Total and Nonresidual Concentrations of Selected Elements in Two Soil Series on the Island of Hawaii[1]

WALTHER M. BARNARD AND JOSEPH B. HALBIG[2]

ABSTRACT: Thirty Aridisol soil samples of the Kawaihae soil series on the dry, leeward, northwestern side of the island of Hawaii and 13 Histosol samples of the Papai series on the wet, windward, eastern side of the island were subjected to (1) complete dissolution by a mixture of HNO_3, HCl, and HF to determine total concentrations of Co, Cr, Cu, Fe, Mn, Ni, and Zn and (2) extraction of these metals by shaking 10 g soil : 100 mL $0.5M$ HCl solutions for 16 hr to determine nonresidual concentrations. Analyses were performed mainly by flame and electrothermal atomic absorption spectrophotometry. Loss on ignition (LOI) and soil pH were also determined.

Total metal concentrations, quantity extracted, LOI, and soil pH were analyzed statistically. Compared to the Histosol, the Aridisol samples typically contain more Co, Cr, Fe, and Mn, less Cu, similar concentrations of Ni and Zn, and have less LOI and higher pH. The Aridisol exhibits a high degree of correlation between total Cr and Ni, while a strong negative correlation occurs between Cu, Mn, Co, and Fe individually with LOI in the Histosol. The mean concentrations of these metals in both soils are significantly greater than those which occur in soils of the conterminous United States.

The effectiveness of extraction by the acid solution, as measured by the percentage of metal extracted, is approximately Mn > Co > Cu > Cr > Fe > Zn ≈ Ni for the Aridisol and Cu ≈ Zn > Co ≈ Mn > Fe ≈ Ni > Cr for the Histosol; the difference is attributed to weathering under different climatic conditions. The latter soils exhibit a higher degree of correlation for percentages of metals extracted among the various metals and with LOI.

THE ISLAND OF HAWAII has a variety of soils as a result of wide differences in climate, vegetation, relief, drainage, and age and type of parent materials. The soils have been described, mapped, and classified (Sato et al. 1973) according to the Soil Taxonomy System adopted by the U.S. government in 1970. Additional study of these soils has been undertaken by the College of Tropical Agriculture at the University of Hawaii and by the State of Hawaii Department of Agriculture. Most of the chemical investigation up to the present time has been related to nutrient elements of importance in crop production. Little work has been done on characterizing the total and nonresidual concentrations of heavy metals.

This investigation is part of a study started in 1981 in three geographic areas on the island (Figure 1) to characterize the natural environment prior to possible industrial development. The purposes of this paper are (1) to present statistical analyses and comparisons of total and nonresidual quantities of Co, Cr, Cu, Fe, Mn, Ni, and Zn in soil samples representing two soil series on the island that have developed from volcanic parent materials

[2] Professor of Geosciences, State University of New York College at Fredonia, Fredonia, NY 14063, and Professor of Geology, University of Hawaii at Hilo, Hilo, HI 96720, respectively.
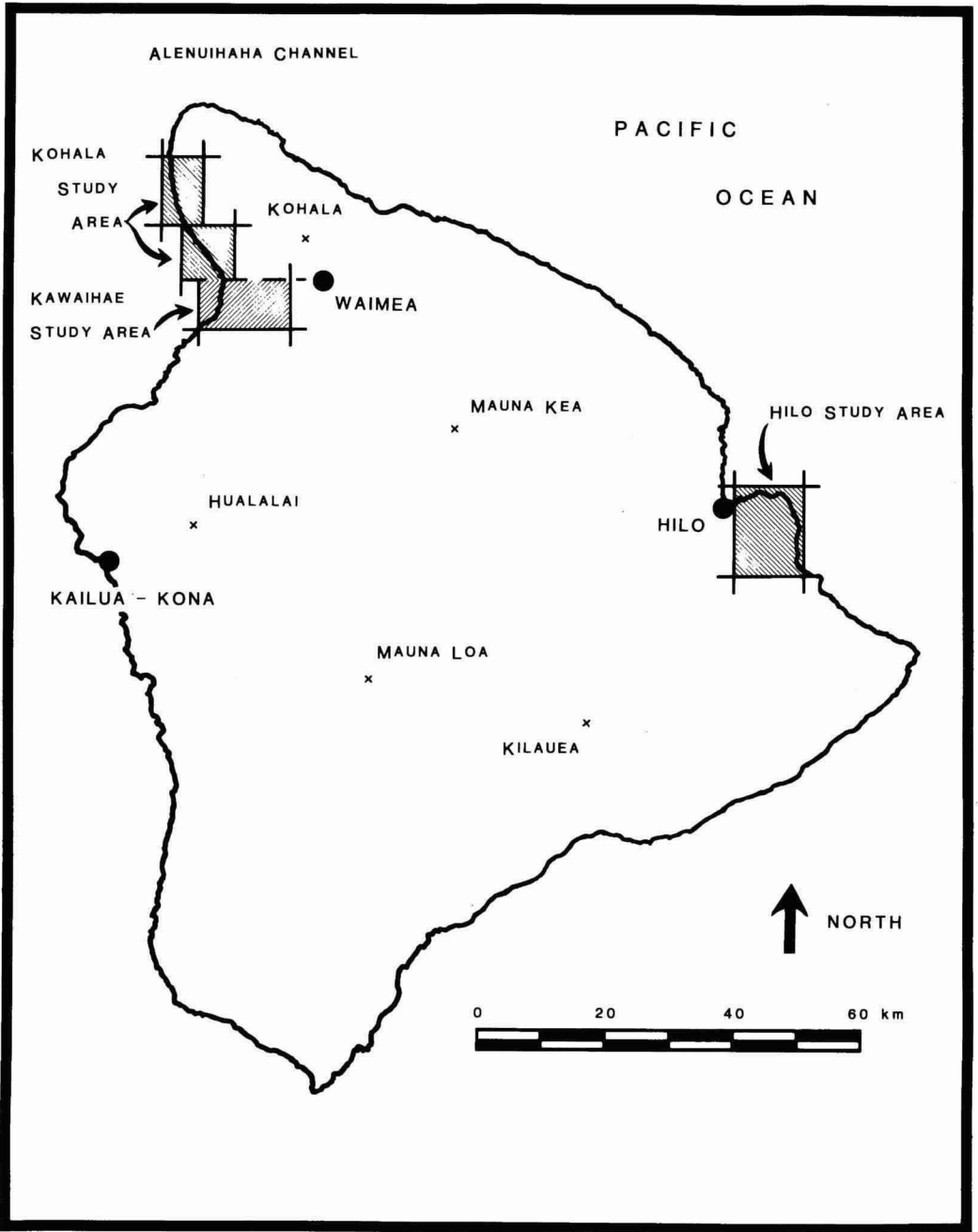
FIGURE 1. Study areas on the island of Hawaii.

under different climatic conditions, (2) to establish correlations between individual metals and between metals, organic content, and pH in these soils, (3) to compare the metal concentrations of these Hawaiian soils with those in common sediments in other areas, (4) to compare the effectiveness of extraction of these metals from the Hawaiian Aridisol and Histosol by $0.5M$ HCl solution, and (5) to ascertain whether the order of effectiveness of extraction of these metals is the same for soils formed under different climatic conditions.

The nonresidual component in soil is that portion adsorbed on sediment particles or present in the form of sparingly soluble salts and organic complexes. Total element concentrations include the nonresidual component plus metal in the silicate matrix. Analytical data on nonresidual metal content are especially informative in the detection of pollution, inasmuch as adsorption, complexation, and precipitation are the main forms in which metals from polluting sources are retained in the soil. In addition, the nonresidual metal content is closely related to the labile metal available to plant roots. Data on total concentrations are important because changes in conditions (such as oxidation-reduction or pH) may result in mobilization of the metal component fixed in the silicate matrix.

MATERIALS AND METHODS

Soils

The soils from the adjacent Kohala and Kawaihae areas considered in this study are Kawaihae extremely stony very fine sandy loam and Kawaihae very rocky very fine sandy loam. The two soils are similar, except that rock outcrops occupy more of the surface in the latter. Both belong to the Kawaihae series, which is a medial, ashy, isohyperthermic Aridisol (subgroup Ustollic Camborthids). These somewhat excessively drained stony soils formed in volcanic ash of uncertain origin (see the section on Parent Material and Soil Genesis) on gentle to moderate (6 to 12%) slopes on the leeward coastal plains of Mauna Kea and Kohala Mountain at an elevation

ranging from sea level to 460 m. Annual rainfall is 12 to 50 cm, and mean annual soil temperature is between 23 and 25°C. Typically these soils have a very thin, dark reddish-brown, stony, very fine sandy loam surface layer overlying dark reddish-brown and dusky-red stony silt loam and loam. The surface layer is neutral; the subsoil is neutral to mildly alkaline. Generally, the A horizon is from 5 to 10 cm thick and the B horizon is 30 to 46 cm thick (Sato et al. 1973: pp. 26, 100, 101).

The Hilo area soil considered here is mapped (Sato et al. 1973) as Papai extremely stony muck, an euic, isohyperthermic Histosol (subgroup Typic Tropofolists). It is described as being a well-drained, thin, extremely stony organic soil overlying fragmental basalt and typically having a surface O horizon up to 30 cm thick. The samples studied here were developed on Mauna Loa tholeiites, and some in reality were not especially organic-rich (as is evident from the weight loss on ignition statistics listed in Table 1). The soil occurs on gentle to steep (3 to 25%) slopes on the windward sides of Mauna Kea and Mauna Loa at an elevation ranging from near sea level to 300 m. Annual precipitation is from 230 to greater than 380 cm, and soil temperature is 22 to 23°C (Sato et al. 1973: pp. 46, 100, 101).

Extractant

The extracting solution employed is $0.5 M$ HCl. This extractant, among others, was evaluated and applied by Agemian and Chau (1976, 1977) and by Bradshaw et al. (1974) to aquatic sediments and soil profile sampling in exploration geochemistry. The Inland Waters Directorate of Canada (1980) specifies the procedure as being applicable to the determination of nonresidual Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn in sediments. It has also been used for the extraction of As (Reed and Sturgis 1936; Deuel and Swoboda 1972: Johnston and Barnard 1979) and can probably be extended to other elements. When employed on acid, neutral, and mildly alkaline soils, a 10 g soil: 100 mL $0.5M$ HCl solution retains a pH less than 2.

Collection and Initial Preparation of Soil Samples

Soil sampling stations were established at the corners of a 1.6-km² grid system which had its axes oriented geographically north-south and east-west. This plan provided for unbiased sampling and achieved coverage of the three study areas with a reasonable number of samples. Stations were located in the field with the use of a Brunton compass and altimeter and with the aid of aerial photographs. Thirty soil samples collected from the Kawaihae and Kohala areas belonged to the Kawaihae soil series; 13 soil samples of the Papai series were obtained from the Hilo area.

Soil samples were collected at each station by means of a small garden trowel. To avoid contamination, the trowel was wiped clean with tissue paper, and to remove any further surface residues it was worked into soil immediately adjacent (within a meter) to the area from which the sample was retrieved. Samples were taken from the surface to a depth of approximately 10 to 15 cm within a 250-cm² area, except where the depth of soil sampling was limited to just a few centimeters (particularly at some locations in the Hilo area) due to shallow soil development. The Kawaihae samples were taken mainly from the A horizon and probably included the uppermost part of the B horizon. The Hilo area samples were from the surface horizon, which included an O horizon in some instances. Chunks of rocks and mats of vegetation were excluded as much as possible at the time of collection. Two samples (one for archival storage), each about 400 cm³ in volume, were collected at each site and placed in cloth bags for transport to the laboratory.

In the laboratory the soil samples were spread out on plastic wrapping material, covered with porous tissue paper, and allowed to air-dry overnight. The exposure resulted in slight weight changes of less than 2% for the Kohala/Kawaihae soils, but for some of the high-moisture, organic-rich soils from the Hilo area weight losses were estimated to be greater than 10%. The soils were then placed in 1-liter plastic containers and mechanically mixed by shaking in order to break apart and homogenize clotted masses. The mixed soils were fractionated by sieving through 2-mm plastic mesh. The <2 mm size fraction was used in all of the analytical determinations. The coarser fraction, which was discarded, consisted of less than 20% by weight of the total sample in all cases; in the great majority of the Kohala/Kawaihae soils the coarser fraction was less than 5% of the total sample weight. The sieved fractions were stored for analysis in airtight plastic containers.

Determination of Total and Nonresidual Metal Concentrations

Analysis of total metals in soil by atomic absorption spectrophotometry (AAS) required complete destruction of the sample, which was achieved by treatment with a mixture of acids and heating in a sealed vessel. The decomposition method used in this study is a modification of a technique employed by the laboratories of the Inland Waters Directorate of Canada (1978). One hundred milligrams of soil contained in a 125-mL linear polyethylene bottle was reacted overnight with 4.0 mL of concentrated HNO_3, followed by addition of 1.0 mL of concentrated HCl and 6.0 mL of HF (48%). The tightly capped bottle was heated in an oven at 100°C for 6 hr and then opened under a hood and allowed to cool. Approximately 50 mL of deionized water and 5.6 g of H_3BO_3 were added to the solution, which was stirred to dissolve the boric acid; the solution was quantitatively transferred to a 100-mL glass volumetric flask, diluted to volume, and returned to a polyethylene bottle for storage prior to analysis.

Soil samples for the determination of nonresidual metals were prepared by adding 100 mL of 0.5 M HCl to 10 g of previously air-dried and sieved soil in 125-mL polyethylene bottles. Following agitation of the soil–solvent mixture for 16 hr on a reciprocating shaker, the suspensions were filtered through 0.45 μm pore size Millipore filters and the filtrates were stored in polyethylene bottles until time of analysis.

Analysis of the prepared aqueous samples

was mainly by conventional flame AAS. Where the metals were present in very low concentrations, as was often the case for Co and Cu, determinations were made by electrothermal AAS. Perkin-Elmer Models 603 and 303 AA spectrophotometers equipped with accessory background correctors and a P-E HGA-70 heated graphite atomizer were employed.

Standards were prepared from commercially available stock solutions (MCB Reagents) which were diluted with a solution corresponding to the matrix of the extracting or dissolving solution. Analysis by the standard additions method was performed in all instances when matrix interferences were indicated. Four reference soil standards, certified by the Canada Centre for Mineral and Energy Technology (Bowman et al. 1979), were prepared and analyzed in the same manner as the Hawaiian soil samples, and comparison of the results of metal determinations with the certified and noncertified values served as a measure of quality control on the analytical techniques.

For many of the samples, determinations of total iron were supplemented by neutron activation/gamma-ray spectroscopic analysis and determinations of total manganese were supplemented by both neutron activation/ gamma-ray spectroscopy and x-ray fluorescence spectrometry. These methods were principally employed for determination of other elements and on additional soil samples other than those considered here (Halbig et al. 1985), but the additional determinations did serve as another measure of quality control for iron and manganese determinations by AAS. Where minor differences occurred in the total iron and manganese values determined by the three analytical techniques, the averaged values are reported here as the total concentrations.

Determination of Oven-Dry Weight, LOI, and pH

The procedures for determination of ovendry weight, loss on ignition (LOI), and pH closely followed those outlined by McKeague (1978). Approximately 2 g of soil, weighed to

the nearest 0.1 mg, was placed in a porcelain evaporating dish and heated in an oven at 90 to 95°C for a minimum of 16 hr. Soils were dried at a temperature lower than that normally recommended (105°C, McKeague 1978:p. 42; 110°C, Chin and Jackson 1982: p. 4) in order to reduce possible error caused by the decomposition (oxidation) of organic material. After the samples were allowed to cool in a desiccator, they were reweighed to determine oven-dry weight and then reheated to determine weight loss on ignition. The samples were ignited in a muffle furnace at 420°C for 2 hr and again reweighed after cooling in a desiccator; the resulting weight loss can be taken as an estimate of the original content of organic matter. To a lesser extent, water loss from soil colloids may be a contributing factor in the LOI determinations. At the ignition temperature used, carbonate decomposition and structural water loss is probably insignificant (McKeague 1978:p. 149). LOI was calculated on the basis of weight percentage of the soil weight after drying (that is, the ovendry weight). In order to achieve an indication of the reliability of the determinative methods involving drying and ignition, several duplicate samples were processed and some samples were subjected to longer periods of heat treatment. In all cases the results showed a variation of less than 1% between different samples of the same soil.

Soil samples were prepared for pH determination (McKeague 1978:p. 67) by mixing 20 g of soil with 20 mL of deionized water (pH = 5.9) in a 50-mL beaker. For samples with a large content of organic matter, a soil/water ratio of 1 : 2 was used. The suspensions were stirred several times over a 10-min period and allowed to stand for 30 min before the glass and calomel electrodes were placed in the supernatant solution for a pH reading. Several duplicate soil samples were tested in order to check the reliability of the technique. Replications were in all cases within ±0.2 pH units.

Statistical Analysis

Statistical analysis of data was performed on line with the Burroughs 6800 (subsequent-

ly 7900) computer at State University of New York College at Fredonia, using the statistical package Minitab, a computing system of Minitab, Inc., State College, Pennsylvania.

RESULTS AND DISCUSSION

Total Concentrations of Metals

Table 1 is a statistical analysis of total concentrations of Co, Cr, Cu, Fe, Mn, Ni, and Zn, the loss on ignition, and soil pH of 30 Kohala/Kawaihae area soil samples of the Kawaihae soil series and 13 Hilo area samples representing soils of the Papai soil series. (The primary data are presented in Halbig et al. 1985.) Concentration values are calculated to express their concentration in oven-dry weight; loss on ignition values are expressed as percentages of oven-dry weight.

Table 1 lists the mean, median, trimmed mean (TMEAN), standard deviation (STDEV), standard error of the mean (SEMEAN), maximum (MAX), minimum (MIN), third quartile (Q3), and first quartile (Q1) values. TMEAN is a 5% trimmed mean; the smallest 5% (rounded to the nearest integer) and the largest 5% of the values are trimmed, and the middle 90% are averaged. SEMEAN is calculated as $STDEV/N$. Q1 and Q3 are the positions at $(N + 1)/4$ and $3(N + 1)/4$, respectively, in a list of data ordered from smallest to largest; if the position is not an integer, interpolation is used.

Table 2 presents standard statistical one-way analyses of variance and "two-sample" t tests for the primary data. The analysis of variance output gives (1) an analysis of variance table for each constituent/property in the soil samples of the two series; (2) the sample size, sample mean, and standard deviation corresponding to each population (or factor level); (3) the pooled estimate, $s_p = \sqrt{\text{mean square error}}$, of the common standard deviation; and (4) a display of individual 95% confidence intervals (CI) for each population mean. Each confidence interval is calculated by $\bar{x}_i - t^* s_p/\sqrt{n_i}$ to $\bar{x}_i + t^* s_p/\sqrt{n_i}$, where $\bar{x}_i$ and n_i are the sample mean and sample size corresponding to population i,

and t^* is the value from a t table corresponding to 95% confidence and the degrees of freedom associated with the mean square error. The "two-sample" t test does a t test of H_0: $(\mu_1 = \mu_2)$, where μ_i is the mean of population i, and a confidence interval of $(\mu_1 - \mu_2)$, using a procedure that does not assume the two populations have equal variance. The output gives (1) the confidence interval and (2) the t test $\mu_1 = \mu_2$ (versus $\mu_1 \neq \mu_2$) with test statistic (T), attained significance (P), and degrees of freedom (DF) (Ryan et al. 1976).

In general, the data of Tables 1 and 2 reveal that the Kawaihae series (the Aridisol) has distinctively greater concentrations of Fe and Mn (no overlap of the 95% CI), greater concentrations of Co and Cr (with considerable overlap of CI), and less Cu (with overlap of CI). The 95% CI for both Ni and Zn in the Kawaihae series are contained within the corresponding CI in the Papai series (the Histosol). Kawaihae soils typically have less LOI and higher pH than do the Papai samples.

The major element analysis of samples of a single profile of Kawaihae very fine sandy loam is provided by Sato et al. (1973; pp. 104–105). For the A horizon, Fe_2O_3 (incorrectly labeled Fe) is 23.68 wt % (Fe is 16.564 wt %, or 165,640 mg/kg), MnO is 0.38 wt % (Mn is 0.294 wt %, or 2940 mg/kg), soil pH (soil/water ratio of 1 : 5) is 7.1, and LOI is 11.30 wt % (method and basis not stated). By comparison, this one sample has somewhat greater Fe, Mn, and LOI and slightly lower pH than the mean and median values of the Kawaihae series samples considered in this study.

The total concentrations of elements in the Hawaiian soils can be compared to concentrations of elements in "average" or "normal" soils. Vinogradov and co-workers present data for the average concentrations of 50 elements in "normal soils of different zones from different continents, but mainly from Europe and North America" (Vinogradov 1959: p. 185 and table 126). Swaine (1955) summarized reports of average amounts of elements in soils as given by several investigators in his bibliography of trace element reports on soils of the world. The most complete review and summary of all individual elements in soils are

TABLE 1

Statistical Analysis of Selected Metals, Weight Loss on Ignition, and Soil pH in Two Hawaiian Soil Series

	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (wt %)	Mn (wt %)	Ni (mg/kg)	Zn (mg/kg)	LOI (wt %)	pH
				A. Kawaihae Soil Series					
MEAN*	55.1	398	92.3	12.95	0.2207	261	117.6	10.42	7.320
MEDIAN	52.5	319	95.5	13.35	0.2150	216	119.0	9.85	7.200
TMEAN	54.9	359	91.0	13.03	0.2188	239	116.7	9.53	7.315
STDEV	15.8	307	52.5	2.25	0.0406	159	21.1	6.05	0.554
SEMEAN	2.9	56	9.6	0.41	0.0074	29	3.8	1.10	0.101
MAX	98.0	1365	196.0	17.50	0.3200	787	188.0	38.80	8.800
MIN	22.0	97	10.0	6.16	0.1570	80	78.0	4.50	6.200
Q3	65.0	524	132.3	14.50	0.2500	297	131.3	11.72	7.600
Q1	46.0	170	32.7	11.36	0.1897	170	104.3	6.98	7.100
				B. Papai Soil Series					
MEAN*	44.69	305	120.2	7.27	0.1146	293	113.6	15.8	6.409
MEDIAN	46.00	318	124.0	7.74	0.1200	256	87.0	9.7	6.600
TMEAN	45.45	307	121.2	7.56	0.1168	293	93.9	12.3	6.422
STDEV	9.89	139	34.3	1.53	0.0207	122	82.8	19.5	0.559
SEMEAN	2.74	39	9.5	0.42	0.0057	43	23.0	5.4	0.169
MAX	60.00	551	189.0	8.63	0.1350	475	380.0	68.0	7.200
MIN	21.00	40	40.0	2.69	0.0700	158	64.0	1.3	5.500
Q3	51.50	416	138.5	8.22	0.1275	431	103.5	16.8	6.800
Q1	37.50	205	108.0	6.90	0.1075	198	80.5	3.1	6.100

* See text for explanation of factors.

TABLE 2

ONE-WAY ANALYSES OF VARIANCE AND "TWO-SAMPLE" t TESTS FOR TOTAL METAL CONCENTRATIONS, WEIGHT LOSS ON IGNITION, AND SOIL pH

A. COBALT

Analysis of variance

Source	DF	SS	MS	F
Factor	1	989	989	4.84
Error	41	8374	204	
Total	42	9393		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	55.13	15.76
Papai	13	44.69	9.89
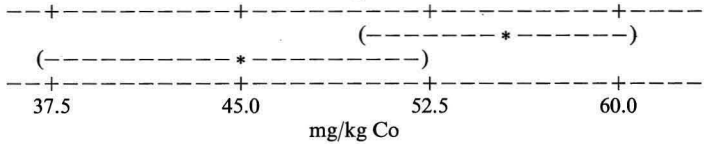
```
     --+---------+---------+---------+----
                               (-------*------)
  (-----------*----------)
     --+---------+---------+---------+----
     37.5       45.0      52.5      60.0
```

Pooled STDEV = 14.29   mg/kg Co

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (2.4, 18.5)
t test μ Kawaihae $= \mu$ Papai (vs. $\neq$): $T = 2.63$, $P = 0.013$, DF $= 35.3$

B. CHROMIUM

Analysis of variance

Source	DF	SS	MS	F
Factor	1	78748	78748	1.09
Error	41	2959352	72179	
Total	42	3038100		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	398.3	306.6
Papai	13	305.2	139.2

```
  -----+---------+---------+---------+-
                 (---------*---------)
  (-----------------*---------------)
  -----+---------+---------+---------+-
     200        300       400       500
```
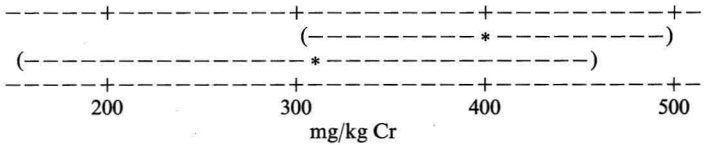
Pooled STDEV = 268.7   mg/kg Cr

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (-44, 231)
t test μ Kawaihae $= \mu$ Papai (vs. $\neq$): $T = 1.37$, $P = 0.18$, DF $= 40.8$

C. COPPER

Analysis of variance

Source	DF	SS	MS	F
Factor	1	7054	7054	3.08
Error	41	93950	2291	
Total	42	101003		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	92.27	52.46
Papai	13	120.15	34.31
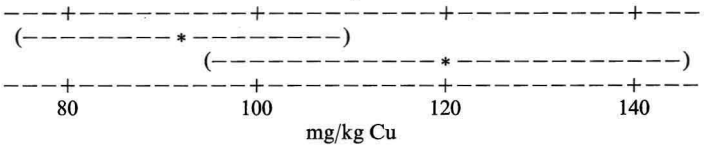
```
  --+---------+---------+---------+---
  (--------*---------)
               (-------------*-------------)
  --+---------+---------+---------+---
    80        100       120       140
```

Pooled STDEV = 47.87   mg/kg Cu

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (-55.3, -0.4)
t test μ Kawaihae $= \mu$ Papai (vs. $\neq$): $T = -2.07$, $P = 0.047$, DF $= 34.1$

D. IRON

Analysis of variance

Source	DF	SS	MS	F
Factor	1	292.82	292.82	68.59
Error	41	175.03	4.27	
Total	42	467.85		

TABLE 2 (continued)

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	12.952	2.251
Papai	13	7.270	1.529

```
Individual 95% CI for mean based on pooled STDEV
-----+----------+----------+----------+-
                                            (-- * --)
(---- * ----)
-----+----------+----------+----------+-
    7.2        9.6        12.0        14.4
              wt % Fe
```

Pooled STDEV = 2.066
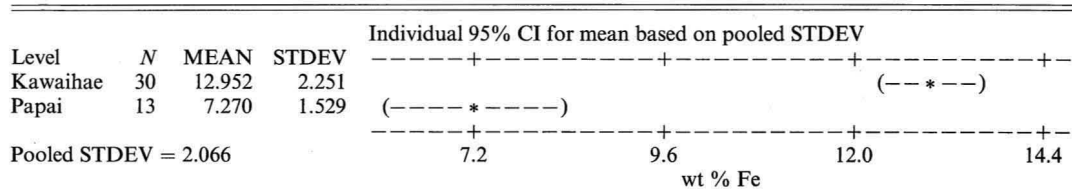
"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (4.48, 6.88)
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = 9.62$, $P = 0.0000$, DF $= 33.1$

E. MANGANESE

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.10213	0.10213	79.05
Error	41	0.05297	0.00129	
Total	42	0.15511		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	0.2207	0.0406
Papai	13	0.1146	0.0207

```
Individual 95% CI for mean based on pooled STDEV
-------+----------+----------+----------
                                      (-- * --)
(---- * ----)
-------+----------+----------+----------
     0.120       0.160       0.200
              wt % Mn
```

Pooled STDEV = 0.0359
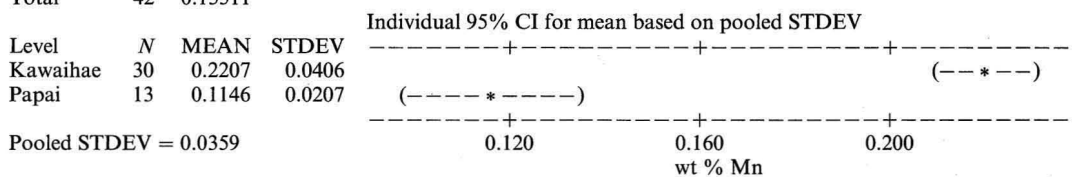
"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (0.0872, 0.1251)
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = 11.32$, $P = 0.0000$, DF $= 39.7$

F. NICKEL

Analysis of variance

Source	DF	SS	MS	F
Factor	1	6521	6521	0.28
Error	36	834837	23190	
Total	37	841359		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	260.9	158.7
Papai	8	293.0	122.4

```
Individual 95% CI for mean based on pooled STDEV
----------+----------+----------+------
       (--------- * ---------)
(-------------------- * ---------------)
----------+----------+----------+------
        240        400        360
              mg/kg Ni
```

Pooled STDEV = 152.3
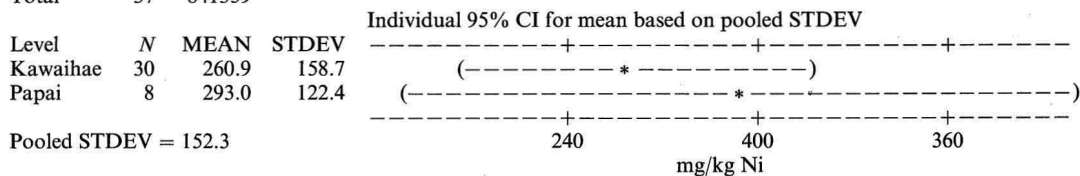
"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: $(-145, 80)$
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = -0.62$, $P = 0.55$, DF $= 14.0$

G. ZINC

Analysis of variance

Source	DF	SS	MS	F
Factor	1	144	144	0.06
Error	41	95234	2323	
Total	42	95378		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	117.6	21.1
Papai	13	113.6	82.8

```
Individual 95% CI for mean based on pooled STDEV
------+----------+----------+----------+
         (---------- * ----------)
(------------------ * ----------------)
------+----------+----------+----------+
     96         112        128        144
              mg/kg Zn
```

Pooled STDEV = 48.2

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: $(-46.8, 55)$
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = 0.17$, $P = 0.87$, DF $= 12.7$

TABLE 2 (continued)

H. LOI

Analysis of variance

Source	DF	SS	MS	F
Factor	1	261	261	1.90
Error	41	5627	137	
Total	42	5887		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV	
Kawaihae	30	10.42	6.05	(———————— * ————————)
Papai	13	15.78	19.50	(————————————— * —————————————)

```
            ————————+——————————+——————————+————————
              10.0           15.0           20.0
                            wt % LOI
```

Pooled STDEV = 11.71

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: $(-17.3, 6.6)$
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = -0.97$, $P = 0.35$, DF $= 13.0$

I. SOIL pH

Analysis of variance

Source	DF	SS	MS	F
Factor	1	6.679	6.679	21.67
Error	39	12.017	0.308	
Total	40	18.696		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV	
Kawaihae	30	7.320	0.554	(———— * ————)
Papai	11	6.409	0.559	(———————— * ————————)

```
            ————————+——————————+——————————+————————
              6.4            6.8            7.2
                           pH units
```

Pooled STDEV = 0.555

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (0.50, 1.33)
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = 4.63$, $P = 0.0000$, DF $= 17.7$

NOTE: In the analysis of variance tables, DF is degrees of freedom and SS is sum of squares broken down into two sources (variation due to differences between the two populations and variation within each population—"factor" and "error," respectively). MS is mean square due to the factor and mean square due to error; each mean square is the ratio of the corresponding sums of squares and degrees of freedom. F is the F ratio, or (MS factor)/(MS error).

In "two-sample" t tests, T is the test statistic, P is attained significance, and DF is degrees of freedom; μ is mean of the population.

presented in the *Handbook of Geochemistry* (Wedepohl 1969–1978). Probably the most extensive investigation of element composition of surficial materials in the United States is that of Shacklette et al. (1971); 863 samples of soils or other regolith, unaltered or very little altered from their natural conditions and supporting plant life, were taken at a depth of approximately 20 cm from locations about 80 km apart throughout the conterminous United States, sieved, and analyzed for 35 elements in the minus 200 mesh fraction. In Table 3 the mean total concentrations of the elements considered in this study in the Kawaihae and Papai series samples are juxtaposed with the means of those in samples from

the conterminous United States. In comparison, the Hawaiian soil samples contain somewhat higher concentrations of each of these elements, but all (except for iron in the Kawaihae samples?) are below the maximum concentration for each element in soil considered little altered.

As part of the statistical analyses in the present study, correlations were sought between the individual elements, between each metal and LOI, and between metals and pH. Pearson product moment correlation coefficients were calculated for these relationships.

Among the total concentrations of metals in the 30 Kawaihae series samples, Cr and Ni have a correlation coefficient of 0.954; all

TABLE 3

MEAN CONCENTRATIONS OF SELECTED ELEMENTS IN SURFICIAL MATERIALS OF THE CONTERMINOUS UNITED STATES
(SHACKLETTE ET AL. 1971) AND IN THE KAWAIHAE AND PAPAI SERIES SAMPLES

| | UNITED STATES* | | KAWAIHAE | PAPAI |
ELEMENT	MEAN (mg/kg)	RANGE (mg/kg)	MEAN (mg/kg)	MEAN (mg/kg)
Co	10	<3–70	55.1	44.69
Cr	53	1–1500	398	305
Cu	25	<1–300	92.3	120.2
Fe	25,000	100–>100,000	129,500	72,700
Mn	560	<1–7000	2207	1146
Ni	20	<5–700	261	293
Zn	54	<25–2000	117.6	113.6

*Based on 863 samples of soils or other regolith, unaltered or very little altered from their natural conditions and supporting plant life, taken at a depth of about 20 cm from locations about 80 km apart.

others have coefficients less than 0.6. Co and Cu have positive but weak correlations with the other metals, and other metal/metal correlations are weak and of mixed sign. Correlation coefficients of metals with LOI are all negative and small; the largest is with Fe (-0.603) and results from a poor distribution of values. Metal/pH coefficients are less than ± 0.3.

In the 13 Papai soil samples, the strongest metal/metal correlations (and corresponding coefficients) occur for Cu/Fe (0.632), Fe/Mn (0.648), Co/Cu (0.654), Co/Fe (0.729), and Co/Ni (0.822). However, the first four result from a poor distribution of values, and the last is based on only eight samples. Ni and Fe exhibit positive correlation with all other metals, but other metal/metal relationships are of mixed sign. Coefficients of total metal concentrations with LOI are all negative; the largest values are for Cu (-0.702), Mn (-0.805), Co (-0.846), and Fe (-0.880). Metal/pH relationships have their strongest correlations with Ni (0.541) and Mn (0.621).

Nonresidual Metal Concentrations and Effectiveness of Extractant

Nonresidual metals were extracted by shaking 10 g soil:100 mL $0.5M$ HCl for 16 hr. The effectiveness of extraction by the acid solution for any given metal in a soil sample is measured by comparing the amount of metal released to its total concentration (that is, the ratio of extracted to total concentration, or percentage of total). The statistical analyses in Table 4 are for these ratios. (The primary data are given in Halbig et al. 1985.)

Table 5 presents one-way analyses of variance and "two-sample" t tests for these ratios; these analyses are analogous to those presented earlier for the total metal concentrations, LOI, and soil pH.

Comparison of the mean, median, trimmed mean, maximum, minimum, and quartile values (Table 4) reveals that for all these statistical values Co and Mn have larger ratios in Kawaihae series soils, while Ni and Zn have larger ratios in Papai soils. Except for the MAX value in Hilo soils, Mn ratios are larger in Kawaihae soils, and except where the MAX values for Cu are about equal in both soil series, all Cu ratios are larger for Kawaihae soils. For Fe the statistical values of ratios as a group are not significantly greater or lower in either soil series. Thus, in general, $0.5M$ HCl extracts greater percentages of Co, Cr, Cu, and Mn from Kawaihae soils, greater percentages of Ni and Zn from Papai soils, and similar percentages of Fe from both soils. Inspection of the 95% confidence interval graphics (Table 5) confirms these results: Kawaihae series intervals for Co, Cr, and Mn are greater, and for Ni and Zn are less, than the corresponding intervals in the Papai series, and with no display of overlap; Cu displays minor overlap, and the Fe intervals are almost entirely overlapping.

TABLE 4

Statistical Analysis of Ratios of Metals Extracted to Total Concentrations
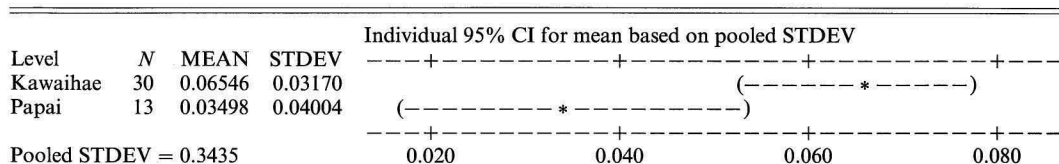
	Co	Cr	Cu	Fe	Mn	Ni	Zn
			A. Kawaihae Soil Series				
MEAN*	0.3409	0.0655	0.257	0.0608	0.373	0.0426	0.0579
MEDIAN	0.3166	0.0700	0.203	0.0609	0.375	0.0412	0.0407
TMEAN	0.3362	0.0644	0.237	0.0610	0.367	0.0424	0.0509
STDEV	0.0991	0.0317	0.169	0.0203	0.132	0.0148	0.0464
SEMEAN	0.0181	0.0058	0.031	0.0037	0.024	0.0027	0.0085
MAX	0.5870	0.1351	0.800	0.1108	0.718	0.0750	0.2262
MIN	0.1846	0.0168	0.050	0.0135	0.170	0.0176	0.0163
Q3	0.4187	0.0841	0.338	0.0763	0.484	0.0560	0.0765
Q1	0.2681	0.0310	0.134	0.0500	0.275	0.0322	0.0295
			B. Papai Soil Series				
MEAN*	0.1199	0.0350	0.1610	0.0694	0.144	0.0672	0.194
MEDIAN	0.0962	0.0174	0.1680	0.0448	0.080	0.0682	0.131
TMEAN	0.1163	0.0268	0.1535	0.0578	0.114	0.0672	0.172
STDEV	0.0626	0.0400	0.0858	0.0641	0.154	0.0193	0.176
SEMEAN	0.0174	0.0111	0.0238	0.0178	0.043	0.0068	0.049
MAX	0.2381	0.1500	0.3500	0.2498	0.586	0.0949	0.594
MIN	0.0408	0.0101	0.0544	0.0162	0.029	0.0379	0.034
Q3	0.1760	0.0484	0.2199	0.0818	0.185	0.0822	0.358
Q1	0.0711	0.0120	0.0816	0.0288	0.050	0.0493	0.043

Note: Metals extracted by shaking 10 g soil : 100 mL $0.5M$ HCl solution for 16 hr.
* See text for explanation of factors.

TABLE 5

One-Way Analyses of Variance and "Two-Sample" t Tests for Ratios of Metals Extracted to Total Concentrations

A. COBALT

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.44291	0.44291	54.78
Error	41	0.33151	0.00809	
Total	42	0.77442		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV
Kawaihae	30	0.3409	0.0991
Papai	13	0.1199	0.0626

```
----+---------+---------+---------+--
                                      (--*--)
(----*----)
----+---------+---------+---------+--
   0.10      0.20      0.30      0.40
```

Pooled STDEV = 0.0899

"Two-sample" t test
95% CI for μ Kawaihae $-$ μ Papai: (0.170, 0.272)
t test μ Kawaihae $=$ μ Papai (vs. $\neq$): $T = 8.82$, $P = 0.0000$, DF $= 35.1$

B. CHROMIUM

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.00842	0.00842	7.14
Error	41	0.04837	0.00118	
Total	42	0.05679		

TABLE 5 (continued)

Level	N	MEAN	STDEV
Kawaihae	30	0.06546	0.03170
Papai	13	0.03498	0.04004

Individual 95% CI for mean based on pooled STDEV

```
   ---+--------+--------+--------+---
                              (------*-----)
   (--------*---------)
   ---+--------+--------+--------+---
   0.020    0.040    0.060    0.080
```

Pooled STDEV = 0.3435

"Two-sample" *t* test
95% CI for μ Kawaihae − μ Papai: (0.0042, 0.057)
t test μ Kawaihae = μ Papai (vs. ≠): T = 2.43, P = 0.026, DF = 18.8

C. COPPER

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.0843	0.0843	3.78
Error	41	0.9137	0.0223	
Total	42	0.9979		

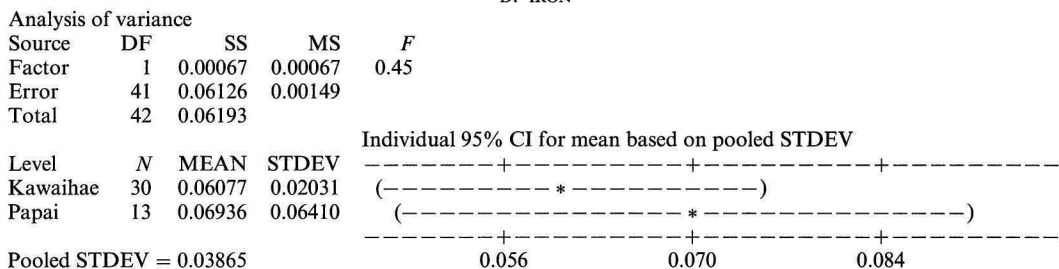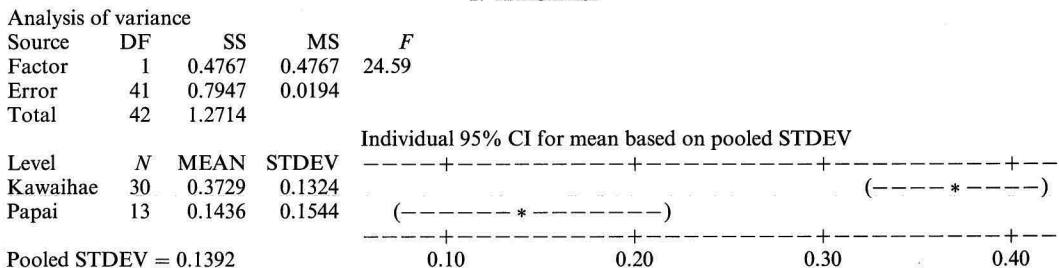| Level	N	MEAN	STDEV
Kawaihae	30	0.2574	0.1687
Papai	13	0.1610	0.0858

Individual 95% CI for mean based on pooled STDEV

```
   ----------+---------+---------+------
                            (-----*------)
   (------------*----------)
   ----------+---------+---------+------
           0.150     0.225     0.300
```

Pooled STDEV = 0.1493

"Two-sample" *t* test
95% CI for μ Kawaihae − μ Papai: (0.018, 0.175)
t test μ Kawaihae = μ Papai (vs. ≠): T = 2.48, P = 0.018, DF = 39.7

D. IRON

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.00067	0.00067	0.45
Error	41	0.06126	0.00149	
Total	42	0.06193		

Level	N	MEAN	STDEV
Kawaihae	30	0.06077	0.02031
Papai	13	0.06936	0.06410

Individual 95% CI for mean based on pooled STDEV

```
   -------+---------+---------+---------
   (----------*----------)
      (----------------*----------------)
   -------+---------+---------+---------
        0.056     0.070     0.084
```

Pooled STDEV = 0.03865

"Two-sample" *t* test
95% CI for μ Kawaihae − μ Papai: (−0.0478, 0.031)
t test μ Kawaihae = μ Papai (vs. ≠): T = −0.47, P = 0.64, DF = 13.1

E. MANGANESE

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.4767	0.4767	24.59
Error	41	0.7947	0.0194	
Total	42	1.2714		

Level	N	MEAN	STDEV
Kawaihae	30	0.3729	0.1324
Papai	13	0.1436	0.1544

Individual 95% CI for mean based on pooled STDEV

```
   ----+---------+---------+---------+--
                                 (----*----)
      (------*-------)
   ----+---------+---------+---------+--
      0.10      0.20      0.30      0.40
```

Pooled STDEV = 0.1392

"Two-sample" *t* test
95% CI for μ Kawaihae − μ Papai: (0.127, 0.332)
t test μ Kawaihae = μ Papai (vs. ≠): T = 4.66, P = 0.0000, DF = 20.0

TABLE 5 (continued)

F. NICKEL

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.003818	0.003818	15.34
Error	36	0.008958	0.000249	
Total	37	0.012776		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV				
				----------+----------+----------+------			
Kawaihae	30	0.04261	0.01479	(----*---)			
Papai	8	0.06720	0.01933			(--------*--------)	
				----------+----------+----------+------			

Pooled STDEV = 0.01577

	0.048	0.060	0.072

"Two-sample" t test
95% CI for μ Kawaihae − μ Papai: (−0.0412, −0.0080)
t test μ Kawaihae = μ Papai (vs. $\neq$): T = −3.35, P = 0.0086, DF = 9.3

G. ZINC

Analysis of variance

Source	DF	SS	MS	F
Factor	1	0.1686	0.1686	15.97
Error	41	0.4328	0.0106	
Total	42	0.6014		

Individual 95% CI for mean based on pooled STDEV

Level	N	MEAN	STDEV				
				--------+----------+----------+--------			
Kawaihae	30	0.05795	0.04636	(----*----)			
Papai	13	0.19427	0.17571			(-------*-------)	
				--------+----------+----------+--------			

Pooled STDEV = 0.10274

	0.075	0.150	0.225

"Two-sample" t test
95% CI for μ Kawaihae − μ Papai: (−0.2441, −0.029)
t test μ Kawaihae = μ Papai (vs. $\neq$): T = −2.76, P = 0.017, DF = 12.7

The relative effectiveness of the extractant for individual metals is, with some exceptions, $Mn > Co > Cu > Cr > Fe \geq Zn \approx Ni$ for Kawaihae soils and $Cu \approx Zn > Co \approx Mn > Fe \approx Ni > Cr$ for Papai soils. Because the soils are relatively pristine (without undue contamination by adsorbed, complexed, and precipitated metals and metal compounds that might be easily removed by the extracting solution), the difference in the effectiveness of removal of individual metals probably results from weathering under different climatic conditions.

Correlations between extracted and total concentrations of any given metal in the 30 Kawaihae soil samples are all positive; the largest coefficients are for Cr (0.610), Co (0.694), Cu (0.747), and Ni (0.893). For the 13 Papai soils, the coefficients are of mixed sign, with larger values for Ni (0.680), obtained on only eight samples, and for Zn (0.924), but with a poor distribution of values.

An analysis of the correlations of the ratios of extracted to total concentrations yields only two coefficients greater than 0.5 for the Kawaihae soils (Mn/Zn, 0.567; Co/Mn, 0.657), but for Papai soils there are several greater than 0.7 (Fe/Zn, 0.707; Cu/Zn, 0.765; Co/Fe, 0.766; Co/Mn, 0.895; Mn/Zn, 0.905; and Co/Zn, 0.916). The relationships between individual ratios and LOI are weak for Kawaihae soils (the only coefficient greater than 0.4 is for Zn, 0.643, with a poor distribution of values); Papai soils, however, have relatively strong correlations for several ratios with LOI (Cu, 0.636; Fe, 0.793; Co, 0.806; Zn, 0.830; and Mn, 0.882).

In a related study, Kanehiro and Sherman (1967) investigated the relationship between $0.1 M$ HCl-extractable Zn and total Zn in 94

soil samples from 19 soil profiles from five different islands in Hawaii. In that study 20-g soil samples were shaken with 200 mL of 0.1 M HCl for 45 min. Most important among their findings were: (1) extractable Zn decreased with soil depth, (2) a highly significant positive correlation was noted between extractable Zn and total Zn, (3) no correlation was noted between extractable Zn and pH, and (4) the occurrence of Zn-deficient plants was better correlated with acid-extractable Zn values than with total Zn concentrations. In the present study, 30 samples from the Kawaihae soil series, taken at 0 to 15 cm depth, were found to have mean concentrations of 6.8 mg/kg non-residual Zn and 117.6 mg/kg total Zn; the corresponding values for the one Kawaihae soil sample reported by Kanehiro and Sherman are 12.4 mg/kg and 136 mg/kg (at 0 to 10 cm depth) and 8.8 mg/kg and 119 mg/kg (at 10 to 30 cm depth). Similarly, the 13 samples of the Papai series (Hilo area) in the present study have mean concentrations of 22.0 mg/kg and 113.6 mg/kg for nonresidual and total Zn, respectively; the corresponding values for a Hilo silty clay loam (Hydrandept) reported by Kanehiro and Sherman are 17.5 mg/kg and 164 mg/kg (0 to 20 cm depth). Thus the analytical data for Zn presented in this study are generally in good agreement with those of Kanehiro and Sherman (1967).

Parent Material and Soil Genesis

Total metal concentrations and the ratios of extractable to total metals in soils depend upon the mineralogical and chemical composition of the parent materials and on the physiochemical conditions of the weathering environment. Under surface conditions the geochemical behavior may be determined by degree of hydrolysis of metal compounds, capacity to form complexes (including natural organic compounds), and changes in oxidation state.

Unfortunately, the mineralogical and chemical compositions of the parent materials for these soil series are not well established. The principal parent material for the Kawaihae soil series is Pahala Ash; throughout most of its extent this widespread pyroclastic,

once-glassy material has been weathered to a mixture of clay minerals and hydrated oxides of aluminum and iron, making it impossible to determine the original composition or its exact source (Macdonald et al. 1983).

The Papai soil series samples were developed on Mauna Loa tholeiite flows for which there are no analytical data known to these writers for samples in the immediate soil-sampling area. However, analytical data on Mauna Loa basalts from several other localities are available. In Table 6 the mean concentrations and standard deviations of metals in the Papai samples are listed with those for 13 tholeiites from the summit, south and northeast rifts, and the northwest slope of Mauna Loa (Leeman et al. 1980) and for 117 Mauna Loa basalts (which probably include olivine basalts and oceanites in addition to tholeiites) given by the Basaltic Volcanism Study Project (1981:app. A-6). The two sets of rock data have nearly identical concentrations of Fe and Mn; in comparison, the Papai soil samples average 85% and 92% of the averaged mean rock concentrations of Fe and Mn, respectively, but some of this "depletion" results from dilution of the weathered rock and metal constituents by organic matter not originally present. Mean soil Cr is intermediate between the means of 13 tholeiites and 9 "basalts," and mean soil Co is only 6% greater than that of the tholeiites. Ni is markedly enriched in the soils (three times the rock concentration). There are no rock data for Cu and Zn. The lack of additional data on parent materials precludes a conclusive discussion on the soil-forming processes of these two soil series.

CONCLUSIONS

Concentrations of total Co, Cr, Cu, Fe, Mn, Ni, and Zn and nonresidual quantities of these metals, expressed as ratios of extracted to total concentrations, are established for an Aridisol (the Kawaihae series) and a Histosol (the Papai series) which developed from volcanic materials under different climatic conditions on the island of Hawaii. The Aridisol has distinctively greater Fe and Mn, generally

TABLE 6

MEAN METAL CONCENTRATIONS AND STANDARD DEVIATIONS FOR PAPAI SOIL SAMPLES AND MAUNA LOA BASALTS

| | | MAUNA LOA BASALTS | |
ELEMENT	PAPAI SOILS	13 THOLEIITES*	117 BASALTS[†]
Co (mg/kg)	44.69 ± 9.89	42 ± 1	—
Cr (mg/kg)	305 ± 139	260 ± 27	340 ± 140[‡]
Cu (mg/kg)	120.2 ± 34.3	—	—
Fe (wt %)	7.27 ± 1.53	8.47 ± 0.16	8.59 ± 1.94
Mn (wt %)	0.1146 ± 0.0207	0.126 ± 0.009	0.124 ± 0.023
Ni (mg/kg)	293 ± 122	95 ± 25	—
Zn (mg/kg)	113.6 ± 82.8	—	—

* Leeman et al. (1980).
[†] Probably a composite of tholeiite basalts, olivine basalts, and oceanites; Basaltic Volcanism Study Project (1981).
[‡] Nine samples only.

greater Co and Cr, and less Cu than does the Histosol; the 95% confidence intervals for both Ni and Zn in the former series are contained within the corresponding intervals for the latter series. LOI is typically lower, and soil pH higher, in the Aridisol.

A strong degree of correlation between total Cr and Ni exists in the Aridisol. The Histosol exhibits strong negative (inverse) correlation between Cu, Mn, Co, and Fe individually with weight loss on ignition. Compared to mean concentrations of metals in other soils throughout the conterminous United States, these Hawaiian soils contain elevated mean concentrations of each metal.

The $0.5 M$ HCl method employed here removes significantly different percentages of individual metals from each soil series, and the relative order of its effectiveness differs in the two series. For the Aridisol (Kawaihae series) the order is Mn > Co > Cu > Cr > Fe ≥ Zn ≈ Ni; for the Histosol (Papai series), Cu ≈ Zn > Co ≈ Mn > Fe ≈ Ni > Cr. Because the soils are relatively pristine, the difference most probably results from weathering under different climatic conditions.

Correlations between LOI (which includes organic matter and water loss from soil colloids) and percentages of any given metal extracted are weak in Kawaihae soils but relatively strong for Cu, Fe, Co, Zn, and Mn in Papai soils.

Relative to its parent rock, the Histosol is moderately depleted in Fe and Mn, moderately enriched in Co and possibly Cr, and

markedly enriched in Ni. Lack of data on Cu and Zn in the Histosol parent tholeiite and limited knowledge of the original nature and source of the volcanic ash which is the parent material for the Aridisol contribute to the problem of discussing parent materials and soil genesis in a definitive manner.

LITERATURE CITED

AGEMIAN, H., and A.S.Y. CHAU. 1976. Evaluation of extraction techniques for the determination of metals in aquatic sediments. Analyst 101:761–767.

———. 1977. A study of different analytical extraction methods for nondetrital heavy metals in aquatic sediments. Arch. Environ. Contam. Toxicol. 6:69–82.

BASALTIC VOLCANISM STUDY PROJECT. 1981. Oceanic intraplate volcanism. Pages 161–192 and App. A-6 in Basaltic volcanism on the terrestrial planets. Pergamon Press, New York.

BOWMAN, W. S., G. H. FAYE, R. SUTARNO,

J. A. MCKEAGUE, and H. KODAMA. 1979. Soil Samples SO-1, SO-2, SO-3, and SO-4 —Certified Reference Materials. Canada Centre for Mineral and Energy Technology, Report 79-3, Energy, Mines and Resources Canada, Ottawa.

BRADSHAW, P.M.D., I. THOMAS, B. W. SMEE, and J. O. LARSSON. 1974. The application of different analytical extractions and soil profile sampling in exploration geochemistry. J. Geochem. Explor. 3:209–225.

CHIN HUAT LIM, and M. L. JACKSON. 1982. Dissolution for total elemental analysis. In A. L. Page, R. H. Miller, and D. R. Keeney, eds., Methods of soil analysis, Pt. 2— Chemical and microbiological properties. 2nd ed. American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin.

DEUEL, L. E. and A. R. SWOBODA. 1972. Arsenic toxicity to cotton and soybeans. J. Environ. Qual. 1:317–320.

HALBIG, J. B., W. M. BARNARD, S. E. JOHNSTON, R. A. BUTTS, and S. A. BARTLETT. 1985. A baseline study of soil geochemistry in selected areas on the Island of Hawaii. State of Hawaii Department of Planning and Economic Development, Honolulu.

INLAND WATERS DIRECTORATE, WATER QUALITY BRANCH. 1978. Determination of metals in sediments: Total (bomb digestion). Analytical methods manual 1979. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada.

———.1980. Non-residual metals in sediments (0.5 N hydrochloric acid extraction). Analytical methods manual 1979. Inland Waters Directorate, Water Quality Branch, Ottawa, Canada. (This open-end manual contains contributions from several years, with updates.)

JOHNSTON, S. E., and W. M. BARNARD. 1979. Comparative effectiveness of fourteen solutions for extracting arsenic from four western New York soils. Soil Sci. Soc. Am. J. 43:304–308.

KANEHIRO, Y., and G. D. SHERMAN. 1967. Distribution of total and 0.1 normal hydrochloric acid-extractable zinc in Hawaiian soil profiles. Soil Sci. Soc. Am. Proc. 31:394–399.

LEEMAN, W. P., J. R. BUDAHN, D. C. GERLACH, D. R. SMITH, and B. N. POWELL. 1980. Origin of Hawaiian tholeiites: Trace element constraints. Am. J. Sci. 280-A:794–819.

MACDONALD, G. A., A. T. ABBOTT, and F. L. PETERSON. 1983. Volcanoes in the sea: The geology of Hawaii. 2nd ed. University of Hawaii Press, Honolulu.

MCKEAGUE, J. A., ED. 1978. Manual on soil sampling methods of analysis. 2nd ed. Canadian Society of Soil Science, Ottawa.

REED, J. F., and M. B. STURGIS. 1936. Toxicity from arsenic compounds to rice on flooded soils. J. Am. Soc. Agron. 28:432–436.

RYAN, T. A., JR., B. L. JOINER, and B. F. RYAN. 1976. Minitab student handbook. Duxbury Press, North Scituate, Mass

SATO, H. H., W. IKEDA, R. PAETH, R. SMYTHE, and M. TAKEHIRO, JR. 1973. Soil survey of island of Hawaii, State of Hawaii. U.S. Government Printing Office, Washington, D.C.

SHACKLETTE, H. T., J. C. HAMILTON, J. G. BOERNGEN, and J. M. BOWLES. 1971. Elemental composition of surficial materials in the conterminous United States. U.S. Geological Survey Professional Paper 574-D. U.S. Government Printing Office, Washington, D.C.

SWAINE, D. J. 1955. The trace-element content of soils. Commonwealth Bureau of Soil Sci., Tech. Comm. No. 48, Farnham Royal, Bucks, U.K.

VINOGRADOV, A. P. 1959. The geochemistry of rare and dispersed chemical elements in soils. 2nd ed. (revised and enlarged, translated from Russian). Consultants Bureau, Inc., New York.

WEDEPOHL, K. H., ED. 1969–1978. Handbook of geochemistry. Springer-Verlag, Berlin.