Isotopic Clues to Sources of Natural and Anthropogenic Lead in Sediments and Soils from O'ahu, Hawai'i[1]

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ABSTRACT: Stable Pb isotopes, Pb elemental concentrations, and, for some samples, Nd and Sr isotopes and concentrations have been analyzed on soils and on stream and estuarine sediments to evaluate the provenance of major inputs of Pb to the O'ahu, Hawai'i, environment. Core samples from the Ala Wai Canal, a major estuary draining urban Honolulu, preserve a historical record of anthropogenic lead input that peaked during the 1970s, the period of heaviest leaded-gas usage in Hawai'i. The timing of the Pb concentration peak and the simultaneous rise in Zn and Cd concentrations, two elements used in tire vulcanization, strongly suggest that the source of this Pb was tetraethyl Pb used in leaded gasoline. The changing Pb isotopic composition in these sediments reflects changing sources of ore from which tetraethyl lead was produced. These isotopic signatures can be used to fingerprint anthropogenic Pb elsewhere on O'ahu. Although leaded gasoline has been phased out of production in the United States and in many other countries, elevated amounts of lead continue to deposit from the Ala Wai Canal's watershed. Sediment samples from Mānoa Stream, a principal tributary, suggest that relatively uncontaminated sediments are eroded from its headwaters while a source (or sources) of lead continues to discharge into the stream as it nears the south end of Mānoa Valley. The isotopic composition of this lead is similar to that measured in recently deposited sediments cored from the Ala Wai Canal. An atmospheric dust-enriched soil collected on the island of Hawai'i contains elevated Pb concentrations (55 ppm) and a Pb isotopic composition similar to North Pacific pelagic sediment. In addition, this sample contains unradiogenic Nd ($\varepsilon = -6$) and radiogenic Sr ($^{87}Sr/^{86}Sr = 0.722527$) confirming an old, continentally derived provenance. Soils collected in Ha'ikū Valley, a windward O'ahu valley subject to high rainfall, contain variable Pb concentrations and Sr, Nd, and Pb isotopes trending toward the isotopic composition of the dust-enriched sample. This confirms that the Ha'ikū Valley soils contain an aerosol component. Soils enriched in this component could have natural lead concentrations higher than soils made up solely of weathered Hawaiian rocks. Hawai'i's soils and sediments have naturally derived variations in Pb concentration that are caused by differences in provenance and degree of weathering. Superimposed on this natural concentration variation is a variable anthropogenic signal. These variations should be factored into environmental monitoring programs.

LEAD (Pb), AN ENVIRONMENTAL toxin, has been used extensively by humans since the days of early civilizations. Since the mid-twentieth century, its wide dispersion in the environment has resulted from its use as an antiknock agent in gasoline. Although leaded gasoline has been nearly phased out in the United States, leaded gasoline emissions continue from other countries. Some lead continues to be released to the environment in the United States from a variety of sources as well (i.e., leaded paint released from older homes, discarded storage batteries, plumbing fixtures, and emissions from coal-fired power plants and metal smelting). In addition to current emissions, thousands of tons of lead that were used to make leaded gasoline remain in the environment. The areas that are likely repositories for this lead should be identified and their levels of lead assessed.

During the 1950s–1980s, Oʻahu's population, auto mileage, and gasoline consumption increased dramatically (Eshleman 1973, Armstrong 1983). De Carlo et al. (1992) and De Carlo and Spencer (1995) have measured high (up to ca. 750 ppm) levels of lead in estuarine sediments in the Ala Wai Canal, an artificial estuary draining urban Honolulu, with peak concentrations coinciding with the years of heaviest leaded gasoline consumption. Likewise, lead levels may be anthropogenically elevated in soils from rural Oʻahu (mean = 18 ppm [Steven Spengler, pers. comm.]) and in the city of Hilo (mean = 6.4 ppm [Halbig et al. 1985]) on the island of Hawaiʻi relative to soils collected in rural locations on the same island (mean = 4.4 ppm [Halbig et al. 1985]).

Isotopic and chemical studies can distinguish the natural variation in lead baseline from contamination. Lead isotopes have documented the concentrations and sources of anthropogenic lead in atmospheric aerosols (Settle and Patterson 1982, Patterson and Settle 1987, Sturgis and Barrie 1987, Hamelin et al. 1989, Maring et al. 1989, Church et al. 1990), nearshore ocean basins (Ng and Patterson 1982), lakes (Flegal et al. 1989, Graney et al. 1992, Ritson and Flegal 1992), rivers, estuaries, and streams (Elbaz-Poulichet et al. 1984, Trefry et al. 1985, Erel et al.

1991), deep-water sediments (Flegal and Patterson 1983, Patterson 1987), and freshwater sediments (Shirahata et al. 1980).

We therefore evaluated the concentrations and stable isotopic compositions of lead from both natural and human (anthropogenic) sources in soils and sediments from several sites on Oʻahu, a tropical ocean island that has undergone rapid development. The Ala Wai Canal is a highly polluted urban estuary that contains a stratigraphic record of lead pollution resulting from increasing urbanization and the use of leaded gasoline in urban Honolulu. The Pb isotope record preserved in these sediments can be used to test for the presence of anthropogenic lead with a similar isotopic composition elsewhere on Oʻahu and discriminate these Pb inputs from other natural or anthropogenic signals. We collected samples from several rural locations on Oʻahu to estimate the natural and anthropogenic contributions to the Pb baseline away from urban development.

Pb in the Hawaiian Environment

To survey environmental lead contamination accurately, the Pb intrinsic to a locality must be discriminated from lead contamination. This baseline must be sensitive to variables that affect the soil geochemistry. In the state of Hawaiʻi, a tropical ocean-island environment, these include the average rainfall and prevailing winds that influence the amount of aerosol deposition, some of which originates in northeastern Asia (Jackson et al. 1971, Dymond et al. 1974, Duce et al. 1980); the extent of weathering, which affects the (variable) mobility of elements in residual soils; and the history of land use in an area.

Soils and terriginous sediments typically derive most of their naturally occurring lead from the rocks that decompose to form them. On Oʻahu, the principal rock types are shield-building basalts that contain low (ca. 0.2–1 ppm) lead concentrations and "post-erosional" Honolulu Series volcanics (i.e., Diamond Head, Punchbowl, Koko Head, Salt Lake Crater, etc. [see Stearns 1939 or Winchell 1947]) that, based on comparative trace element concentrations, might in-

clude up to an order of magnitude more Pb than the shield tholeiites (Roden et al. 1984, Tatsumoto et al. 1987). Although volumetrically insignificant compared with the size of the shields, these late-stage volcanics erupted from numerous vents in the southeastern Ko'olau range and draped (or built almost entirely, in the case of Hawai'i Kai) large areas of eastern O'ahu with lava and ash deposits (Stearns 1939). Finally, carbonate (reef) deposits are present in some areas of O'ahu, such as downtown Honolulu and Waimānalo, that were submerged during former high stands of the sea. Uncontaminated carbonate reef should contain sub-ppm quantities of Pb (Shen and Boyle 1987).

In addition to the Pb contributed from decomposing bedrock, naturally occurring Pb is contributed by atmospheric dust that transports weathered rock debris to the Islands from elsewhere (Jackson et al. 1971). Loess, a likely component in dust, contains ca. 15–20 ppm Pb (Taylor and McLennan 1985). Open-ocean dust deposition in the central Pacific basin has been estimated to be ca. 0.3–0.4 cm/1000 yr (Duce et al. 1980, Tsunogai and Kondo 1982, Uematsu et al. 1983) and contributes to the formation of pelagic sediments, which can contain > 30 ppm Pb (Ben Othman et al. 1989). On the Hawaiian Islands, dust concentrations in the soil can locally be higher than the open-ocean average because dust is scavenged by orographic rainfall and deposited in greater quantities in wet areas. This is especially true in intermountain basins, where dust can make up a sizable fraction of the soil (Jackson et al. 1971). Dust-enriched soils could therefore contain higher natural lead concentrations than soils made up of volcanic-rock debris alone.

Although the island's initial rock (and dust) chemistry constrains the natural Pb baseline, chemical or mechanical mobility during tropical pedogenesis determines how fast elements are removed to the sea. Metals such as Mg, Ca, K, Na, and silica are dissolved rapidly out of the rocks and transported downstream, whereas heavy metals (including Pb) and rare-earth elements (REE) are at least temporarily enriched in the soil residue, whose inorganic components are enriched in aluminum and iron hydroxides, minerals highly surface-reactive to heavy metals (Hayes and Leckie 1986, Erel et al. 1990). Thus, Pb and other heavy metals concentrations might be at least temporarily enriched in developing soils relative to the Pb concentration in the host rock (Halbig et al. 1985), exclusive of anthropogenic input. Over time, however, even heavy metals are leached out of soils by extreme, wet, tropical weathering.

Superimposed on the "geologic" baseline could be a variable anthropogenic lead signal. We hypothesize that much of the anthropogenic lead present on O'ahu was introduced locally by automotive use and that it is pervasive in heavily urbanized corridors, as shown by Jernigan (1969) and Eshleman (1973). Away from traffic corridors, anthropogenic lead levels probably show locally high concentrations near point-sources of heavy metal pollution, such as shipyards and fuel storage areas (both civilian and military), and near the outfalls of streams or trenches that drain polluted watersheds. Industrial contaminants can also be brought in as aerosols from distant sources (e.g., Maring et al. 1989) and potentially can raise baseline Pb concentrations. Finally, Pb has been released to the soils from chips of pre-1960s vintage paint, which can contain up to 50% Pb (Dr. P. Heu, State of Hawai'i Department of Health, pers. comm.). Paint-derived Pb is probably present in soils found in neighborhoods developed before the 1960s. It can be released as homes are remodeled, as a consequence of the natural weathering and peeling of paint, or during demolition of older structures.

MATERIALS AND METHODS

Stream and estuarine sediments were collected from the Ala Wai Canal and its watershed in Honolulu on the southern side of the island of O'ahu (Figure 1). The Ala Wai Canal is an artificial estuary developed by the U.S. Army Corps of Engineers in 1927 and currently drains a highly developed residen-
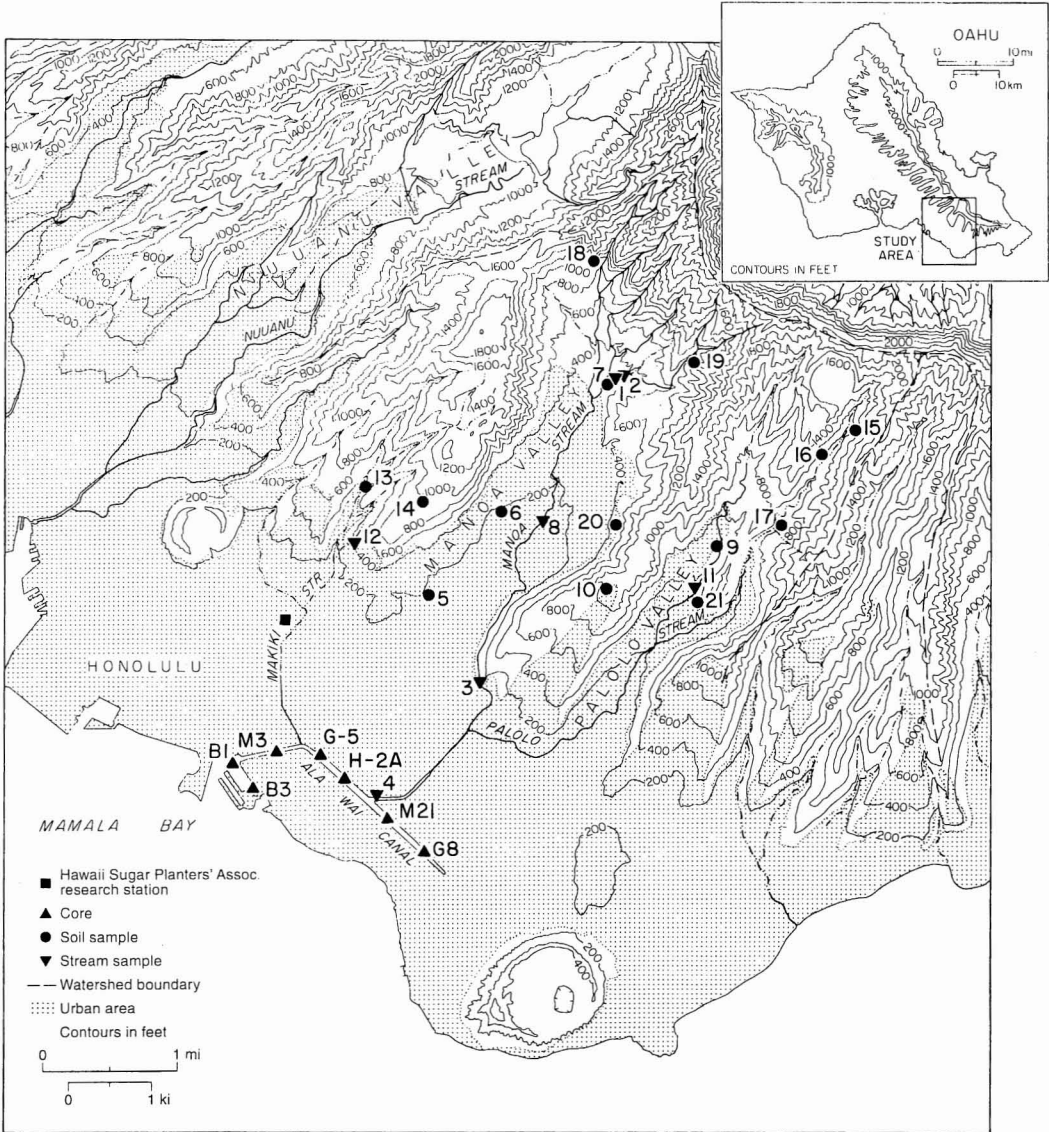
FIGURE 1. Map of the Ala Wai Canal watershed with an inset map showing its location on O'ahu. The samples analyzed from the canal and Mānoa Stream (Table 1) were collected at locations 2, 3, and 8 along Mānoa Stream and at location G-8 in the Ala Wai Canal.

tial and commercial district that has been subjected to heavy auto use. Makiki, Mānoa, and Pālolo Streams and numerous drainage culverts empty into the Ala Wai Canal. Sedimentation rates are between 1 and 4 cm/yr, and the canal exhibits highly anoxic conditions that have minimized bioturbation.

Although the canal has been dredged several times since its creation, we obtained a core (Gonzalez-8) collected in a location that had not been dredged and thus contains a complete history of canal sedimentation. All canal data presented in this paper are from the Gonzales-8 core. A fuller description of

the Ala Wai Canal can be found in Laws et al. (1993).

Canal sediments were collected using precleaned 5-cm-diameter DSDP core-liners that were driven into the sediment by hand from a small boat. Sediment tubes were frozen, sawed longitudinally, and then sectioned along the tube axis to produce sample intervals of about 4 cm for chemical and dating analysis. Three sediment samples from Mānoa Stream (one from the headwaters and two farther downstream [see Figure 1]) were collected using a hand trowel, wet-sieved, and size-fractioned. Samples were homogenized, sieved, and freeze-dried. Care was taken to exclude material that contacted the core-liner or saw blade. Subsequent handling was done under Class-100 conditions. Chemical analyses were made on the < 45-μm fraction of these sediments.

Canal samples analyzed for lead isotopes were taken from splits that had been analyzed for total chemical analysis by inductively coupled plasma optical emission spectroscopy (ICP/OES) and atomic absorption spectroscopy (AAS) and analyzed for ^{210}Pb and ^{137}Cs for dating purposes. Analytical procedures and blanks for these other techniques have been reported by De Carlo and Spencer (1995) for ICP/OES and AAS and by McMurtry et al. (1995) for ^{210}Pb and ^{137}Cs.

We collected soil samples near the heads of Ha'ikū and North Hālawa Valleys, close to the spine of the Ko'olau range on O'ahu (Figure 2). The Ha'ikū Valley site is on the windward side of the Ko'olau range and was developed as a U.S. Navy base during World War II, turned over to the U.S. Coast Guard in 1973, and is currently near the site of a major freeway construction project. The Hālawa soil was collected in a similar location relative to the spine of the Ko'olaus but on the lee side of the ridge. A sample from the island of Hawai'i, near Hilo, is highly enriched in eolian soil-derived dust and was provided by Rollin Jones (University of Hawai'i Department of Tropical Agriculture). We have analyzed it to help define the isotopic composition of the dust-enriched end-member in Hawaiian soils.

Ha'ikū soils, collected by Woodward-Clyde Geological Consultants, and the Hālawa soil, collected by E.H.D., were sampled using precleaned disposable hand trowels and placed into precleaned glass jars. Our sample selection was based on soil analyses (including lead concentrations) provided by Woodward-Clyde; we analyzed samples spanning the range of lead concentrations measured at the site.

Soil samples were opened and handled in the University of Hawai'i School of Ocean and Earth Science and Technology (SOEST) isotope geochemistry clean laboratory. They were sieved to remove large roots and pebbles but were then processed without further attempt to separate organic from nonorganic components. Samples were dried overnight at 95°C and ground to a powder in a precleaned alumina mortar. The powders were x-rayed to determine their mineralogy and to look for quartz fragments. Quartz can occur in Hawaiian soils as a result of aerosol dust input from continental sources (Jackson et al. 1971) or by inclusion of hydrothermal quartz found near the Ko'olau or Wai'anae calderas (Macdonald and Abbott 1970). The soil samples from this study were collected in the vicinity of the Ko'olau caldera.

To obtain Pb abundances on carbonates formed before humans began using Pb, we collected 0.5-myr-old coral skeletal fragments from the Ka'ena-stand reef (Stearns 1974) and carbonate rock fragments from a nearby eolianite deposited on the 0.125-myr-old Waimānalo-stand reef (Sherman et al. 1993) at Ka'ena Point, O'ahu. These samples were collected by first breaking off several centimeters of material to expose a fresh rock surface and then collecting unweathered material from the interior. Samples were coarsely broken up (ca. 2- to 4-mm fragments) and hand picked under a binocular microscope to exclude altered or contaminated material.

These samples were then analyzed by thermal ionization mass spectrometry (TIMS) to determine their Pb isotopic compositions (ICMS) and their Pb concentrations by isotope dilution (IDMS). For ICMS and IDMS measurements, ca. 40–50 mg of each sample was chemically processed for Pb (and selected
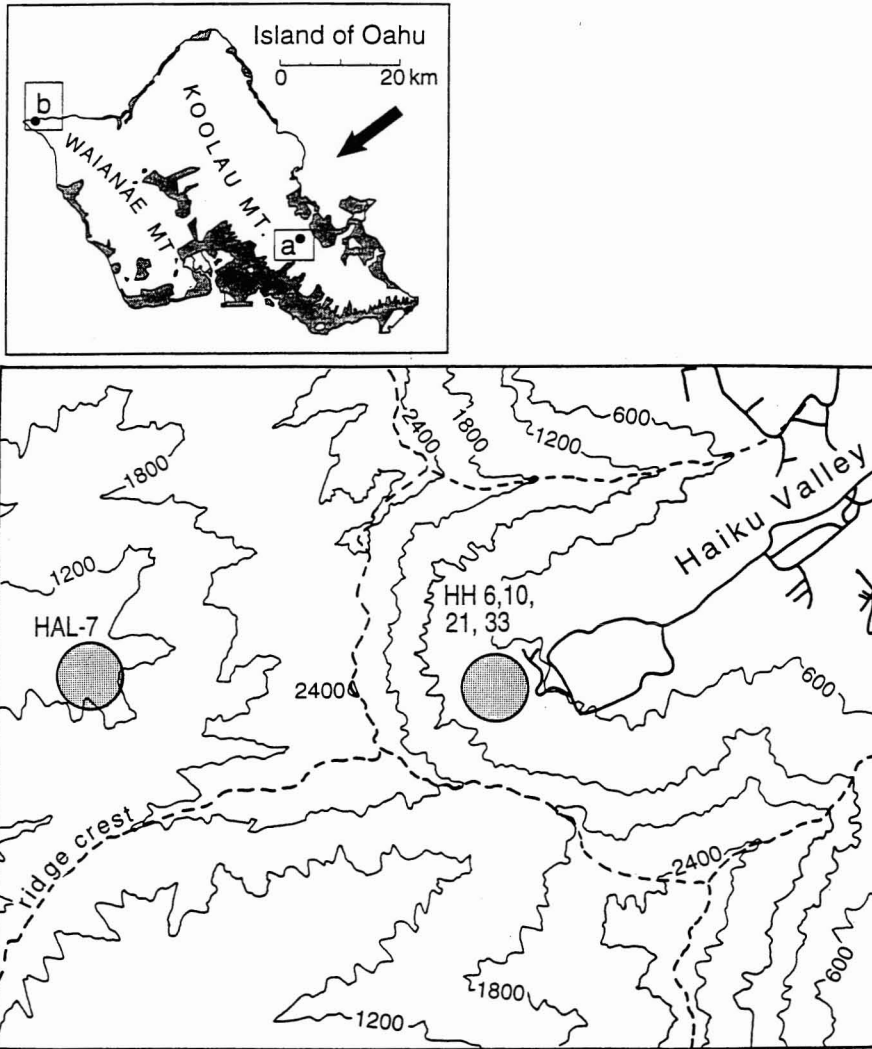
FIGURE 2. The top map is of Oʻahu, Hawaiʻi, showing urban, military, and industrial areas in dark stipple (taken from Armstrong 1983). The arrow indicates the prevailing wind direction for most of the year (North Pacific easterlies). Box *a* notes the location of the Haʻikū/Hālawa Valley samples and box *b* the location of the Kaʻena Point samples. The larger topographic map (bottom) shows sample locations (shaded circles) in Haʻikū and North Hālawa Valleys.

samples for Nd and Sr) following the clean protocols developed in the SOEST isotope geochemistry laboratory (Mahoney et al. 1991). In addition to the normal $HF : HNO_3$ digestion usually used to decompose silicates, these soil and sediment samples were subjected to an attack by several milliliters of hot $HCl : HNO_3$ for 24 hr in a tightly capped

15-ml FEP beaker to decompose organic matter.

After the $HF : HNO_3$ and aqua regia steps, samples were redissolved in 2N HCl and split ca. 10 : 1; the smaller split was then spiked with a ^{206}Pb tracer for IDMS. During this procedure, some solution usually stuck to the walls of the original sample beaker, probably

because of residual organic material. Because of this recovery and splitting problem, which was never completely solved, our IDMS measurements are slightly less accurate than the 1% value reported by Mahoney et al. (1991) for silicates.

Total Pb blanks reported in our laboratory for silicate analyses are routinely 20–40 pg (Mahoney et al. 1991) or less, and similar values were measured during this study. Nonetheless, we estimate that our blanks on sediments and soils could be somewhat higher because of the additional time and handling required by these samples. Although the additional reagent blank would only be a few picograms (our reagents used for analyzing Pb isotopes contain subpicogram Pb concentrations), the additional handling required by "difficult" sample material (i.e., sample sticking to the sides of the beaker, etc.) could add to the sample blank even though it did not show up in the actual "blank" (control) analysis. In any case, even if our blank were doubled, this would not likely be a significant source of error in our ICMS measurements. For example, a 45-mg sample containing 3.3 ppm Pb would have a sample/blank ratio of about 2000 if it included an 80-pg blank. The uncertainty in the isotopic composition measurement due to this much blank would be far smaller than our analytical uncertainty. The only sample for which an IDMS (concentration) measurement would be seriously in error would be the Ka'ena Point coral fragment; a 10–40% reduction in its actual Pb concentration would be appropriate for a 10- to 80-pg blank.

Samples were analyzed using the single–Re filament, silica gel–phosphoric acid technique. Mass spectrometric procedures used in the SOEST isotope geochemistry laboratory have been described in Mahoney et al. (1991).

Stable Isotopes as Clues to the Origin of Pb Components

To make use of isotopes to discover the sources of anthropogenic and natural lead present in an area, the various input signals must be characterized. The volcanic units on O'ahu, the Ko'olau and Wai'anae shield volcanoes and the Honolulu Series posterosional volcanics, have been analyzed for Pb, Nd, and Sr isotopes (Roden et al. 1984, Stille et al. 1983, 1986); these data from the literature are shown as fields in Figures 3–6.

The atmospherically transported silicate dust component in Hawaiian soils is isotopically distinct from Hawaiian lavas. Dymond et al. (1974) and Jackson et al. (1971) reported Sr isotope ratios and Rb-Sr concentrations measured on mineral separates collected from soils on O'ahu located in areas subject to high orographic rainfall. Sr isotope ratios in these mineral separates ($^{87}Sr/^{86}Sr$ ca. 0.722) are too high to evolve from Hawaiian igneous rocks (ca. 0.7033–0.7045) and require an old continental source. North Pacific pelagic sediments, however, are derived primarily from this dust; Figure 3a shows their lead isotope field (Chow and Patterson 1959, Ben Othman et al. 1989; D. G. Waggoner, pers. comm.). Data for these sediments fall at higher $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios than those of O'ahu's volcanic rocks.

Hawai'i soils that are mixtures of native volcanic weathering products and continental silicate aerosols should, therefore, have isotopic compositions lying on mixing lines defined by these end-members. It may be possible to model the aerosol input if suitable constraints can be placed on the isotopic compositions, elemental concentrations, and relative mobility of the elements. In addition, soils containing a silicate aerosol component should have attributes such as quartz fragments, discernible by X-ray diffraction analysis, derived from dust; such information could act as parallel lines of evidence of a pervasive silicate aerosol component (Fan et al. 1995).

Anthropogenic lead mined in the United States has Pb isotope ratios that fall, for the most part, into different fields than those of mixtures of lead derived from Hawaiian volcanic rocks and natural silicate aerosols. To a first approximation, anthropogenic Pb 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." These iso-

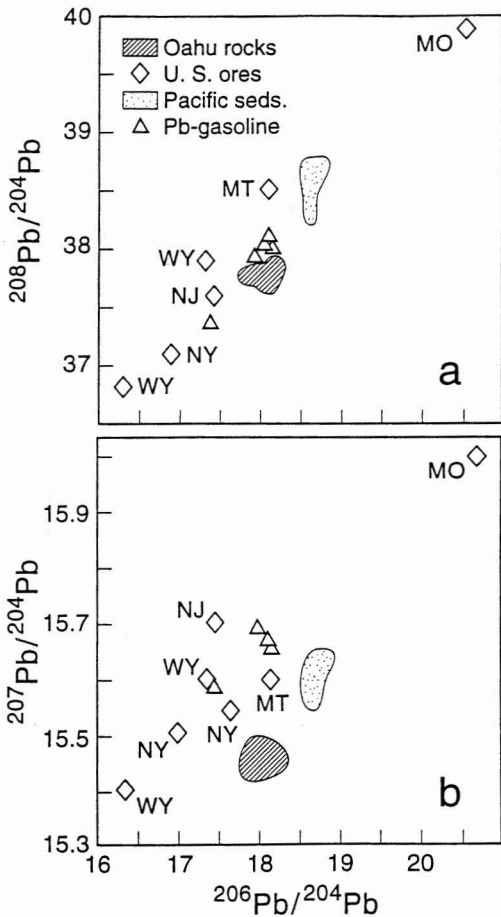FIGURE 3. (a) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and (b) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ data for selected ore bodies in the United States (open diamonds with state locations, from Facchetti et al. 1982). O'ahu volcanic rocks define a diagonally lined field (data taken from Stille et al. 1983, 1986), North Pacific Ocean sediments define a stippled field (data taken from Ben Othman et al. 1989, Chow and Patterson 1959; and D. G. Waggoner, unpublished Leg 136 ODP data), and gasolines sold in southern California during the 1960s are shown as triangles (data taken from Chow and Johnston 1965).

topic compositions can be seen in Figure 3. Even when there is overlap between the fields of naturally occurring and anthropogenic (ore) lead in the $^{206}Pb/^{204}Pb$ ratio, these particular ore data often have small but measurable differences in, for example, $^{207}Pb/^{204}Pb$ for a given $^{206}Pb/^{204}Pb$ (Figure 3b).

In addition to measuring their Pb isotopes, we have analyzed selected samples for Nd and Sr isotopes. Nd, a rare-earth element, should help identify material containing an atmospheric dust component because dust would have a history of Sm/Nd depletion different than that of the Islands (i.e., ocean-island basalt formed in the earth's mantle versus dusts formed from old continental crust) and may have an isotopic signature less radiogenic than that of O'ahu volcanic rocks. As shown by Jackson et al. (1971), the $^{87}Sr/^{86}Sr$ ratio of atmospheric dust is highly radiogenic compared with that of Hawaiian rocks and should provide evidence for an aerosol (continental) component. Finally, samples containing a carbonate component should have $^{87}Sr/^{86}Sr$ (ca. 0.709) dominated by a seawater signature, but because pristine reef carbonate has very low Nd and Pb concentrations, the Pb and Nd isotope ratios in such material would be overwhelmed by the signals of terrigenous components.

RESULTS AND DISCUSSION

The Ala Wai Canal and Its Watershed

Two of the Ala Wai Canal sediment samples we analyzed for their Pb isotopes were selected from a core depth (176–180 cm and 196–200 cm) near the original bottom of the canal; others were analyzed from levels corresponding to sedimentation during the early 1940s through the early 1980s, assuming an average sedimentation rate of ca. 2.5 cm/yr for the Gonzalez-8 core (based on ^{137}Cs measurements [McMurtry et al. 1995]). These data are shown in Table 1.

Lead concentrations in the two bottom (and presumably earliest canal) sediments are 3.2 and 6.4 ppm. Chemically, these two samples differ from each other in that the 3.2-ppm sample contains a greater carbonate fraction, whereas the 6.4-ppm sample contains more terrigenous clays (De Carlo and Spencer 1995). Lead concentrations in samples deposited during the urbanization of Honolulu show a smooth rise with decreasing sediment depth, a concentration maximum

TABLE 1

ELEMENTAL CONCENTRATION (IN ppm) AND ISOTOPE RATIO DATA FOR SAMPLES MEASURED FOR THIS STUDY AND VOLCANIC ROCK DATA FROM SOURCES QUOTED IN NOTES

SAMPLE	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{143}Nd/^{144}Nd	εNd	^{87}Sr/^{86}Sr	Pb	Sr	Sm	Nd
Mānoa Stream 2	18.316	15.568	38.058	0.512913	5.3	0.705603	16.6	73.6	9.18	39.79
Mānoa Stream 3	18.430	15.560	38.022				284			
Mānoa Stream 8	18.210	15.574	37.942				37.1			
Ha'ikū/Hālawa valley soils										
HAL-7	17.840	15.544	37.605	0.512725	1.7	0.712708	11.0	1.76	0.64	3.83
HH-6	18.422	15.605	38.387	0.512738	1.9	0.709341	48.8	68.8	2.85	16.85
HH-10	18.443	15.593	38.223	0.512892	4.9	0.707069	13.5	60.3	2.57	15.09
HH-33	18.353	15.541	38.219	0.512854	4.2	0.707356	7.15	41.5	2.52	12.39
HH-21	19.090	15.660	38.680				429			
Ala Wai Canal Gonzalez-8 core sediments										
G-8 8–12 cm	18.417	15.619	38.079							
G-8 20–24 cm	18.307	15.583	37.923							
G-8 36–40 cm	18.145	15.585	37.819				506			
G-8 56–60 cm	17.932	15.573	37.735							
G-8 68–72 cm	18.300	15.607	38.137							
G-8 72–76 cm	18.451	15.628	38.275							
G-8 76–80 cm	18.479	15.620	38.270							
G-8 100–104 cm	18.292	15.575	38.008							
G-8 172–176 cm	18.142	15.565	38.050				3.68			
G-8 196–200 cm	18.042	15.555	37.926				7.02			
Tropospheric dust, Hawai'i	18.680	15.612	38.715	0.512315	−6.3	0.722545	55.3	76.5	6.26	30.2
Ka'ena Point coral							0.002			
Ka'ena Point eolianite	17.666	15.510	37.347	0.512632	−0.2		4.07		0.07	0.28
*Ko'olau avg.	17.91	15.46	37.75	0.51271	1.7	0.7041		446	6.1	23.5
*Honolulu Series avg.	18.13	15.45	37.77	0.51305	7.8	0.7033		1300	12.2	56.6

NOTES: Average Sr, Nd, and Sm concentrations and isotopic compositions for Ko'olau and Honolulu Series volcanics are from Roden et al. (1984). The quoted averages for their isotopic compositions are from Roden et al. (1984) and Stille et al. (1983, 1986). Isotopic fractionation factors are ^{148}Nd/^{144}Nd = 0.241572, ^{86}Sr/^{88}Sr = 0.1194. Standard values for LaJolla Nd is ^{143}Nd/^{144}Nd = 0.511855 ± 0.000012 (0.2 epsilon units) and for SRM 987 is ^{87}Sr/^{86}Sr = 0.71025 ± 0.000022 (both 2 − σ). Pb topes are corrected for fractionation using the values of Todt et al. (1984), and the total ranges measured on NBS 981 are ±0.008 for ^{206}Pb/^{204}Pb, 0.008 for ^{207}Pb/^{204}Pb, and 0.030 for ^{208}Pb/^{204}Pb. Errors for individual samples are less than the stated uncertainties on standards. Total procedural blanks are <60 pg for Pb, <20 pg for Nd, <120 pg for Sr. εNd corresponds to ^{143}Nd/^{144}Nd = 0.512640 for ^{147}Sm/^{144}Nd = 0.1967. Nd Sm, and Sr abundances measured by isotope dilution are known to be better than 0.2%, 0.2%, and 0.4%, respectively. Pb abundance uncertainties may be greater than 1% because of problems splitting samples for ID/IC when organic residues were present.

(ca. 750 ppm) corresponding to the period of time (based on ^{137}Cs measurements) when automotive leaded gasoline was in heaviest use, a subsequent decrease after leaded gasoline was phased out, and a strong covariation with Zn concentrations through 1975 (De Carlo et al. 1992, De Carlo and Spencer 1995). High Pb concentrations have also been measured in other estuarine environments that have been heavily developed, such as Narragansett Bay, Rhode Island (Bricker 1992). High lead concentrations (300 ppm) remain in the most recently deposited sediments measured in this core, and similarly elevated Pb concentrations have been mea-

sured in several other Ala Wai Canal cores (De Carlo and Spencer 1995).

We have chosen to present our Pb isotope data on a $^{207}Pb/^{208}Pb$ versus $^{206}Pb/^{204}Pb$ isotope diagram because it discriminates anthropogenic from natural components in our samples. These data are shown in Figure 4. The "O'ahu rocks" and "Pacific sediments" data fall into two distinct fields, whereas presumed anthropogenic lead from the Ala Wai Canal falls largely outside these fields.

The two samples from the lowest sections of the core have, in addition to low lead concentrations, lead isotopic compositions that fall within a field consistent with mixing of O'ahu volcanics and North Pacific pelagic sediments and might, therefore, contain a silicate aerosol component. This relationship is more clearly seen on a conventional $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ isotope diagram, depicted in Figure 5a and b. The lead concentrations in the bottommost core samples might approximate the natural lead values in this system. At worst, they are the least contaminated samples in the core.

The isotopic compositions of lead in the presumed contaminated Ala Wai samples plot in a roughly linear pattern suggestive of mixing of unradiogenic and radiogenic lead ore isotopic compositions. This mixing line is displaced to higher $^{207}Pb/^{208}Pb$ for a given $^{206}Pb/^{204}Pb$, compared with the Pb data for the O'ahu volcanics and the North Pacific pelagic sediments. The canal Pb isotope data further suggest a temporal variation of lead sources. Recently deposited (0–20 cm) samples and those at the 74- to 78-cm interval contain the greatest concentration of J-like lead relative to low $^{206}Pb/^{204}Pb$ ore lead, but differ significantly in their $^{207}Pb/^{208}Pb$ for a given $^{206}Pb/^{204}Pb$. Shirahata et al. (1980) noted a temporal change in lead isotopic compositions measured on sediments deposited in an alpine lake in California and attributed it to the increased mining of J-lead relative to unradiogenic lead (such as produced at Balmat, New York, or Franklin, New Jersey) during the 1960s and 1970s in the United States.

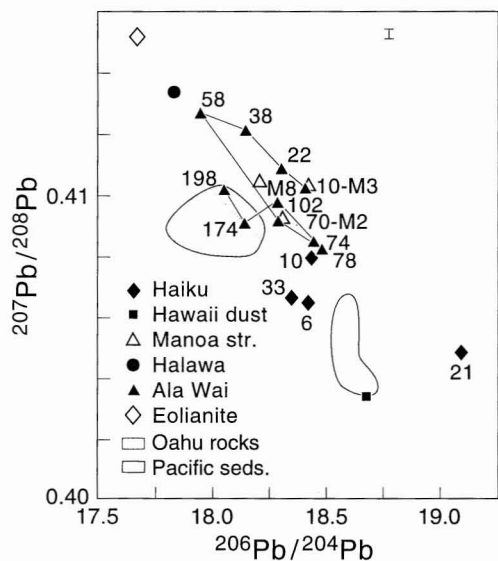In contrast to the (low) Pb concentrations measured in the bottommost core samples,

FIGURE 4. $^{207}Pb/^{208}Pb$ versus $^{206}Pb/^{204}Pb$ results for this study. The fields for O'ahu volcanic rocks and North Pacific pelagic sediments are as described in Figure 3. Unradiogenic ores mined in the United States (e.g., Balmat, New York, and Franklin, New Jersey) and ores used in Japan would have high $^{207}Pb/^{208}Pb$ and low $^{206}Pb/^{204}Pb$ ratios and lie off of the diagram to the upper left. Radiogenic ores mined in the United States (Mississippi Valley "J" Pb) would have low $^{207}Pb/^{208}Pb$ and high $^{206}Pb/^{204}Pb$ ratios and lie off of the diagram to the lower right. The numbers on the Ala Wai Canal symbols are core depths and are connected in stratigraphic order. The Mānoa Stream symbols are shown with their sample numbers from Figure 1. Ha'ikū Valley samples are labeled with their sample numbers. Uncertainties are smaller than the symbol size.
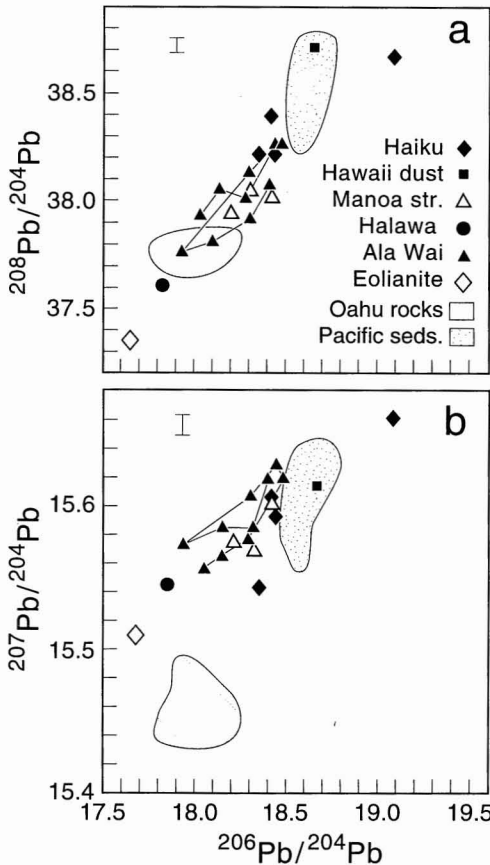
FIGURE 5. (a) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ results from this study. Symbols and fields are as described in Figures 3 and 4. Sample numbers for the Ala Wai Canal and Mānoa Stream data points are omitted for clarity. (b) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ results from this study. Symbols and fields are as described in Figures 3 and 4.

Pb concentrations measured in recently deposited sediments indicate that they have been polluted to levels approximately one to two orders of magnitude above normal. The temporal relationship of Pb concentrations to leaded gasoline consumption, and the association with elevated Zn (De Carlo and Spencer 1995), a metal used in auto tire vulcanization, indicates that this lead was most likely contributed by leaded gasoline combustion and deposition.

The high (100–300 ppm) Pb concentrations present in the topmost canal sediments

from this and several other cores in the Ala Wai Canal (De Carlo and Spencer 1995) indicate that Pb continues to be transported out of the Ala Wai Canal's watershed. To gauge where this Pb originates, we analyzed the <45-μm fraction from three Mānoa Stream samples (Figure 1) for Pb isotopes and concentrations.

The three samples show increasing lead concentrations as one moves down the valley, a highly developed residential area. Sample M-2, which was collected near the headwaters of the stream, contains rather low (16.6 ppm) Pb concentrations, whereas M-8, collected about 1.5 km downstream, contains 37.1 ppm Pb. Sample M-3, collected at the Dole Street bridge near the University of Hawai'i at Mānoa, contains nearly an order of magnitude higher Pb concentrations than the other two (Table 1). Although it is not clear at this time whether this progression indicates a steady addition of Pb to the stream as it progresses through the valley or whether a single point-source of Pb pollution is located between M-3 and M-8, it should be noted that for decades Dole Street and nearby roadways have been heavily used, carrying traffic into and out of Mānoa Valley, and one might expect soils near these roads to be highly contaminated with Pb from auto emissions. Erosion of such soils into the stream might explain the high Pb concentrations measured at this site.

All three samples plot outside the field of natural mixtures and within the Ala Wai Canal lead isotope field in Figure 4 and, therefore, all presumably contain anthropogenic Pb. It is interesting that even at the low Pb concentrations measured on M-2 and M-8, a substantial amount of the Pb present is of anthropogenic origin. Sample M-3, containing 284 ppm Pb, plots approximately along the trace of Ala Wai Canal Pb isotope data between the 22-cm and 10-cm sample intervals (Figures 4 and 5). Therefore, contaminated stream sediments draining out of Mānoa Valley (and possibly other residential valleys) may be among the sources of the contaminated sediments that have been deposited in the canal since the phaseout of leaded gasoline in the state of Hawai'i.

The isotopic signatures of this recently deposited Pb are distinct from those of the Pb deposited at earlier times in the canal's history (see Figures 4 and 5). Therefore, at least some of the Pb in the recently deposited sediment has been either (1) introduced to the watershed since the 1970s from a radiogenic source, or (2) stored in the watershed for a considerable time and released recently. We think that the most likely scenario to explain these data is that highly radiogenic, or J-type (e.g., $^{206}Pb/^{204}Pb > 20$; $^{208}Pb/^{204}Pb \sim 40$), Pb released to the environment since the 1970s is mixing with older, low $^{206}Pb/^{204}Pb$ already present; this Pb finds its way downstream into the canal. Leaded paint chips and auto exhaust–derived Pb, deposited before the 1970s and having low $^{206}Pb/^{204}Pb$ ratios, are mixing with recently added J-Pb contributed by combusted gasoline and from other industrial sources.

Sources of Pb in Selected Soils as Deduced from Nd and Sr Isotope Data

Hawaiian soils contain elements and minerals of continental origin derived from silicate aerosols (e.g., Jackson et al. 1971, Dymond et al. 1974). Although the Pb isotopes and concentrations in these aerosols may differ substantially from those of Pb in Hawaiian volcanic rocks, a potential problem arises in distinguishing this Pb from low-level human contamination. We have therefore analyzed several soil samples from Ha'ikū Valley on O'ahu (Figure 2) and one soil sample enriched in silicate dust, collected on the island of Hawai'i, for Pb, Nd, and Sr isotopes and elemental concentrations to see if a systematic pattern exists in the isotopic signature of these elements in soil mixtures. We hypothesized that Pb derived from silicate dust should be coupled to Sr and Nd derived from this dust, but Pb derived from local or long-range pollution should have an isotopic composition different from that of O'ahu's rocks and decoupled from other isotopic systems. A potential problem arises in testing this hypothesis because of the possible differential mobility of these elements during tropical pedogenesis.

The dust-enriched soil collected on the island of Hawai'i contains 55.3 ppm Pb, a concentration higher than average values for loess (Taylor and McLennan 1985), but similar to concentrations measured in pelagic sediments (Ben Othman et al. 1989). Its lead isotope ratios fall in the field of Pb isotopes measured on North Pacific pelagic sediments (Figures 4 and 5) and do not suggest contamination by Pb that has an isotopic composition similar to that measured in polluted Ala Wai Canal sediments.

Other stable isotope systems confirm a probable continental origin for this sample. Its unradiogenic Nd composition ($\varepsilon = -6$) is far more negative than any value measured on O'ahu volcanic rocks (Figure 6a) and similar to values measured on Pacific deep-sea sediments (Ben Othman et al. 1989; D. G. Waggoner, pers. comm.). Its Sr isotopic composition ($^{87}Sr^{86}Sr = 0.722545$ [Figure 6b]) is likewise outside the range measured on oceanic igneous rocks (White 1985) and is more radiogenic than Sr measured on Pacific pelagic sediments (Ben Othman et al. 1989). Unlike deep-sea sediments, however, which can exchange Sr with seawater (modern $^{87}Sr^{86}Sr \sim 0.709$ [Capo and DePaolo 1990]), this sample most likely preserves its source's Sr isotopic composition. These Pb, Nd, and Sr data indicate that the source of this material was most likely continental. If the high Pb concentrations found in this sample are representative of dust deposited on O'ahu, then a small amount of this material added to a soil would dramatically raise its lead concentration and change its Pb isotopic composition.

Soil HH-33 has the lowest lead concentration (7.2 ppm) of the Ha'ikū Valley soils we analyzed, whereas HH-10 contains 13.5 ppm. These samples had powder X-ray patterns indicating a small quartz component. Their Pb isotopic composition falls outside the field of that of Hawaiian volcanic rocks and indicates that additional components are present. HH-33 lies midway between fields of Pb similar to North Pacific pelagic sediments and Pb from Hawaiian volcanic rocks, suggesting that its Pb is derived from a mixture of these two sources. HH-10, as seen in Figure 4,
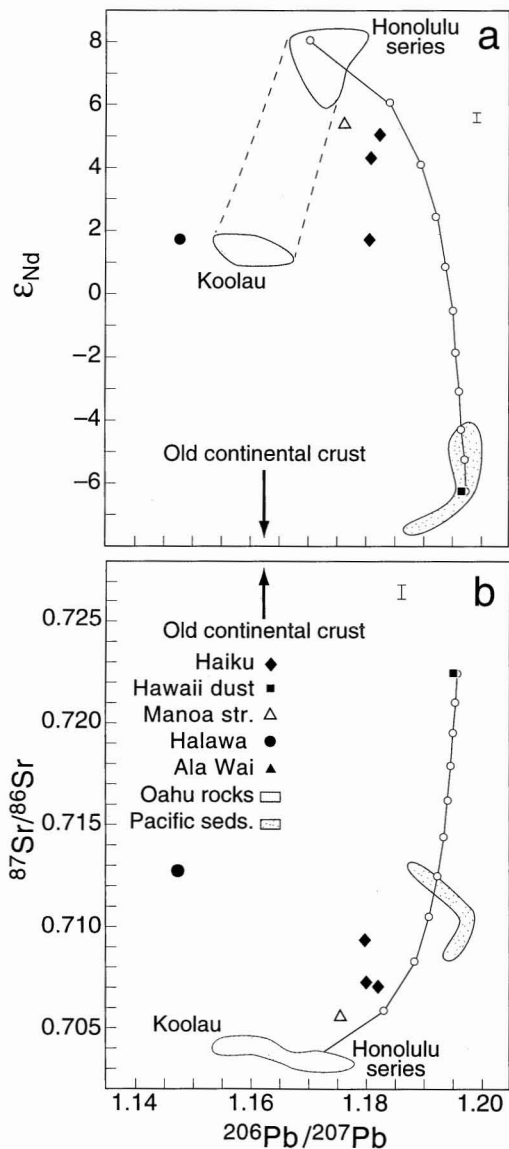
has a higher $^{207}Pb/^{208}Pb$ for a given $^{206}Pb/^{204}Pb$ than HH-33. Its isotopic composition could be explained as a mixture of HH-33-type Pb mixing with a small amount of anthropogenic Pb similar to that found in the 74- to 78-cm layers of the Ala Wai Canal.

Soil HH-21, containing 429 ppm Pb, is far more enriched in J-Pb than the Pb found in the Ala Wai Canal. This sample was located far from known roads and near a dump site that contained discarded leaded products and represents a point-source of lead contamination rather than auto exhaust–related Pb deposition.

Soil sample HH-6 contains 48.8 ppm lead and 1 ppm As. Although the As is most likely of anthropogenic origin, this sample's Pb has an isotopic composition similar to that of HH-33. HH-6 has, in addition, a strong quartz line in its X-ray pattern. The higher quartz concentration in this soil may indicate that a much larger dust component is present, perhaps explaining its higher Pb concentration. But if HH-6, like HH-21, was contaminated with anthropogenic Pb enriched in a J-component rather than containing a larger dust component, this sample should contain Sr or Nd with an isotopic composition similar to that of the other soils.

In Figure 5a and b, HH-6 lies on permissible mixing lines between HH-33 and the pelagic sediment field in Pb-Pb space, rather than on trends toward J-Pb. Figure 6a and b shows Pb-Nd and Pb-Sr systematics for the soils, O'ahu volcanic rocks, and Pacific pelagic sediments. Ha'ikū soils HH-6, HH-10, and HH-33 show an increase in $^{87}Sr/^{86}Sr$, and a decrease in epsilon Nd that is consistent with mixing of Pb, Nd, and Sr derived from O'ahu volcanic rocks and from atmospheric dust. HH-6 indeed has a significantly lower epsilon value and higher $^{87}Sr/^{86}Sr$ than HH-33 or HH-10, suggesting that at least some of the additional Pb found in this soil is derived from natural sources.

FIGURE 6. (a) Epsilon Nd versus $^{206}Pb/^{207}Pb$ variation diagram. Symbols are as described in Figure 4. A model mixing curve connects Honolulu Series volcanics data to the island of Hawai'i tropospheric silicate dust sample (solid box) and is marked in 10% increments. This calculation uses local soil and dust derived end-members with the following model parameters: local soil, 20 ppm Nd with epsilon = +8 and 5 ppm Pb with $^{206}Pb/^{207}Pb = 1.17$; dust, 30 ppm Nd with epsilon = −6.3 and 50 ppm Pb with $^{206}Pb/^{207}Pb = 1.197$. (b) $^{87}Sr/^{86}Sr$ versus $^{206}Pb/^{207}Pb$ variation diagram for O'ahu rocks and soil samples. Data sources and symbols are as described in Figure 4. The mixing curve uses the same Pb parameters used in Figure 4, assumes Sr concentrations of 55 ppm for a soil derived from a rock and 76 ppm for a dust-derived soil, and assumes $^{87}Sr/^{86}Sr = 0.7033$ for a rock-derived soil and $^{87}Sr/^{86}Sr = 0.7225$ for a silicate dust–derived soil.

The Ha'ikū Valley soils contain variable amounts of atmospheric dust–derived Pb. Perhaps HH-10 contains some Pb derived from combusted gasoline that was carried in as an aerosol from the town of Kāne'ohe, which is upwind of the site, whereas HH-6 may contain some J-type anthropogenic Pb, in addition to their natural Pb. Sample HH-21 has clearly been contaminated severely with a substance containing J-Pb and is isotopically distinct from the Pb measured in the urban Honolulu watershed.

A soil sample we analyzed from the lee side of the Ko'olau ridge crest in the headlands of Hālawa Valley (HAL-7 [see Figure 2]) was formed in a region subject to intense orographic rainfall. We thought it might contain a significant silicate aerosol component. However, this gibbsite-enriched soil was strongly depleted in Nd and Sr (3.8 ppm Nd, 1.76 ppm Sr), although it contains 11 ppm Pb. Because its Sr and Nd concentrations are so low compared with those of any of the rocks or dusts that could be parental, although its Pb concentrations are similar or higher, we hypothesize that most of the lead could be anthropogenic and added during the last 50–100 yr.

This sample has a Pb isotopic composition distinct from those of O'ahu volcanic rocks and Pacific pelagic sediment but similar to that of anthropogenic Pb measured from the ~58-cm level of the Ala Wai Canal (Figures 4 and 5). Nd isotopes provide equivocal evidence of provenance, falling at the least radiogenic extreme of Ko'olau volcano data (Figure 6a). However, Sr isotopes (Figure 6b) require that much of the Sr that remains in this sample was derived from eolian dust. To explain the origin of the Pb in this sample, we suggest one of two possibilities: either this sample was contaminated with Pb during collection or transportation to the laboratory, a possibility we consider unlikely because of the large blank this would require, or it contains a component of anthropogenic Pb. Because this soil has experienced extreme Nd and Sr loss, and because of its Pb's isotopic similarity to locally derived anthropogenic Pb, we conjecture that its Pb was anthropogenic and probably added to the soil too recently to have been removed by rain or groundwater as the naturally derived Nd and Sr have.

We analyzed the least contaminated Mānoa Stream sample for Nd and Sr isotopes to determine the nature of the source of natural Pb in this sediment; these data are shown in Figure 6a and b. Nd isotopes can be explained by mixing Ko'olau and Honolulu Series volcanic material, both of which may be present in upper Mānoa Valley (Macdonald and Abbott 1970). The relatively high epsilon value and the high Nd and Sr concentrations suggest that Honolulu Volcanic Series–derived material (Table 1) may be a major source of silicate in the sample. $^{87}Sr/^{86}Sr$ is somewhat higher than found in mixtures of O'ahu volcanics and confirms that a small but measurable amount of atmospheric silicate dust-derived Sr is present. The Pb in this sample might therefore be primarily a mixture of volcanic-derived and anthropogenic Pb and contain a minor amount of eolian Pb.

Thus far we have not attempted to model the proportions of soil components (see for example, Amacher et al. 1986, 1988, 1990) because these soils exhibit variable to extreme loss of Nd and Sr as compared with unweathered rocks and with less weathered soils analyzed for REE on the island of Hawai'i. Halbig et al. (1985) reported that Hawai'i Island soils can be enriched in REE over their host rocks by about a factor of 2 to 2.5 and depleted in Ca by 50–80%. Quantitative modeling of end-member proportions would have to take into account the variable mobility of REE, Pb, and Sr during the sometimes extreme tropical pedogenesis seen on O'ahu. Such modeling is beyond the scope of this paper.

Nd abundances in these soils (exclusive of the Mānoa Stream sediment sample) are, for example, similar or far lower than abundances measured in six Ko'olau tholeiites and far lower than measured in Honolulu Series posterosional volcanics (Roden et al. 1984; see Table 1). Dilution of inorganic soil components by water and organic material (samples were dried at 95°C but not corrected for loss on ignition [LOI] or analyzed for

total organic carbon) could explain somewhat lower abundances of Nd and Sr. However, the extremely low Nd concentrations (3.8 ppm) measured in the highly weathered gibbsite-enriched soil that contained little organic matter suggest that leaching rather than dilution is the cause of the low Nd abundance in this case.

Pb Concentrations in Ancient Carbonates on Oʻahu

A 0.5-myr-old coral skeletal fragment from the 30-m Kaʻena-stand reef (Sherman et al. 1993) at Kaʻena Point, Oʻahu, and an eolianite deposited on a 0.125-myr-old-Waimānalo-stand reef, ca. 100 m east of the Kaʻena reef sample (Figure 2), were collected to gauge the amount of Pb in Oʻahu's prehistoric reef deposits. Reef coral underlies much of Oʻahu's coastal plains (downtown Honolulu and Waimānalo, for example). Prehistoric reef coral should be exceptionally clean, containing far less than 1 ppm Pb (Shen and Boyle 1987) and should not contribute measurably to the Pb baseline. These two samples were analyzed for Pb concentrations (coral data provided by D. G. Waggoner), and the eolianite was analyzed for its Pb isotopic composition.

The coral fragments were x-rayed and found to be a mixture of calcite and aragonite. They were subsequently hand picked under a binocular microscope to obtain samples without discoloration or obvious alteration; this material was x-rayed and found to be pure aragonite. A clean split was subsequently dissolved using ultra-clean HCl and HNO_3.

The coral contained 2 ppb Pb (1 nM Pb/M Ca) suggesting that uncontaminated prehistoric reef corals on Oʻahu are not a significant source of Pb in the environment. It is interesting that this Pb concentration is about four times lower than the amount that Shen and Boyle (1987) found in a modern Fijian coral, which, being farthest from major Northern Hemisphere sources of anthropogenic Pb, had the lowest concentrations they measured. Because our sample was unaltered (and contained 7000 ppm Sr with a Sr

isotopic composition consistent with that of 0.5-myr-old seawater [D. G. Waggoner, pers. comm.]), its chemistry can be used to estimate prehistoric surface Pb concentrations in the ocean near Hawaiʻi. Assuming an approximate coral/ocean water K_D of 2.5 for Pb partitioning between coral aragonite and ocean water (we did not determine the species of coral, and the exact K_D is species-dependent [e.g., Shen and Boyle 1987]), this sample suggests 0.5-myr-old Pb concentrations in Pacific Ocean surface waters near Oʻahu of ca. 4 pM.

It is surprising that the eolianite contained 4.1 ppm Pb, considerably higher than the coral skeleton. In Figure 4, the eolianite Pb plots on a low $^{206}Pb/^{204}Pb$ extension of the Ala Wai Canal ("anthropogenic") Pb field, suggesting that this sample was contaminated. As shown on Figure 5, the isotopic composition of its Pb is less radiogenic than those of either Oʻahu volcanic Pb or Pacific pelagic sediment Pb and trends toward a low $^{206}Pb/^{204}Pb$, ore Pb composition (Figure 3). The sample was subsequently analyzed for its Nd isotopes and concentration to determine if the Pb in the sample could be contributed by a dust with Pb and Nd signatures different from those of the Pacific pelagic sediment field (Figure 6a).

The isotopic composition of the Nd in this sample, corresponding to an epsilon value of -0.16, suggests a mixture of Nd from dust and from Hawaiian rocks (Figure 6a), but the extremely low Nd concentration of 0.28 ppm and low Nd/Pb ratio of 0.082 suggest that only a very small silicate-derived component is present. Nd/Pb ratios of Hawaiian basalts are variable (West et al. 1992), but average around 15, whereas Nd/Pb for average loess or continental crust is ca. 1.3–1.5 (Taylor and McLennan 1985). Therefore, the natural Pb concentrations in this sample should be < 0.1 ppm.

We think that the most likely scenario to explain the Pb in the eolianite is that anthropogenic Pb was added either through atmospheric deposition from a distant source or by the deposit of auto exhaust released nearby (this area has recently been placed off-limits to auto traffic but is near a trail

formerly used by off-road motor vehicles). Even though we removed several centimeters of surface material, it is evident that rainwater (or some transport medium) percolating through the porous cement of the eolianite transported Pb into the interior of the outcrop. The intrinsically low initial Pb concentrations of this sample have been overwhelmed by the anthropogenic component.

Anthropogenic Pb from Distant Aerosols?

It is interesting that the Pb isotopic composition of the eolianite is most similar to that of the Hālawa soil. Perhaps both of these samples are contaminated with similar atmospherically derived Pb from a distant source, because neither sample was collected near a major road. The relatively low $^{206}Pb/^{204}Pb = 17.67$ and $^{206}Pb/^{207}Pb = 1.14$ suggest that the source of anthropogenic Pb could include anthropogenic aerosols transported from Japan or other parts of Asia (Asian/Japanese $^{206}Pb/^{207}Pb \sim 1.16$ [Table III in Patterson and Settle 1987]). This would not be surprising because much of the silicate dust found in Hawai'i is derived from Asia (e.g., Duce et al. 1980). The amount of anthropogenic Pb found in the ridge top soil (~ 11 ppm), a wet location, is higher than that found in the eolianite (~ 4.1 ppm), a dry location (Armstrong 1983). Assuming that the amount of atmospheric deposition roughly correlates with rainfall, this association would be consistent with delivery of this Pb by atmospheric anthropogenic aerosols.

CONCLUSIONS

The Ala Wai Canal, a highly polluted artificial estuary, drains residential and commercial (i.e., cottage industry and tourism) neighborhoods in Honolulu that contain no heavy industry. Anoxic sediments cored from the canal preserve a record of Pb isotopic compositions and abundances that can be used to model the Pb pollution history of the watershed draining into it. Lead concentrations in the canal sediments follow leaded gasoline use; concentrations measured in most re-

cently deposited canal sediments are up to 50 times higher than those measured in the bottommost samples, suggesting that large amounts of anthropogenically derived lead continue to be transported out of the watershed. An upper watershed source for at least some of this Pb has been verified by the measurement of a polluted sample of sediment from Mānoa Stream.

The lead deposited in the Ala Wai Canal since the mid-1970s, after the peak years and subsequent phaseout of leaded gasoline, has a different isotopic composition than lead deposited in older sediments. If the increase in J-Pb component in these recently deposited core samples indicates that the Pb has been more recently mined and used (e.g., Shirahata et al. 1980), then at least some of this Pb has been added to the local environment during the last 20 yr, and it is mixing with Pb added earlier in the century. Pb may be released to the streams draining into the canal gradually, by soil erosion, or it could be released in massive sporadic doses during the excavation of contaminated soils or by the dumping of stored wastes containing Pb.

Because the Ala Wai Canal's watershed contains a significant portion of urban Honolulu, we think its anthropogenic lead isotopic signature is a good representation of locally produced pollution present elsewhere on the Islands. Some material that appears contaminated with Pb but that differs isotopically from the Ala Wai Canal samples, such as a Hālawa Valley soil, may reflect the presence of aerosol input of Pb from distant sources.

Selected soils from high rainfall areas show an association between quartz fragments, Pb concentrations, and Sr-Nd-Pb isotopic systematics that suggests a continental affinity, thus verifying the presence of an atmospheric dust component in these samples. Soils containing a dust component would probably contain higher concentrations of Pb than soils composed of volcanic rock debris alone because of the higher average Pb concentrations in continental crust and soil. Dust-enriched soils might be identified by the presence of quartz crystals. This fingerprint would not apply to areas of O'ahu where indiginous quartz is found, such as

in the Koʻolau caldera or in parts of the Waiʻanae range where quartz-saturated rocks crop out.

The use of several isotopic systems in combination (Nd-Pb or Sr-Pb, for example) provides a method of discriminating natural from anthropogenic Pb sources in soils and sediments. Source materials for soils may have different origins, geochemistries, and thus metals concentrations; attempts to model geologically relevant metal baseline concentrations should take these factors into account.

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