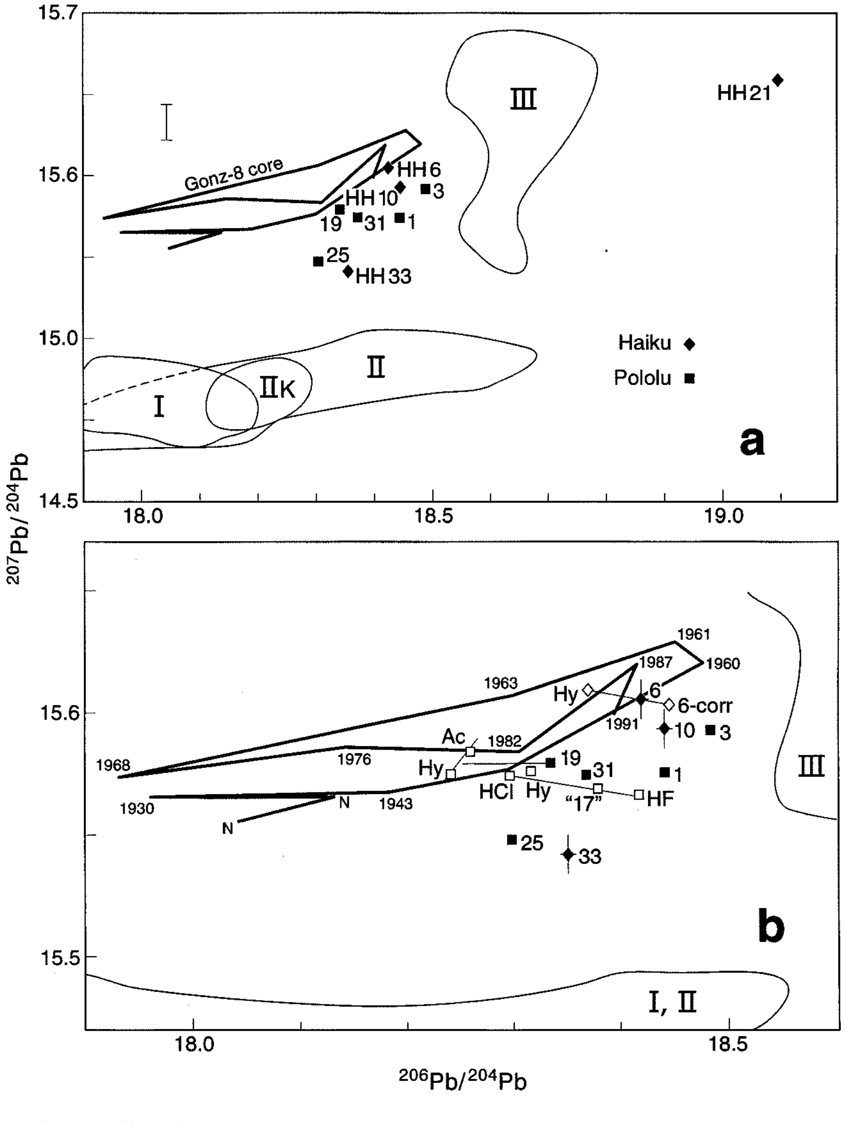

Figure 10 (a) ^{207}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb isotope ratios for unleached Haiku and Pololu samples. The fields correspond to data from Oahu (I), Hawaii (II), Kohala Volcano on Hawaii (IIK), and North Pacific pelagic sediments (III); data sources are cited in the text. (b) Enlargement of (a) showing the route taken by leaches and residues of Pololu samples 17 and 19 and Haiku sample 6. Parts of the fields shown in (a) are included for reference.

HH-6 might have been derived from very localized traffic and wind patterns on the site. If the ‘anthropogenic’ component is subtracted from this sample, the corrected ‘natural’ lead concentration would be 31 ppm. This is still much higher than would be produced by the weathering of Hawaiian rocks, but may be within the range of concentrations possible if a large atmospheric dust component is included. The strontium isotopic composition and the presence of a strong quartz XRD line[24] support the latter interpretation. For example, an extremely dust-enriched soil, collected north of Hilo on the island of Hawaii (Rollin Jones, UH School of Tropical Agriculture, personal communication), contains 55 ppm lead, a strong quartz XRD peak and $^{87}Sr/^{86}Sr = 0.72255$.[24] The anthropogenic overprint of about 16 ppm would average out to about 0.6 ppm/yr^{-1} for the period 1945–1980, which is similar to the average non-urban deposition rate calculated by McMurtry *et al.*[56] Nonetheless, nearby surface soils varied by an order of magnitude in their total lead concentration, suggesting that lead deposition is extremely non-uniform, as suggested by Eschelman.[5]

We are currently studying a core taken in Pololu Valley, a rural location on the North Kohala peninsula of the island of Hawaii (Fig. 1).[63] The core was recovered near the shoreline of a wetland fed by a small stream that drains the valley. The valley itself is currently unoccupied but contains the scattered remains of an old farm, long since abandoned. The valley wetlands are accessed by a trail approximately 0.75 km long, starting at the end of a paved road at the top of 130-m-high cliffs overlooking the valley.

Measurements of lead isotopes on unleached samples, shown in Fig. 10(a), can be interpreted as attributable to a mixture of volcanic and dust-derived lead. There is no unambiguous evidence of anthropogenic lead in the ‘bulk’ isotope ratios, but the concentration profile (Fig. 11) shows a recent increase suggestive of contamination. Leaching experiments can test between two hypotheses: (1) The concentration profile is the result of natural variations in chemical components in the soil, possibly influenced by bioturbation and chemical mobilization; (2) The profile results from the deposition of anthropogenic lead used within the valley or transported to the valley by rain or surface water.

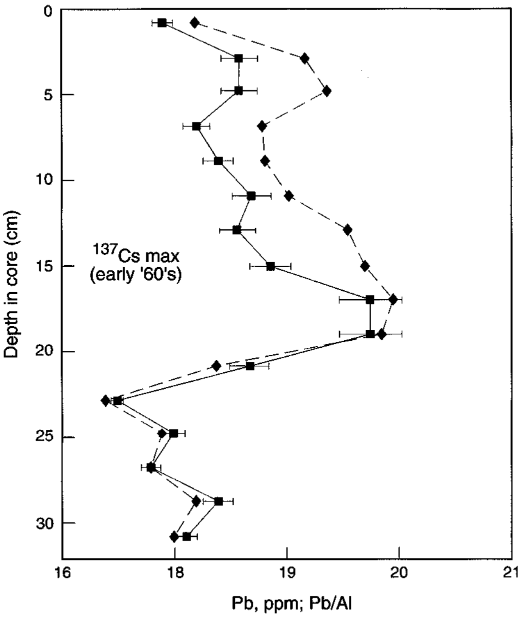

Figure 11 Plot of lead concentrations in ppm (solid line) and Pb/A1 (10 × ppm/% wt; dashed line) for Pololu Stream core samples.

$^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ isotopic results for leaching experiments on samples Pololu-17 and Pololu-19 are shown in Fig. 10(b). Both samples contain leachable lead (ammonium acetate, hydroxylamine–HCl and 1 M HCl) that is lower in $^{206}Pb/^{204}Pb$ than the bulk sample and perhaps somewhat higher in $^{207}Pb/^{204}Pb$. The leaches lie within or very close to the field of Ala Wai G8 anthropogenic lead. A quantitative recovery of this leachable lead in Pololu-17 by isotope dilution shows that ~0.3% of the estimated total lead (total lead is based on graphite furnace AA analysis) was removed with a pH of 3, hydroxylamine–HCl leach and ~28% by a 1 M HCl leach. Thus, 72% of the lead remained in the solid fraction and was subsequently decomposed in HF/NHO_3. The isotopic composition of the residue can be explained as a mixture of volcanic- and dust-derived lead. A continental signal is also suggested by the $^{87}Sr/^{86}Sr$ measured on the residue from leaching (0.70585), which is considerably higher than values measured in Hawaiian volcanic rocks and which should also be free of strontium sorbed from seaspray; the latter would have been removed by leaching.

Lead in the HCl and hydroxylamine–HCl leaches is not likely to be present as mixtures of natural components. The lead isotope measurements tended more towards those on the Ala Wai Canal anthropogenic field deposited approximately during the 1950s, rather than towards those of the 'rock' or 'dust' fields. $^{87}Sr/^{86}Sr$ measured on the 1 M HCl leach of Pololu-17 is more radiogenic than that measured on the residue. If the higher $^{87}Sr/^{86}Sr$ value measured on the leach was caused by an increasing dust component in the leach, then the lead isotopes ratio should move closer to the dust field unless the lead is overwhelmed by an anthropogenic component. The 1 M HCl leach on this sample is more easily explained as containing anthropogenic lead and a mixture of strontium from seawater, dust, and volcanic sources.

Measures of ^{137}Cs on the Pololu Stream samples[63] suggest the 17 and 19 cm core sections were deposited during the mid to late 1950s. The two model ages produce broadly similar results. Interestingly, the increase in included anthropogenic lead concentration occurs prior to the peak lead emissions in the USA and in Hawaii during the 1960s and 1970s, when automobile mileage was higher than during the 1950s and when higher-performance engines used gasoline with higher concentrations of alkyl-leads. Because the lead maximum does not coincide with peak Hawaii or US usage, we believe that anthropogenic lead was probably introduced locally as a result of farming activities that occurred when the valley was inhabited.

CONCLUSIONS

This study has assessed the influence of anthropogenic concentrations of lead and other metals in sediments of the Ala Wai Canal. Our results are also indicative of the quality of waters draining into the Ala Wai Canal and provide both a measure of the retention of metallic species within sediments and historic trends of metal inputs. Our work has shown that, as observed elsewhere, significant quantities of heavy metals are transported through stream and street runoff and are subsequently deposited in sediments when they enter estuarine water. There is also evidence of a contribution from atmospheric fallout sources that are resolvable using stable isotopic techniques.

Profiles of lead provide historical records of alkyl-lead fuel additives in automobiles and clearly show the decreased anthropogenic flux of this element on Oahu since the implementation of legislation in 1975 restricting its use. Based upon concentrations and stable-isotope data, most of the lead in post-World War II sediments appears to be derived from automotive use and enters the canal through street runoff. Stream sediment data corroborate this conclusion.

The zinc and cadmium concentrations in the sediments probably reflect increased automotive traffic in Honolulu since the creation of the Ala Wai Canal, particularly since 1960. These two elements, which enter streams and the canal primarily via street runoff, are probably derived in part from the wear of tires on road surfaces. Approximately half to two-thirds of the zinc is of anthropogenic origin, whereas for the cadmium the proportion may exceed 90%.

Sedimentary profiles document a particularly notable increase in the flux of metals during the past ten years. Unlike lead, zinc and cadmium, whose increased fluxes over time are largely attributed to automobile traffic, copper may be derived from other sources such as plumbing, gutters, etc. Concentrations of copper in Manoa Stream sediments are more consistent with residential and commercial sources of copper than antifoulant boat paints. Approximately 50% of the copper in near-surface sediments is natural.

Nickel and cobalt do not appear to have been impacted by anthropogenic activity, although the nickel concentration in core M3 indicates a significant input around 1980. Mineralogical control can be invoked to account for nickel and cobalt concentrations and most of their variability.

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

Sedimentary materials collected in rural locations exhibit small but measurable concentrations of anthropogenic lead. Lead isotopes measured on leachable lead in soils and sediments indicate that up to one-third of the lead in some samples that are often referred to as having 'baseline' concentrations actually exhibits anthropogenic lead overprints. These overprints may be the result of nearby human activity or may be long-traveled aerosols carried in on the prevailing winds. Our measurements on samples from the Haiku and Pololu Valleys are more consistent with local contamination because (1) soils have widely differing lead concentrations that would be difficult to explain using a pervasive, distant aerosol model; and (2) the timing of the peak in anthropogenic overprint in Pololu did not match the peak period of alkyl-lead use either in Hawaii or in the Northern Hemisphere.

This study has provided a historical record of anthropogenic activity in urban and semirural Honolulu and in one rural location on the island of Hawaii. Because complete sedimentary records were obtained from the Ala Wai Canal, including relatively uncontaminated sediments at the bottoms of several cores, results of our study can be used as a comparative basis to evaluate the effect of anthropogenic activity on other watersheds and estuaries in Hawaii and other sub-tropical volcanic island environments.

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