3206

ASSESSMENT OF TRACE ELEMENT CONTAMINATION

IN STREAMBED SEDIMENT AND SPATIAL ASSOCIATIONS

IN PALOLO VALLEY WATERSHED, HONOLULU, O'AHU, HAWAI'I

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ABSTRACT

Trace elements in streambed sediment (<63 micrometers) of Palolo, Pukele, and Waiomao Streams (Palolo Valley Watershed, Honolulu, Hawaii) were investigated. Based on weak hydrochloric acid leaching (0.5 molarity), total digestions, sequential extractions, concentration enrichment ratios, sediment quality guideline comparisons, and national stream comparisons, there was significant lead contamination in Palolo Stream and some concern for copper, nickel, and zinc. Pukele Stream had intermediate trace element contamination, while Waiomao Stream was largely uncontaminated. Palolo Stream had significantly greater concentrations of trace elements than Pukele Stream, and both streams were significantly greater than Waiomao Stream. Since sediment in Palolo Steam was significantly contaminated with trace elements, the biological integrity of Palolo Stream and downstream systems could be impaired. There were great differences in urbanization related to population, storm drains, streets, and vehicle numbers in the sub-basins. These landuse characteristics could contribute to the observed differences among trace elements concentrations in streambed sediment.

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LIST OF ABBREVIATIONS AND SYMBOLS

α	Alpha (Significance Level)
α_{adj}	Alpha Adjusted (Adjusted Significance Level)
Ag	Silver
Al	Aluminum
As	Arsenic
AAS	Atomic Absorption Spectrometry/Spectrophotometry
AFS	Atomic Fluorescence Spectrometry
ANOVA	Analysis of Variance
Ba	Barium
Be	Beryllium
Bi	Bismuth
BCR	Standards, Measurements, and Testing Program (was known as European Community Bureau of Reference)
BCR	BCR sequential extraction procedure
BCR_{Sum}	sum of BCR steps
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
CEC	Cation Exchange Capacity (units $cmol_c/kg$)
CH_3COOH	Acetic acid (HOAc)
$cmol_c/kg$	centimoles of charge / kilogram of dry soil
CRM	Certified Reference Material
CV%	Coefficient of Variation
DC-AES	Direct-Current Arc Emission Spectrometry
EDTA	Ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
ER	Enrichment Ratio
ER_n	Enrichment Ratio of specific element
ERL	Effects Range Low (10^{th} percentile)
ERM	Effects Range Median (50^{th} percentile)
ETAAS	Electrothermal Atomic Absorption Spectrometry
Fe	Iron
g	gram
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GIS	Geographic Information System
h	hour
Hg	Mercury
$HClO_4$	Perchloric acid
HCl	Hydrochloric acid
HF	Hydrofluoric acid

HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
INAA	Instrumental Neutron Activation Analysis
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma-Mass Spectrometry
L	liter
La	Lanthanum
Li	Lithium
Mn	Manganese
μg/L	micrograms / Liter (μg/L = ppb)
μm	micrometers
M	Molarity
mg/L	milligrams / Liters (mg/L = ppm)
mL	milliliter
mm	millimeter
min	minute
MAD	Median absolute deviation from the median
Ni	Nickel
NAWQA	National Assessment of Water Quality
NaOAc	Sodium acetate
$NH_2OH \cdot HCl$	Hydroxylamine hydrochloride
NH_4OAc	Ammonium acetate
OM	Organic Matter
Pb	Lead
PCB	Polychlorinated biphenyls
PEC	Probable Effect Concentrations
PEL	Probable Effect Level
PEL_n	Probable Effect Level of a specific element
ppm	parts per million (ppm = mg/L)
ppb	parts per billion (ppb = μg/L)
RCMV%	Relative coefficient of median variation ([MAD ÷ Median] *100)
Sb	Antimony
Sc	Scandium
Se	Selenium
Sr	Strontium
SD	Standard Deviation
SQG	Sediment Quality Guidelines
Ti	Titanium
Tl	Thallium
TEC	Threshold Effect Concentrations
TEL	Threshold Effect Level
TEL_n	Threshold Effect Level of a specific element

Total	4-acid total digestion
$Total_{est}$	Total digestion estimation from recovery ratios
TXRF	Total X-ray Fluorescence Spectrometry
UCC	Upper Continental Crust
USGS	U.S. Geological Survey
V	Vanadium
XRF	X-ray Fluorescence Spectrometry
Zn	Zinc

1.0. INTRODUCTION

1.1. Element Contamination in the Environment

Trace and major elements are a natural part of an environment found primarily in parent rock and metallic minerals (Adriano 2001). However, there are many anthropogenic sources of elements, particularly metals, which have lead to the degradation of physical environments and biota. Anthropogenic sources include agriculture, metallurgy, energy production, transportation, microelectronics, and waste disposal (Adriano 2001). Elements can be released as gases, liquids, or solids and can originate from point or nonpoint sources (Adriano 2001). Han et al. (2002) estimated the potential industrial age anthropogenic lead (Pb), mercury (Hg), and cadmium (Cd) inputs in the pedosphere (soil) are 9.6, 6.1, and 5.2 times higher than non-anthropogenic levels in the lithosphere rock, respectively.

Although element contamination is sometimes thought to be a product of modern civilizations, anthropogenic inputs could have begun with the domestication of fire more than 500,000 years ago (Ponting 1991). Trace elements deposited in cave environments from firewood burning altered the natural element concentrations (Nriagu 1996). Closer to present day, copper (Cu) smelting began in Anatolia (Turkey) about 8000 years ago and about 1000 years later in Mesopotamia (Ponting 1991). With the discovery of mining and metalworking techniques, the close link between trace elements, trace element contamination, and human history was formed (Nriagu 1996).

Since ancient times, the symptoms of element toxicity have been nonspecific and retrospective; however, there are historical accounts of element contamination and poisonings (Nriagu 1988). Over 2000 years ago, Hippocrates (460-377 B.C.) reported, "cows and horses could not be pastured near the mines of Laurion, near Athens of classical Greece, because they became sick and died" (Faure 1991). Strabo, another Roman, wrote that Pb smelting works needed to be equipped with chimneys so "gas from the ore may be carried high into the air, for it is heavy and deadly" (Ponting 1991). Additionally, the Roman Empire utilized Pb extensively in food preparation, preservation, water pipes, cosmetics, and medicaments (Nriagu 1983). The human symptoms of Pb poisoning described by Hippocrates (460-377 B.C.) in Roman times were a loss of appetite, colic, weight loss, fatigue, and irritability (Faure 1998).

In contemporary times, research has shown that particular elements, especially metals, have no beneficial effect in humans and no known homeostasis mechanism, while other elements are linked to specific diseases such as cardiovascular disease, reproductive impairments, immune suppression, allergies, and cancer (**Table 1.1**).

Table 1.1. Elements associated with specific diseases

No Known Beneficial Effect in Humans	Cardiovascular Disease	Reproductive Impairments	Cancer Associated
Ag, Cd, Hg, Pb, Tl	Cd, Pb	Al, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Sb	Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Sb, Se, Ti, V, Zn

after Nriagu (1988).
Ag (silver), Al (aluminum), As (arsenic), Be (beryllium), Bi (bismuth), Cd (cadmium), Co (cobalt), Cr (chromium), Cu (copper), Fe (iron), Hg (mercury), La (lanthanum), Mn (manganese), Ni (nickel), Pb (lead), Sb (antimony), Se (selenium), Ti (titanium), Tl (thallium), V (vanadium), Zn (zinc).

Lead is a neurotoxin that can be stored in human blood, brain tissue, or bones with calcium (Ca), strontium (Sr), and barium (Ba) (Faure 1998, Lidsky and Schneider 2003). Faure (1998) listed several adverse effects from Pb related to pregnancies, which include:

- the risk of premature birth increases significantly for mothers whose blood contained between 80 and 140 μg/L (0.08 and 0.14 mg/L) of Pb,
- children whose blood in the umbilical cord contained an average of 140 μg/L (0.14 mg/L) of Pb were measurably impaired in their mental development at the age of six months,
- high prenatal Pb blood levels in children are associated with low birth weight and a decrease in their length, and
- the adverse effects of high Pb content in the blood of prenatal children are detectable up to at least 12 months after birth.

In modern times, it has been that argued there is a "silent epidemic of environmental metal poisoning," where over one billion humans are exposed to elevated levels of toxic trace elements (Nriagu 1988). Although the dangers of particular elements are known, many elements have become essential to industrial and developing societies.

1.2. Trace Elements in Fluvial Bed Sediment

Water bodies, such as rivers and lakes, can be used as "sentinel ecosystems," because they collect and integrate the regional sediment of a watershed and preserve long-term information of sediment quality (Carpenter and Cottingham 1997, Smol 2002). Although rivers are dynamic water bodies, typically with shorter sediment residence times, bed sediment can be a valuable medium for investigating environmental change.

A trace element can attach to sediment in several ways, including as "discrete compounds, ions held by cation-exchanging clays, bound by hydrated oxides of Fe or manganese (Mn), or chelated by insoluble humic [organic] substances" (Manahan 2000). Bacteria and algae in sediment can also biologically incorporate trace elements, which can eventually lead to bioaccumulation and/or biomagnification through trophic levels (Hart 1982). Additionally, the process of sedimentation can simply cause the physical entrapment of particulate trace element matter with suspended sediment as they settle out of the water column and are deposited along the streambed (Hart 1982).

In 1998, the US Environmental Protection Agency (EPA) submitted the first survey report to Congress on aquatic sediment contamination in the US. The survey concluded that there were contaminated sediments in all regions of every state and nearly 10 % of the sediment posed a potential risk to people and wildlife (USEPA 1999).

Sediment contamination can change ecosystems at the base of the food chain by influencing the development of aquatic macroinvertebrates, which can lead to a "modification of the whole ecological structure" (Beasley and Kneale 2002). The accumulation of contaminated streambed sediments is the principal reason for reduced biointegrity (Beasley and Kneale 2002). Power and Chapman (1992) list several reasons for establishing sediment quality criteria:

> • various toxic contaminants found in only trace amounts in the water column accumulate in sediments to elevated levels,
> • sediments serve as both a reservoir and a source of contaminants to the water column,
> • sediments integrate contaminant concentrations over time, whereas water column contaminant concentrations are much more variable and dynamic,
> • sediment contaminants, in addition to water column contaminants, affects benthic and other sediment-associated organisms, and
> • sediments are an integral part of the aquatic environment, providing habitat, feeding, and rearing areas for many aquatic biota.

Horowitz (1991) listed two reasons why streambed sediments are preferable as a sampling medium to suspended sediments in the water column. These are:

> • when suspended sediment concentrations are relatively low, <100 mg/L (mg/kg), it is usually far simpler and easier to collect sufficient amounts of bed sediment than suspended sediments to meet the mass requirements for all requisite physical and chemical analyses, and
> • suspended sediments tend to display much more marked spatial and temporal chemical and physical variability than do bed sediments.

As stated above, bed sediments are typically superior to suspended sediment and water column data in contaminant investigations. Finally, Feltz (1980) concluded streambed sediment material data are significant because they can be used:

• as an historical water quality integrator,
• as a reconnaissance tool,
• in planning analytical schedules,
• in conducting short-lived studies,
• for deriving short- and long-term trends, and
• for identification of problem areas.

1.3. Sources, Pathways, and Sinks of Trace Elements

The potential anthropogenic sources of selected trace elements to the environment are listed in **Table 1.2**.

Table 1.2. Potential anthropogenic sources of selected elements in the environment

	Potential Anthropogenic Sources
As [a]	Nonferrous metal mining and smelting, pesticide manufacturing/application, coal combustion, wood preservation, wood combustion, waste incineration, semiconductor manufacturing, and glass production
Cd [b]	Lubricating oils, diesel oils, tires, phosphate fertilizers, sewage sludge, insecticides, electroplating, pigments, batteries, coal and oil combustion, non-ferrous metal production, refuse incineration, iron and steel manufacturing
Cr [c]	Natural gas, oil, and coal combustion, chemical manufacturing industry, electroplating, leather tanning, fly ash from coal-fired power plants, treated wood, cement production, asbestos brake linings, incineration of refuse and sewage sludge, exhaust from catalytic converters, emissions from cooling towers using Cr compounds as rust inhibitors, textile industries.
Cu [b]	Metal plating, bearing and brushing wear, moving engine parts, brake-lining wear, fungicides and insecticides, anti-foulants, corrosion of Cu plumbing, algaecides, concrete and asphalt, rubber, phosphate fertilizers, sewage sludge
Ni [b]	Diesel fuel and vehicle exhaust, lubricating oil, metal plating, brushing wear, brake lining wear, asphalt paving, phosphate fertilizers, and storage batteries
Pb [b]	Leaded gasoline, automobile exhaust, tire wear, lubricating oil and grease, bearing wear, brake lining, rubber, concrete, paint manufacturing, battery manufacturing, insecticides, phosphate fertilizers, and sewage sludge
Zn [b]	Vulcanization of rubber and tire wear, motor oil, grease, batteries, galvanizing, plating, air-conditioning ducts, pesticides, phosphate fertilizers, sewage sludge, transmission fluid, under coating, brake linings, asphalt, concrete, coal combustion, smelting operations, incineration and wood combustion

[a] after US ATSDR (2000a).
[b] after Sutherland (2000b) sources: Lagerwerff and Specht (1970), Frank et al. (1976), Wigington et al. (1983), Moore and Ramamoorthy (1984), Harned (1988), Kabata-Pendias and Pendias (1992), Lee et al. (1994), Alloway (1995), Raine et al. (1995), and Monaci and Bargagli (1997). Councell et al. (2004) for Zn tire wear. Root (2000) for Pb wheel weights
[c] after US EPA (1995) and US ATSDR (2000b).

Streams are sources, pathways, and sinks of water/sediment, and the elements that can be dissolved in water or attached to sediment. **Table 1.3** gives a general depiction of sources, pathways, and sinks of sediment throughout the fluvial environment. There are numerous components that could be a source, pathway, and sink.

Table 1.3. Sources, pathways, and sinks of elements in a fluvial environment

Source	Pathway	Sink
Atmosphere, Rivers Lakes, Soil Pavement, Roads Storm Sewers, Vehicles Pesticides, Fertilizers Mining, Industrial Waste	Atmosphere, Rivers Lakes, Soil Pavement, Roads Storm Sewers, Vehicles Street Sweepers	Ocean, Rivers Lakes, Soil Pavement, Roads Storm Sewers Sewage, Landfill, Tailings

after Combest (1991), Rhoads and Cahill (1999), Charlesworth et al. (2000), Sutherland (2000b), Root (2000), Andrews (2002), Beasley and Kneale (2002), DeCarlo and Anthony (2002), and Councell et al. (2004).

1.4. Variation of Trace Elements in Urban Streams

A number of studies have shown that elevated element concentrations are associated with urban areas where anthropogenic sources are most abundant. Elevated element concentrations have been correlated with greater population or traffic density (Rhoads and Cahill 1999, Rice 1999, Callender and Rice 2000), storm drain sewers (Andrews 2002, Andrews and Sutherland 2004), and leaded gasoline use (Needleman 2000, Sutherland 2000b). Also, increased road densities, traffic numbers, and incidence of braking have been linked to a decline in macroinvertebrates of urban streams (Beasley and Kneale 2002).

In a US Geological Survey (USGS) examination of 20 continental study areas of their National Water Quality Assessment Program (NAWQA), Rice (1999) found 49% of urban sites had concentrations of one or more elements that exceeded "threshold effect levels" (TEL) at which adverse biological effects could occur in aquatic biota. Rice

(1999) also found that the sums of concentrations of several trace elements (Cu, Hg, Pb, and Zn) were well correlated with population density. Callender and Rice (2000) found traffic density was strongly related to Pb and Zn. In another study where sediment quality guidelines (SQGs) were exceeded for Cu, Pb, Zn, Cr, and Ni, these sample sites were in close proximity to storm sewer outfalls (Rhoads and Cahill 1999).

1.5. Sediment Quality Guidelines (SQGs)

There have been several SQGs developed for metals, metalloids, hydrocarbons, organic pesticides, and polychlorinated biphenyls (PCB), which predict the likelihood of adverse biological affects (MacDonald et al. 2000).

Two summary SQGs were complied from previously established guidelines by MacDonald et al. (2000). These were a "threshold effect concentration" (TEC) and a "probable effect concentration" (PEC). **Table 1.4** gives concentrations and predictive abilities of TEC and PEC for several elements. All but one element (As) had a predictive quality >90% for sediment at concentration levels ≥ PEC.

Table 1.4. TEC and PEC concentrations and percent incidence of toxicity

Element	Guideline (mg/kg)		Incidence of Toxicity (%)		
	TEC	PEC	≤TEC	TEC- PEC	≥ PEC
As	9.9	33	26	58	77
Cd	0.99	4.98	20	45	94
Cr	43.4	111	28	64	92
Cu	31.6	149	18	64	92
Hg	0.18	1.06	66	70	100
Ni	22.7	48.6	28	63	91
Pb	35.8	128	18	54	90
Zn	121	459	18	61	90

after MacDonald et al. (2000).

One of the first studies to define SQGs was Long et al. (1995), which was based on matching biological and chemical data from marine and estuarine sediments. The two guidelines developed were “effects range-low” (ERL) and “effects range-median” (ERM). The lower 10th percentile of the effects data was identified as the ERL. The median, or 50th percentile, of the effects range data was identified as the ERM. The ERL and ERM pair of SQGs were also used to develop the TEC and PEC (**Table 1.4**, MacDonald et al. 2000). **Table 1.5** provides the ERL and ERM guideline values and the percent of biological effects based on the ranges established by the two guidelines. Unfortunately, only Cr, Cu, and Pb have predictive abilities >80% at ≥ ERM.

Table 1.5. ERL and ERM concentrations and percent incidence of biological effects

Element	Guideline (mg/kg)		Incidence of Effects (%)		
	ERL	ERM	≤ERL	ERL-ERM	≥ ERM
As	8.2	70	5	11	63
Cd	1.2	9.6	7	37	66
Cr	81	370	3	21	95
Cu	34	270	9	29	84
Hg	0.15	0.71	8	24	42
Ni	20.9	51.6	2	17	17
Pb	46.7	218	8	36	90
Zn	150	410	6	47	70

after Long et al. (1995).

The common pair of SQGs used by the USGS NAWQA program are the “threshold effect level” (TEL) and “probable effect level” (PEL) (**Table 1.6**).

Table 1.6. TEL and PEL concentrations (mg/kg)

Element	TEL	PEL
As	5.9	17
Cd	0.596	3.53
Cr	37.3	90
Cu	35.7	197
Hg	0.174	0.486
Ni	18	36
Pb	35	91.3
Zn	123	315

after Smith et al. (1996), MacDonald et al. (2000).

The TEL and PEL were used to develop the TEC and PEC guidelines (**Table 1.4**, MacDonald et al. 2000). The TEL "represents the concentration below which adverse effects are expected to occur only rarely," while PEL "represents the concentration above which adverse effects are expected to occur frequently" (MacDonald et al. 2000).

1.6. Study Designs

There are numerous study designs that have been employed to investigate trace elements in streambed sediment. The following section will highlight methods commonly used.

1.6.1. *Sampling, Spatial and Temporal Variability*

Representative sampling of bed sediments in spatially and temporally dynamic river environments can be of concern to researchers. If too few samples are taken to adequately represent the location of study, it may be difficult to distinguish a concentration pattern in streambed sediment. Spatial variability can be further complicated when multiple landuses contribute to the river.

The quantification of long-term variations of elements in bed sediment would be ideal when looking at contamination and management of rivers (Birch et al. 2001, USGS 2001, USGS 2004). However, a single sampling period with a suitable suite of spatially distributed samples can provide valuable information about river quality at a particular moment in time (Sutherland 2000b, Andrews 2002, Andrews and Sutherland 2004). A single sampling framework can be used as the basis for establishing a longer term monitoring program.

1.6.2. *Grain Size Partitioning*

Grain size is a significant factor controlling the capacity of sediment to concentrate elements (Horowitz 1991). Because of this, bed sediment samples are usually partitioned into specific size fractions to control for grain size effects. **Table 1.7** shows the general grain size scale used for partitioning sediments.

Table 1.7. Grain size scales for sediment <2000 µm

Size (µm)	Wentworth Size Class
< 2	Clay
2 - 63	Silt
63 - 125	Very Fine Sand
125 - 250	Fine Sand
250 - 500	Medium Sand
500 - 1000	Coarse Sand
1000 - 2000	Very Coarse Sand

after Folk (1974).

In general, there is a strong correlation between decreasing grain size and increasing element concentrations attached to sediment. Horowitz (1991) indicates that "this correlation results from a combination of both physical and chemical factors" of the sediment. As particle size decreases, the physical surface area increases, and cation exchange capacity (CEC) increases (Horowitz 1991), which increases the number of sites for elements to concentrate. **Table 1.8** illustrates some CEC capacities of several materials. The <63 µm grain size fraction (silts and clays) is commonly used for measuring contaminants in bed sediment (Gaiero et al. 1997, Rice 1999, Sutherland 2000b, Birch et al. 2001, Viganò et al. 2003, Andrews and Sutherland 2004, and USGS 20004b). When different grain sizes are analyzed, it becomes difficult to compare the results.

Table 1.8. Cation exchange capacity of selected materials

Material	CEC ($cmol_c/kg$) [a]
Pure Sand	0
Sand Soils	1- 5
Fine Sandy Loams	5 - 10
Loams and Silt Loams	5 - 15
Clay Loams	15 - 30
Clays	30 - 150
Humus (Organic Matter)	100 - 300

after Miller and Gardiner (2001).
[a] $cmol_c/kg$ = centimoles of charge per kilogram.

1.6.3. *Digestion of Sediments: Sequential, Weak, and Total Procedures*

After streambed sediment samples are sorted into size classes, the samples are commonly digested by one or more reagents to bring sediment-associated elements into solution. The varying reagent strengths, result in three basic geochemical approaches to examining elements in sediment: sequential extractions, weak bioavailable leaches, and total digestions.

Sequential extractions are increasingly being applied in environmental and geochemical contaminant research. This technique operationally defines multiple element phases associated with streambed sediments and other solid media. These different chemical phases control the availability of elements to the environment, which is useful in contaminant studies. Tessier et al. (1979) were one of the first to develop a sequential extraction procedures for aquatic environments, which involved separating elements into five operationally defined phases: (1) exchangeable, (2) carbonate bound, (3) Fe and Mn oxide bound, (4) OM bound, and (5) residual. Phases 1-4 are considered labile, with phase 1 the most readily bioavailable, followed by 2, 3, 4, and phase 5 is not bioavailable. Each sequential step applies a harsher reagent to release elements from specific phases. Although sequential extractions have the benefit of quantifying element associations, they are more complicated, time consuming, and costly. Recently, the BCR harmonized and standardized a 3-step procedure plus a 4^{th} and final aqua regia step (hydrochloric acid and nitric acid in a ratio of 3:1) has been employed for sequential extractions (BCR is the European Community Bureau of Reference, now known as the Standards, Measurements, and Testing Program) (Rauret et al. 1999, Sutherland and Tack 2000, 2002, 2003).

Weak single digestion (leaches), such as 0.5 molarity (M) hydrochloric acid (HCl), has been widely used as indicators of trace element bioavailability for aquatic sediments (Campbell et al. 1988, Sutherland et al. 2001). A dilute HCl leach (0.5 M) releases adsorbed, detrital, and non-detrital carbonate-bound trace elements, most trace elements associated with Fe/Mn oxides, and organic materials, while minimally affecting the residual silicate-bound elements (Fiszman et al. 1984, Sutherland and Tolosa 2000). Gasser et al. (1996) also stated that a short leach (1 h) with a dilute solution (0.1 M HCl) could serve as a quick and inexpensive method for determining Pb bioavailability from various solids, which would include streambed sediment. The most readily leached elements from weak digestions can be available to living organisms in aquatic environments, which could negatively impact biota. **Table 1.9** provides a list of common cold or weak reagents thought to be associated with bioavailability.

Table 1.9. Cold and/or dilute reagents commonly used in bioavailable extractions

Reagent	Chemical Formula	Molarity (M)
Acetic acid	CH_3COOH	0.1 - 4.2
Ethylenediaminetetraacetic acid	EDTA	0.05 - 0.5
Hydrochloric acid	HCl	0.07 - 2.0
Nitric acid	HNO_3	0.1 - 4.0
Sodium acetate	NaOAc	1.0

after Sutherland (2000b), Andrews (2002), Andrews and Sutherland (2004).

The third type of digestion procedure, total extraction, allows almost all elements present in sediment to be determined quantitatively. These digestions will break down clays, organic matter (OM), Fe and Mn oxides, carbonates, and most of the crystal matrix (Agemian and Chau 1976). This means that elements from both anthropogenic and natural sources will go into solution, which may not be as useful in environmental investigations. **Table 1.10** provides a list of common hot or strong acids used in total extractions.

Table 1.10. Hot and/or strong acids commonly used in total extractions

Acid	Chemical Formula	Molarity (M)
Hydrochloric acid	HCl	12.1
Hydrofluoric acid	HF	28.9
Nitric acid	HNO_3	15.9
Perchloric acid	$HClO_4$	11.7
Sulfuric acid	H_2SO_4	18.0

after Trefry et al. (1985), Rhoads and Cahill (1999), Rice (1999), Callender and Rice (2000), Sutherland (2000b), Sutherland and Tack (2000), Andrews (2002), DeCarlo and Anthony (2002).

1.6.4. *Analytical Methods of Measuring Trace and Major Elements*

There are several analytical methods to measure the concentrations of elements in solution after the sediment has been digested. These methods are listed in **Table 1.11**. Common methods used include atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS). Since each analytical method has advantages and disadvantages, the selection of the appropriate method(s) is important to consider. There are several references that provide details about AAS (Aruscavage and Crock 1987, Chau and Wong 1989), ICP-AES (Hall 1992, Yamasaki 1996), and ICP-MS (Hall 1992, Yamasaki 1996, Gluodenis 1998, Beauchemin 2004).

Table 1.11. Analytical methods of measuring trace and major elements

Analytical Method	Acronym
Atomic Absorption Spectrometry/Spectrophotometry	AAS
Atomic Fluorescence Spectrometry	AFS
Direct-Current Arc Emission Spectrometry	DC-AES
Electrothermal Atomic Absorption Spectrometry	ETAAS
Graphite Furnace Atomic Absorption Spectrometry	GFAAS
Inductively Coupled Plasma-Atomic Emission Spectroscopy	ICP-AES
Inductively Coupled Plasma-Mass Spectrometry	ICP-MS
Inductively Coupled Plasma-Optical Emission Spectrometry	ICP-OES
Instrumental Neutron Activation Analysis	INAA
Laser Ablation Inductively Coupled Plasma-Mass Spectrometry	LA-ICP-MS
Total X-ray Fluorescence Spectrometry	TXRF
X-ray Fluorescence Spectrometry	XRF

after Reeves and Brooks (1978), Baedecker (1987), Batley (1989).

1.6.5. *Statistical Analysis and Enrichment Ratios (ER)*

Data analysis can be one of the most challenging parts of any study, as there are a variety of possible qualitative and quantitative approaches. Although it is useful to provide basic qualitative and quantitative analysis (mean, median, etc.) of element concentrations, it is important to include analysis of the concentrations relative to established SQGs and other streams to evaluate possible contamination.

One common approach used in geochemistry is to normalize the data to a conservative element and establish enrichment ratios (ER). Conservative elements "are assumed to have a uniform flux from the crustal-rock sources, from the time sediment particles were eroded until the time they were deposited, over a long period of time" (Horowitz 1991). Conservative elements that have previously been used include Al, Cr, cesium (Cs), Fe, lithium (Li), scandium (Sc), and Ti (Loring 1990, Horowitz 1991, Sutherland 2000b). The most commonly used conservative elements are Al and Ti

(Horowitz 1991). A simple ratio, as described by Horowitz (1991) is used to calculate ERs:

$$ER_n = (C_n) / (C_{con}) \quad \textbf{[1.1]}$$

where, in a given sample C_n is the concentration of the element in question and C_{con} is the concentration of the conservative element. **Equation 1.1** was adapted by Sutherland (2000b) for a given element following the work of others (Lee et al. 1994, Lee at al. 1997) and is defined as:

$$ER_n = [(C_n/C_{con})_{\text{sample}}] / [(BE_n/BE_{con})_{\text{background}}] \quad \textbf{[1.2]}$$

where, C_n and C_{con} as before, BE_n is the best estimate of the background concentration of the element in the study area, and BE_{con} is the best estimate of the background concentration of the conservative element in the study area. Although there are no standardized rankings of ER_n, five categories were proposed by Sutherland (2000b):

- $ER_n \leq 2$ depletion to minimal enrichment, suggestive of no or minimal contamination
- $ER_n > 2\text{-}5$ moderate enrichment, suggestive of moderate contamination
- $ER_n > 5\text{-}20$ significant enrichment, suggestive of a significant contamination signal
- $ER_n > 20\text{-}40$ highly enriched, indicating a strong contamination signal
- $ER_n > 40$ extremely enriched, indicating an extreme contamination signal.

1.7. Previous Studies of Streambed Sediment

This section presents a brief review of previous streambed sediment research that has been conducted in international, national, and local rivers. Although the methods of each study vary, a general trend of contamination was common in places affected by industrial and/or urban landuses.

1.7.1. *International*

A selection of international research of element contamination in fluvial bed sediment (summarized in **Table 1.12**) illustrates that a variety of grain sizes, digestion procedures, and analytical methods have been employed. Since there is a lack of international standardization, it becomes difficult to compare results across studies. However, on a qualitative level, element contamination was associated with urbanization, industrial activities, and mining.

Table 1.12. Selected international research of elements in streambed sediment

Geographic Location	Authors	Grain Size (μm)	Digestion [a]	Analysis [b]
South America				
Suquia River System, Argentina	Gaiero et al. (1997)	<63	HCl	AAS
Europe				
River Elbe, Germany and Czech Republic	Aulinger et al. (2002)	<20	HNO_3, HF, HCl	TXRF, ICP-OES, ICP-MS, INAA
Coventry, United Kingdom	Charlesworth et al. (2000)	<63	$HClO_4$, HNO_3, H_2SO_4	AAS
Cávado River Basin, Portugal	Gonçalves et al. (1994)	<63	HNO_3, HCl	AAS, AAS-EA
Po River, Italy	Viganò et al. (2003)	<63	HNO_3, HCl, HF	AAS-EA
Vistula River, Poland	Wardas et al. (1996)	<20, <63	HNO_3	AAS
India				
Rivers of Ganga Plain, India	Singh et al. (2002)	<20	$HClO_4$, HNO_3, HF	AAS
Asia				
Toyohira River, Hokkaido, Japan	Sakai et al. (1986)	<71, 71-460, 460-810, 810-1680	HCl	AAS
Australia				
Sydney, NSW	Birch et al. (2001)	<63	HNO_3, $HClO_4$	AAS

[a] See **Table 1.10** for reagent names.
[b] See **Table 1.11** for analytical methods.

1.7.2. *United States*

During the past few decades, federal agencies (EPA and USGS) have examined the chemical content of bed sediments. The EPA's *Introduction to Contaminated Sediments* (1999) listed several key points related to the history of researching contaminated sediments:

- until the early 1980s few people saw contaminated sediments as a significant environmental problem,
- in the late 1980s, EPA began to document the extent and severity of contaminated sediments,
- under the Water Resources Development Act of 1992, Congress required EPA to conduct a comprehensive survey of the nation's sediments,
- EPA created the National Sediment Quality Survey, and
- efforts are underway to expand sediment monitoring.

There have been numerous published studies in the US related to trace elements in streambed sediments (Trefry et al. 1985, Combest 1991, Breault and Harris 1997, Rhoads and Cahill 1999, Rice 1999, Callender and Rice 2000, Frenzel 2002). Some of these studies were part of the USGS NAWQA program, which has an agency standardized method to study bed sediment throughout the US. Prior to streambed sediment investigations, most studies used suspended sediment or water column samples, which have become less useful compared to streambed sediment in contaminant research (Helsel et al. 1979, Trefry et al. 1985, Alexander and Smith 1988).

1.7.3. *State of Hawaii*

Prior to mid-1990s, there were few studies that looked at elements in soils, plants, or coastal sediments of Hawaii (Barnard and Halbig 1985, Fu et al. 1989, McMurtry et al. 1995). In recent years, there has been more research investigating streambed sediment (DeCarlo and Spencer 1997, USGS 1998, Sutherland 2000a, Sutherland 2000b, Andrews 2002, DeCarlo and Anthony 2002, Andrews and Sutherland 2004).

There have also been recent studies of elements in road-deposited sediments (RDS) (Bussen et al. 2000, Sutherland 2000c, Sutherland and Tolosa 2000, Sutherland et al. 2000, Sutherland et al. 2001, Andrews 2002, Sutherland 2002a, Sutherland 2002b, Sutherland 2003, Sutherland et al. 2003, Andrews and Sutherland 2004) and soil (DeCarlo and Spencer 1997, Sutherland and Tack 2000, Sutherland and Tolosa 2001, DeCarlo and Anthony 2002, Sutherland 2002a).

Since a majority of these recent studies have found elevated concentrations of elements in soils, RDS, and streambed sediment, it would be valuable to expand the spatial understanding of streambed sediment contamination as it could relate to landuse and demographic patterns.

2.0. RESEARCH OBJECTIVES

This thesis will investigate the geographic distribution of elements in the streambed sediment of Palolo Valley, Honolulu, Hawaii. The following outline presents the research objectives of this thesis.

- Quantify and discuss the variation of element concentrations in streambed sediment:
    - Focus on the following trace elements that could be enhanced from anthropogenic sources/activities and had elevated concentrations:
        - As (metalloid), Cd, Cr, Cu, Pb, Ni, and Zn (metals)
    - Utilize and discuss several digestion methods and one concentration calculation method relative to lability and potential bioavailability:
        - BCR sequential extraction digestion
        - Weak HCl digestion
        - Total 4-acid digestion
        - $Total_{est}$ concentration calculation
    - Make comparisons among Palolo Valley's three streams:
        - Palolo Stream, Pukele Stream, and Waiomao Stream
    - Compare Palolo Valley streams to national streams with comparable methods:
        - Nuuanu Stream and Manoa Stream of Honolulu
        - Oahu and US continental streams from USGS NAWQA program

- Discuss the element concentrations relative to SQGs and ERs:
    - Compare established SQGs (TEL and PEL) with trace element concentrations:
        - As (metalloid), Cd, Cr, Cu, Pb, Ni, and Zn (metals)
    - Based on SQG comparisons, determine:
        - if "bioavailable" element concentrations pose a potential threat to aquatic biota and
        - whether Palolo Valley should be further investigated.
    - Calculate and discuss enrichment ratios (ER).

- Illustrate the present spatial relationships between landuse and element concentrations:
    - Look for visual relationships among element concentration, landuse, storm drain lines, storm drain inlets/outlets, demographics, and other spatial information that could influence element concentrations
    - Illustrate these possible relationships with computer generated maps and/or Geographical Information Systems (GIS)

3.0. STUDY SITE & METHODS

3.1. Physical Geography and Geology

The Hawaiian Islands are the most isolated islands from any continental landmass. Oahu (1,564 km^2) is the third largest island in the state of Hawaii, which ranges between 158°20'W to 157°35'W longitude and 21°15'N to 21°45'N latitude in the Pacific Ocean (Oki and Brasher 2003). Palolo Valley watershed (11.4 km^2) is located in southeast Honolulu, Oahu (**Figure 3.1**). It is separated to the west by Kalaepohaku Ridge and Waahila Ridge (St. Louis Heights neighborhood), to the east by Mauumae Ridge (Wilhelmina Rise neighborhood), to the north by the Koolau Mountain Ridge, and to the south by the Kaimuki Dome (Waialae Avenue, Kaimuki neighborhood). There are three principal streams within the valley: Palolo Stream and its two tributaries, Pukele Stream and Waiomao Stream (**Figure 3.2**).

Palolo Valley is carved into remnants of the Koolau Shield Volcano, which forms the eastern mountain range of Oahu. The Koolau Volcano is between 1.8 and 2.7 million years old and is comprised of tholeiitic basalts, olivine basalts, and small amounts of oceanite (Lanphere and Dalrymple 1980, Macdonald et al. 1983, Frey at al. 1994). Additionally, post-erosion volcanism occurred <1 million years ago forming the Honolulu Volcanic Series (HVS), which represents <1% of the Koolau Shield Volcano and is characterized by nephelinite rocks (Clague and Frey 1982, Macdonald et al. 1983). At the head of Palolo Valley, the HVS geology is represented by Kaau Crater (~480 m diameter), however the crater walls are composed of Koolau lavas (Macdonald et al. 1983).

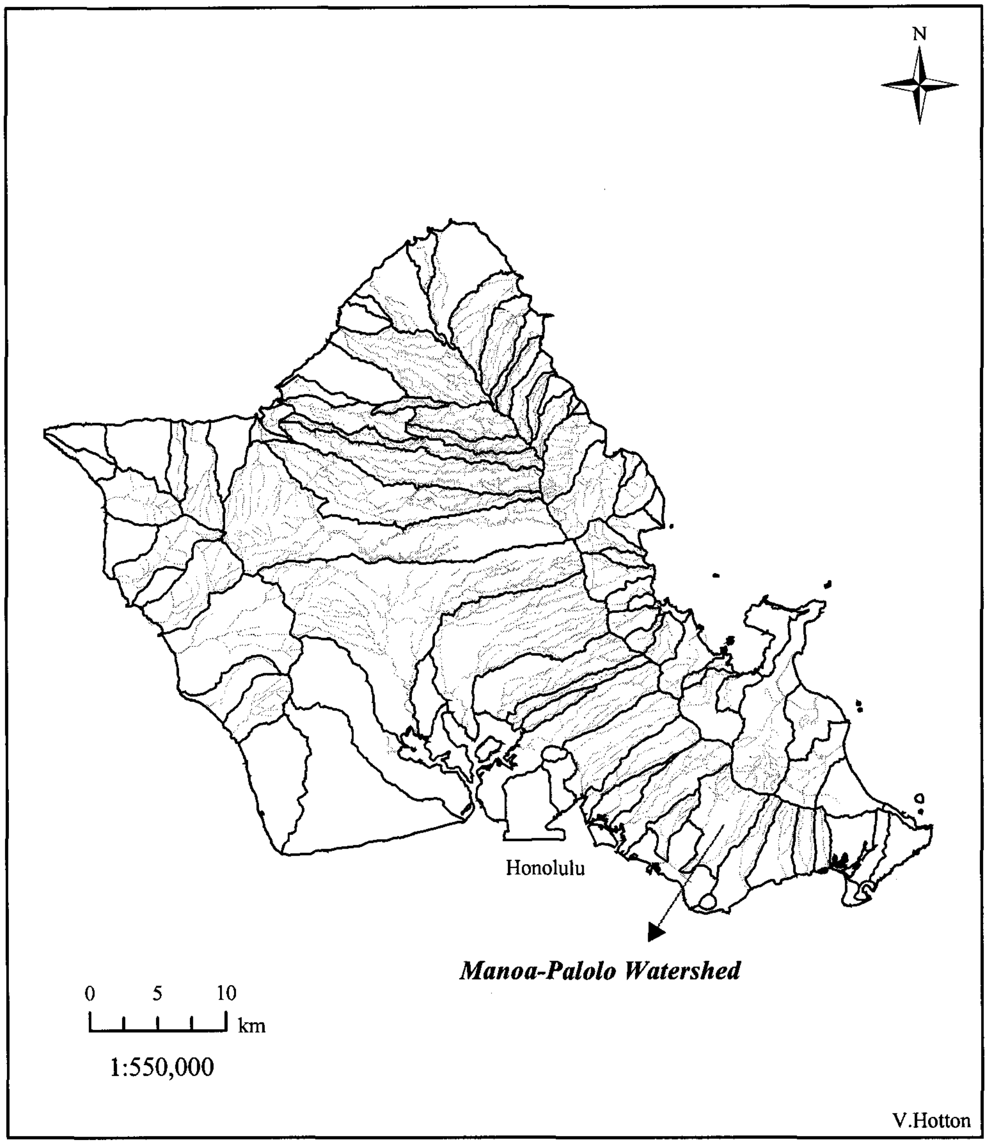


Figure 3.1. Oahu Island's watershed divisions (black lines) and perennial streams (gray lines)

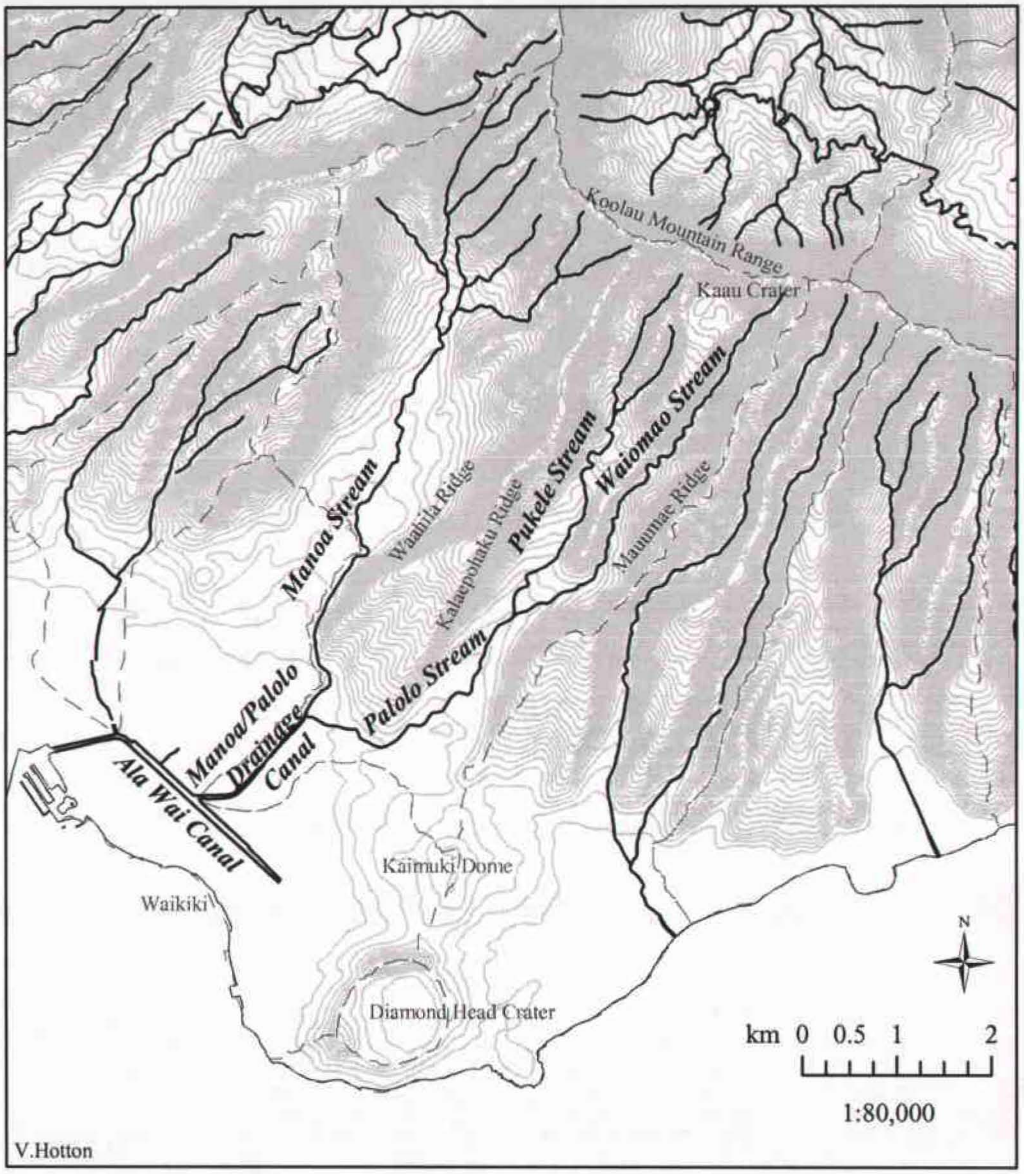


Figure 3.2. Map of Palolo Valley watershed with perennial streams (black lines), 12.2 m contours (40 ft, gray lines), and watershed boundaries (dashed dark gray lines)

Immediately south of Kaau Crater, along the east fork of Pukele Stream, HVS melilite nephelinite lava flow rests on Koolau basalt and talus, which is then overlain by tuff and mudflow debris (Macdonald et al. 1983). Kaimuki Dome is also a HVS feature (**Figure 3.2**). Several soil orders occur in Palolo Valley, which include entisols, histosols, inceptisols, mollisols, oxisols, ultisols, and vertisols (Foote et al. 1972).

3.2. Development and Settlement History of Palolo Valley

3.2.1. *1890 – 1899*

Written accounts of Palolo Valley date from the late nineteenth century when Native Hawaiians living in the valley tended taro fields (Tehranian 1993). An early event was The Battle of Palolo Valley, which occurred on January 7, 1895, along Palolo Hill, also called Maemae (State of Hawaii 1976). The battle was a reaction to Queen Liliuokalani's overthrow in 1893, and was fought between her supporters and the new US territorial government (State of Hawaii 1976).

When the US government took possession of Hawaiian lands, it began selling the land in parcels (Tehranian 1993). In Palolo Valley, some parcels were either converted to homestead lands leased to Native Hawaiians or purchased by businessmen in Honolulu (Tehranian 1993).

3.2.2. *1900 - 1939*

In the early twentieth century, there were several hundred cottages and bungalows built along the one unpaved road in the valley (State of Hawaii 1977, Tehranian 1993). This road is known as 10^{th} Avenue (east side) and Palolo Road (west side), which forms the primary loop through the valley (**Figure 3.3**).

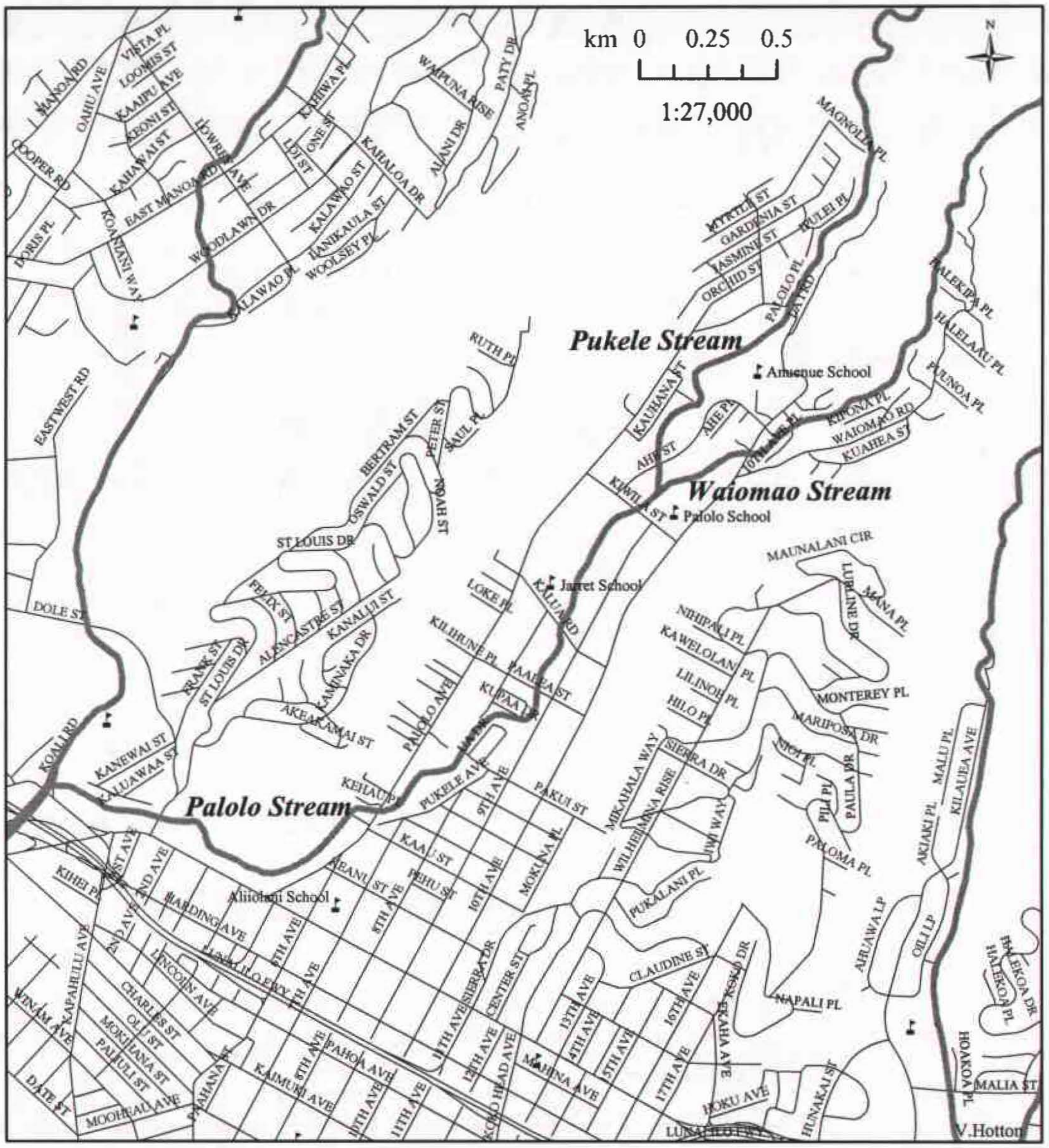


Figure 3.3. Map of Palolo Valley's streets (black lines), public schools (flagged building), and perennial streams (thick gray lines)

Before 1930, there were about 100 people living in the valley (State of Hawaii 1977) and the valley was primarily an agricultural community, which supported dairy, vegetable, and truck farming (City and County of Honolulu 1959). **Figure 3.4** displays a 1913 topographic map of Palolo Valley, which shows the location of buildings throughout the lower portions of the valley and along Palolo Road. There were a few dozen buildings scattered throughout the upper portions of the valley where Palolo Road and 10th Avenue merge.

During the first quarter of the century, the first school, Palolo Elementary, was built east of the Waiomao Stream outlet (**Figure 3.3**) (State of Hawaii 1977). **Figure 3.5** provides a 1928 topographic map of Palolo Valley, which shows an increase in streets and buildings throughout the lower and middle portions of the valley. The upper portions of the valley appeared to have changed minimally since 1913 (**Figure 3.4**).

In 1926, plans to build a municipal 18-hole golf course ($75,000) were announced (Tehranian 1993). The golf course was proposed by land owners/developers in the valley who thought the golf course would bring more residents to the valley (State of Hawaii 1977). In December of 1930, after funding shortages and construction delays, a smaller 9-hole golf course was opened (Tehranian 1993). The course operated for over a decade, although it experienced continuous income loss (Tehranian 1993). The golf course was usually muddy in rainy winters, while during the hot summers the ground was often hard and cracked open where golf balls could fall through to be lost (State of Hawaii 1977). Although the golf course itself was an economic failure, between 1930-32, more than 3,000 new people had moved into Palolo Valley (State of Hawaii 1977).

Figure 3.4. Palolo Valley c. 1913
(Cos A.G.&I. Engineers US Army. 1913. Topographic Map. 1:18,000. N↑)

Figure 3.5. Palolo Valley c. 1928
(USGS. 1928. Honolulu Quadrangle. 1:20,000. N↑)

By 1939, houses lined the entire main road of Palolo Valley (Tehranian 1993). At this time the valley was in transition from an agricultural community to a residential community (Tehranian 1993).

Flooding of Palolo Stream was a common problem for residents who lived along it (Tehranian 1993). In April 1930, floodwaters drowned a woman swept off her lanai next to the river, while several nearby homes were destroyed (Tehranian 1993). In August 1931, the *Honolulu Advertiser* newspaper reported that Palolo Valley accounted for 80% of Honolulu's cesspool pumping operations, costing the city $12,760 annually, which could be saved if Palolo Valley had a sewer line (Tehranian 1993).

3.2.3. *1940 - 1979*

Figure 3.6 provides a 1943 topographic map of Palolo Valley, which did not contain many changes from the 1928 topographic map (**Figure 3.5**). In 1942, during World War II, the Palolo Evacuee Camp was established along 10th Avenue on a portion of the former golf course (Tehranian 1993). The 85 duplex buildings were later opened to the public to relieve the housing shortages in Honolulu (Tehranian 1993). In October of 1943, the administration of the camp was given to the Hawaii Housing Authority and the camp became known as the Palolo Emergency Homes (Chun et al. 1959, Tehranian 1993). Between 1951 and 1955, the original wooden structures were replaced by concrete structures, which were renamed Palolo Homes I & II (Chun et al. 1959). In June 1957, a new low-income project, T.H.1-8, with 118 units was finished adjacent to Palolo Homes II (Chun et al. 1959).

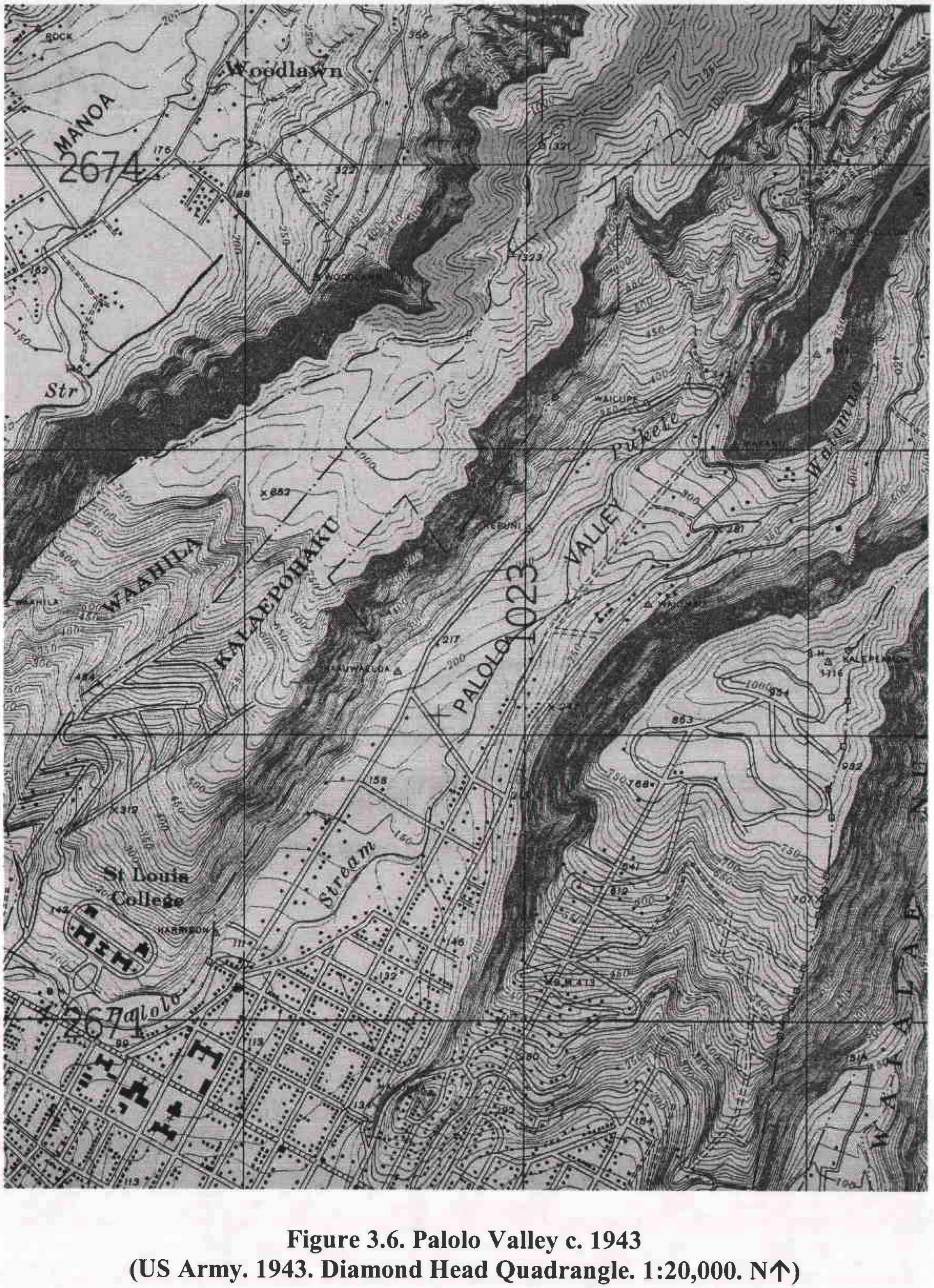


Figure 3.6. Palolo Valley c. 1943
(US Army. 1943. Diamond Head Quadrangle. 1:20,000. N↑)

During the post-World War II building period, which lasted through the late 1950's, over 2,200 new homes were built in Palolo Valley (Tehranian 1993). At the close of 1950, there were almost 3,000 houses in the valley and about 815 homes were built in the following decade (Tehranian 1993). **Figure 3.7** provides a 1959 topographic map of Palolo Valley. Less information is attainable from this topographic map since individual homes are no longer illustrated. As an alternative, shading was used to designate urban/residential areas with only large structures, such as schools, shown.

When another flood along Palolo Stream occurred in 1951, the city began plans to construct a drainage/channelization system extending up to Kalua Street (**Figure 3.3**) (Tehranian 1993), which would direct water from the streets directly into the stream channel. After Palolo Stream was channelized, problems continued to occur and in March 1958 the intersections of Waialae Avenue and 9th Avenue (**Figure 3.3**) were submerged under 0.9 - 1.2 m (3 to 4 ft) of water (Tehranian 1993).

In 1952, the Palolo Community Council (PCC) was formed to pursue similar interests among the several community associations in Palolo Valley (Tehranian 1993). The PCC's first issue was improving Palolo Valley's infrastructure (Tehranian 1993). This council was able to persuade the City and County of Honolulu to invest in a neighborhood renewal project, which was called the Palolo Improvement Plan (PIP) or Palolo Improvement District Program (PIDP) (City and County of Honolulu 1964, City and County of Honolulu 1966, Tehranian 1993). The PIP/PIDP was estimated to cost between $7 - 8.5 million (Tehranian 1993, City and County of Honolulu 1964, City and County of Honolulu 1966).

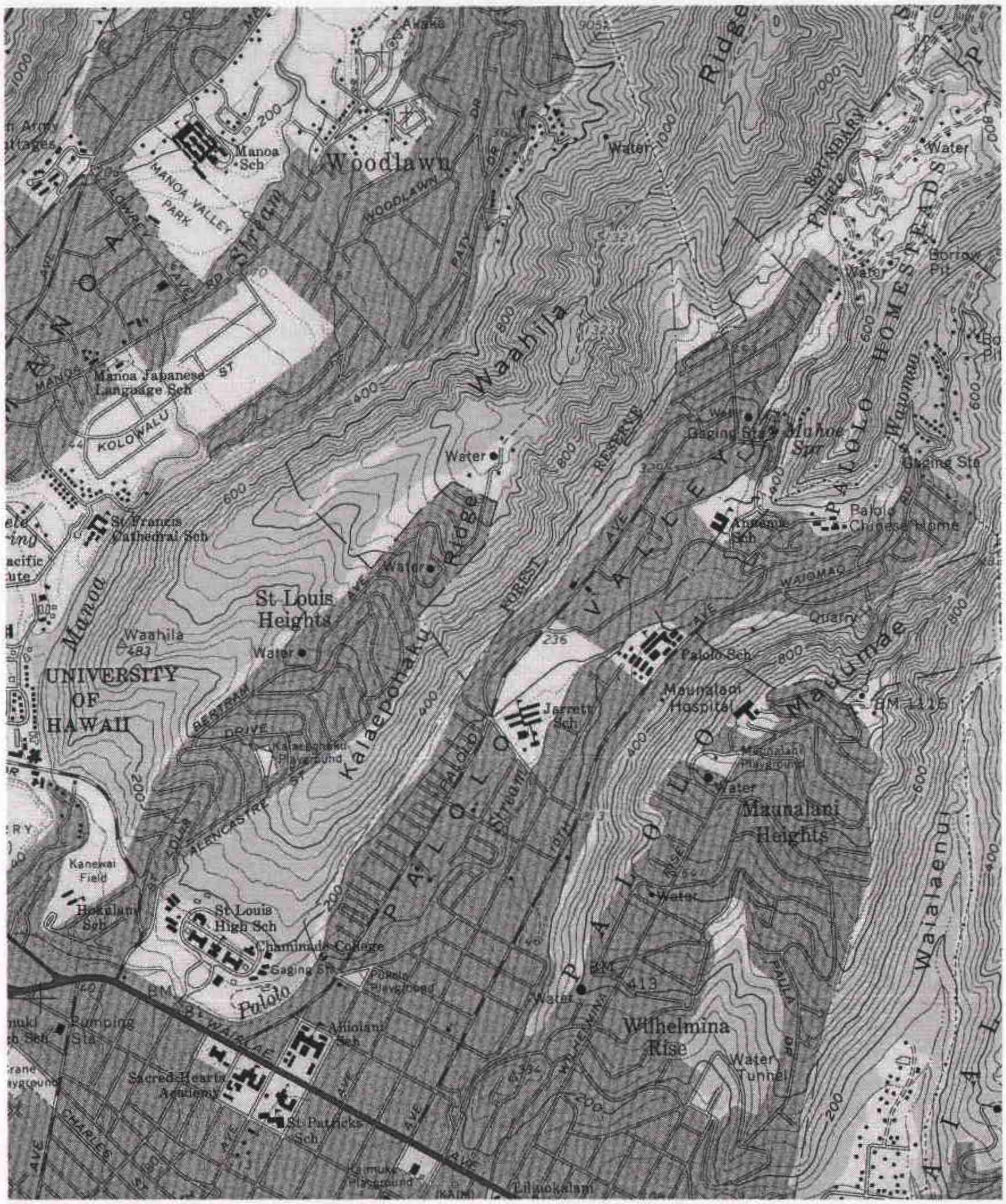


Figure 3.7. Palolo Valley c. 1959
(USGS. 1959. Honolulu Quadrangle. 7.5 Series Topographic. 1:24,000. N↑)

At the time, this was the largest improvement plan undertaken in Hawaii (Tehranian 1993). The PIP/PIDP was designed to comprehensively improve and build public roads, streetlights, sewers, curbs, gutters, and sidewalks (Tehranian 1993). When the project was near completion in early 1967, the valley had gained an estimated 14.5 km (9 mi) of widened and newly paved streets, 29.0 km (18 mi) of concrete sidewalks, and 29.0 km (18 mi) of curbs/gutters along the streets (Tehranian 1993). Two new schools were established during this time: Jarrett Intermediate School in 1955 and Anuenue Elementary School in 1958 (Tehranian 1993).

In 1951, the Hawaiian Construction and Dredging Company sold their 13 ha (33 acre) quarry along Waiomao Stream to realtor Adolf J. Mendoca for $175,000 (Tehranian 1993). The quarry was located south west of Kuahea Street above Waiomao Stream (**Figure 3.3**). During quarry operations, loose soil was pushed over the side towards Waiomao Stream's east bank, which raised the elevation and leveled some of the slope (Tehranian 1993). The quarry can be seen on several USGS topographic maps and an orthrophotoquad from 1959, 69, 78, 83, and 98 (**Figure 3.7 - 3.11**). Additionally, the 1998 USGS topographic map (**Figure 3.11**) includes the "Waiomao Slide Area" between the quarry and Waiomao Stream. Although no date was listed for when the slide occurred. Mendoca divided most of the quarry area, including loose soil portions, into 7,432 m^2 (8,000 ft^2) residential lots (Tehranian 1993). In March 1954, which was shortly after the first homes were completed, soil instability affected a 4 ha (10 acre) residential area for several years (Tehranian 1993).

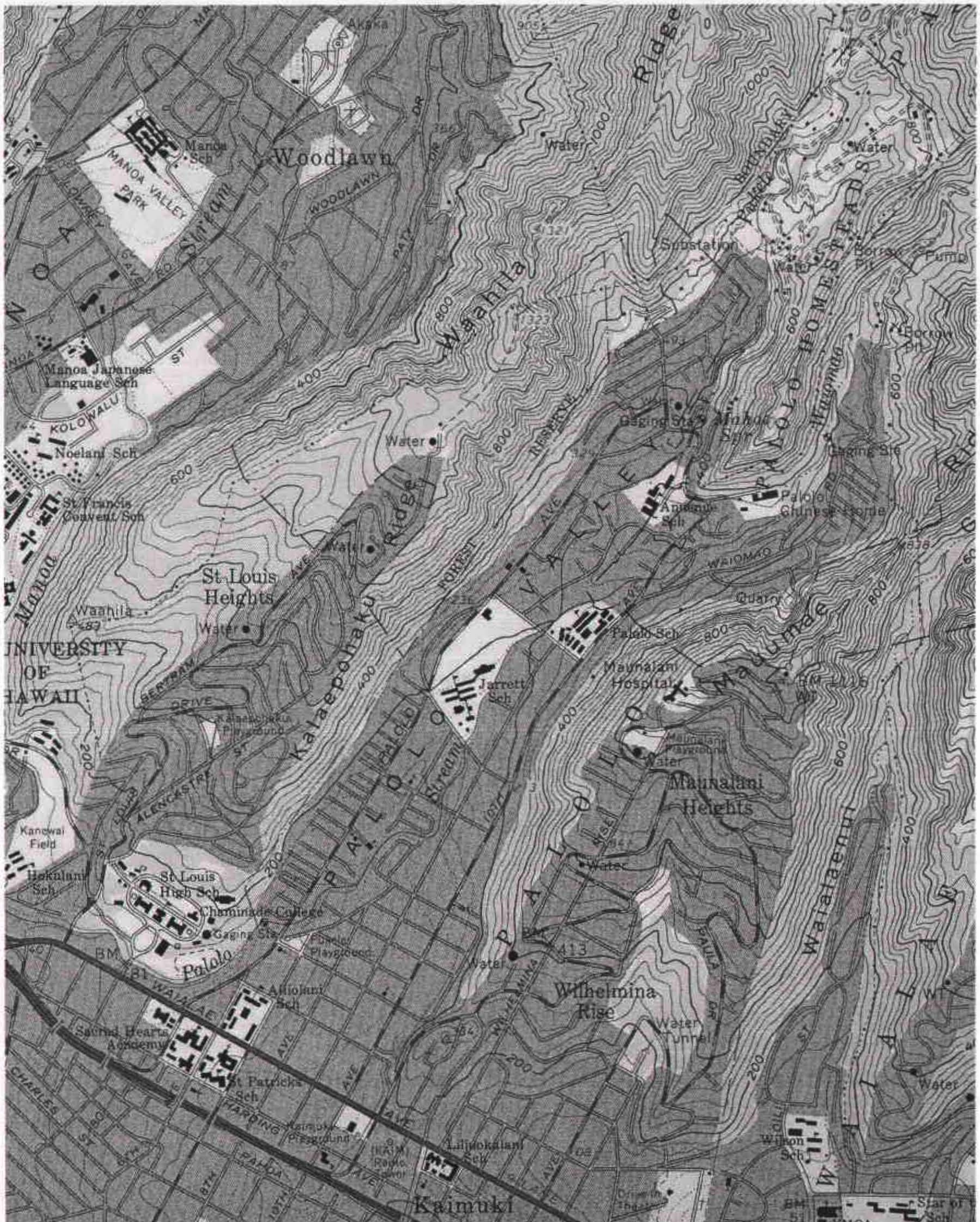


Figure 3.8. Palolo Valley c. 1969
(USGS. 1969. Honolulu Quadrangle. 7.5 Series Topographic. 1:24,000. N↑)

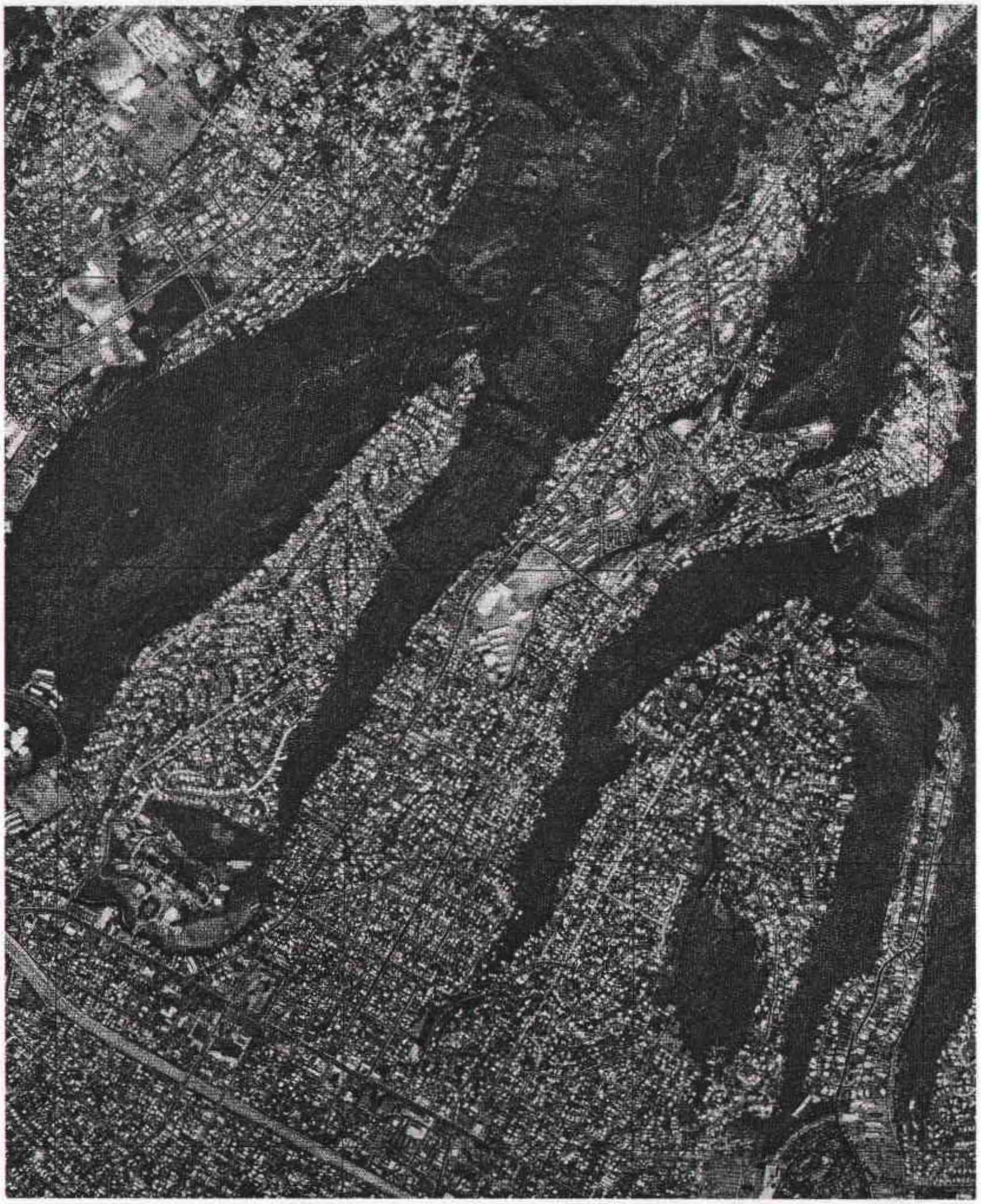


Figure 3.9. Palolo Valley c. 1978
(USGS. 1978. Honolulu Quadrangle, Orthophotoquad. 1:24,000. N↑)

Figure 3.10. Palolo Valley c. 1983
(USGS. 1983. Honolulu Quadrangle. 7.5 Series Topographic. 1:24,000. N↑)

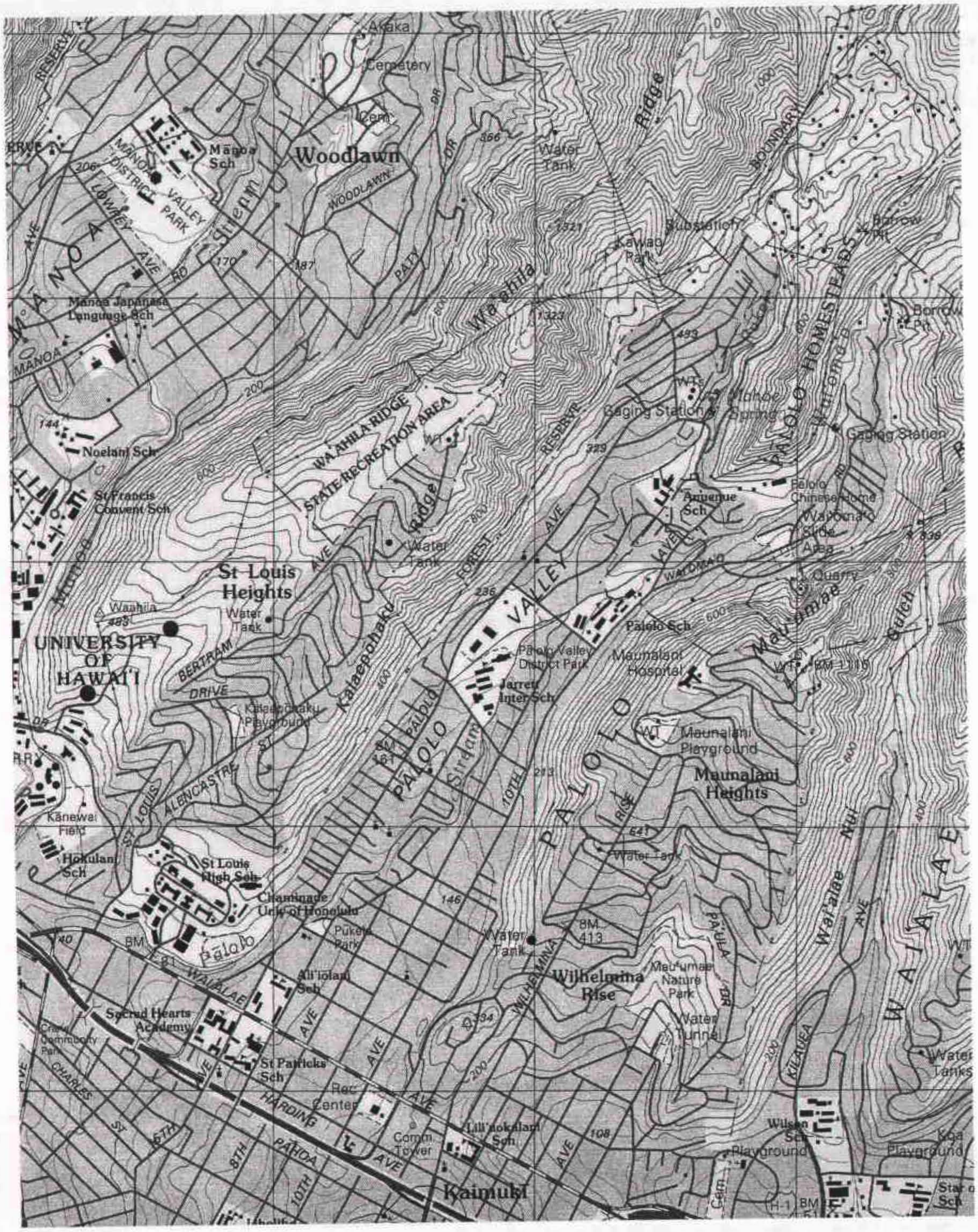


Figure 3.11. Palolo Valley c. 1998
(USGS. 1998. Honolulu Quadrangle. 7.5 Series Topographic. 1:24,000. N↑)

In 1954, two sections of Kuahea Street (**Figure 3.3**) sank about 30 cm (1 ft) and in the following month the city began construction of a storm drain to help alleviate the problem (Tehranian 1993). In 1957, a 61 m (200 ft) wall along Kuolea Street had been finished, which was intended to control the water flow from the quarry during the rainy season; additional drainage was constructed in 1961 (Tehranian 1993). A 1966 study of the area concluded that the new drainage systems had alleviated the problems (Tehranian 1993).

A 1969 topographic map of Palolo Valley (**Figure 3.8**) shows little change within the valley from 1959 (**Figure 3.7**). An important change outside of Palolo Valley is the highway, H-1, present on the 1969 map. A 1978 orthrophotoquad of Palolo Valley is useful since small buildings, such as houses, are discernable at the orthrophotoquad's scale (**Figure 3.9**). Much of Palolo valley had houses through the lower portions of Palolo Stream and into the lower areas of Pukele Stream and Waiomao Stream.

3.2.4. ***1980 - present***

In the early 1980s, a developer, Larry Clapp, planned to build the Palolo Heights Project (Tehranian 1993). The project would consist of 110-single family units at the end of Gardenia Street (**Figure 3.3**), which is on the western slope of Pukele Stream (Tehranian 1993). In the mid-1980s, the developer conducted soil studies, and the city contracted the University of Hawaii to conduct an additional soil survey; both were assumed to be acceptable by Tehranian (1993) since no construction plans were changed. A third survey was initiated in 1988 by a Palolo Valley resident, and at the same time the Emma Corporation, a Taiwanese owned company, purchased the development from

Clapp. Although the third survey concluded the soil was unsuitable for construction, the results were rejected and construction began on March 26, 1990 (Tehranian 1993).

Housing and population numbers for 1990 and 2000 are summarized in **Table 3.1**. In 1980, there were 4,175 housing units in Palolo Valley (State of Hawaii 1996) with 80.1% single-family homes, 10.6% apartment buildings, 8.6% duplexes, and 0.7% townhouses (City and County of Honolulu 1980). In 1990 there were 4,208 housing units (+0.8% from 1980) and in 2000 there were 4,583 housing units (+9.0 % from 1990) (State of Hawaii 2002). In 1990, there were 4,284 households with a resident population of 13,465 (US Census Bureau 2004). By 2000, there was an increase of 5.2% in household numbers to 4,520 and population increased 1.9% to 13,727 (US Census Bureau 2004). The recent landuse classification of Palolo Valley includes 55% undeveloped conservation land, 41% urban land, and 4% agricultural land (Ikeno 1996).

Table 3.1. Housing and population numbers in Palolo Valley in 1990 and 2000

	1990	**2000**	**Change**
Housing Units [a]	4,208	4,583	+9.0%
Households [b]	4,284	4,520	+5.2%
Population [b]	13,465	13,727	+1.9%

[a] State of Hawaii (2002).
[b] US Census Bureau (2004).

A 1983 USGS topographic map of Palolo Valley (**Figure 3.10**) shows little change from the 1969 USGS topographic map (**Figure 3.8**). Additionally, **Figure 3.11** provides a 1998 USGS topographic map of Palolo Valley, which is similar to the 1983 version.

3.3. Contemporary Sources of Trace Elements to Streambed Sediment

The potential sources of trace elements in the Hawaiian Islands differ from continental systems because of the lack of local inputs from anthropogenic sources of smelting, refining, coal-fired energy, or other industrial activity (Sutherland et al. 2003). The primary sources of trace elements in Palolo Valley would include host geology, paint, vehicles, and gasoline, while long-range aerosol transport to the islands could also be a non-point source (Sutherland et al. 2003). Non-point sources of trace elements in Palolo Valley could originate from two automobile service stations and several "back-yard" repair operations throughout the valley (Sutherland et al. 2003). Another non-point source of trace elements could originate from RDS along the streets, which would be from vehicles and residential activities (Bussen et al. 2000, Sutherland 2002b, 2003, Sutherland et al. 2003).

The valley is scheduled for a weekly street sweeping, however, it is subject to the availability of personnel and equipment (Sutherland et al. 2003). Unfortunately, there are also several narrow streets and numerous parked or abandoned vehicles that prevent a comprehensive street sweeping program in Palolo valley (Sutherland et al. 2003). Since RDS are not regularly swept, the trace elements could directly enter the stream during precipitation events. RDS would enter storm drain inlets along the roads, which then connect with storm drains that finally exit directly into the stream through storm drain outlets. A storm runoff study showed that Palolo Stream was affected more adversely by urban runoff than neighboring stream systems (Ikeno 1996), which could lead to a greater amount of RDS entering the stream channel.

There is an estimated 28.1 km of storm drain lines and 722 in/outlets contributing to Palolo Valley's streams (**Figure 3.12**). Examining the data on an individual stream basis is informative: Palolo Stream (19.6 km, 70%; 489 in/outlets, 68%; **Figure 3.13**), Pukele Stream (5.7 km, 20%; 151 in/outlets, 21%), and Waiomao Stream (2.8 km, 10%; 82 in/outlets, 11%; **Figure 3.14**). The data was based on the University of Hawaii at Manoa (UHM) Geography Cartography Lab (2005) data files. The City and County of Honolulu (2005) also has online access to similar data files.

Since streets (**Figure 3.3**) and vehicles are primary pathways and sources of RDS, it is important to quantify their distribution in the valley. Total street length in Palolo Valley is approximately 35.2 km with: Palolo Stream (22.7 km, 65%), Pukele Stream (7.2 km, 20%) and Waiomao Stream (5.5 km, 15%). In 1990, there were an estimated 6,884 vehicles in Palolo Valley with 2,088 (30%) in upper Palolo (Pukele and Waiomao Stream) and 4,796 (70%) in lower Palolo (Palolo Stream) (City and County of Honolulu 1996). The vehicle count in 1990 and 2000 are summarized in **Table 3.2**, which shows a decrease (-14%) in upper Palolo, an increase (+15%) in lower Palolo, and an overall increase (+6%) in Palolo Valley.

Table 3.2. Vehicle numbers in Palolo Valley in 1990 and 2000

Section of Palolo Valley	**1990** [a]	**2000** [b]	**Change**
Lower (Palolo Stream)	4,796	5,520	+15%
Upper (Pukele and Waiomao Stream)	2,088	1,786	-14%
Total	6,884	7,306	+6%

[a] City and County of Honolulu (1996).
[b] US Census Bureau (2004).

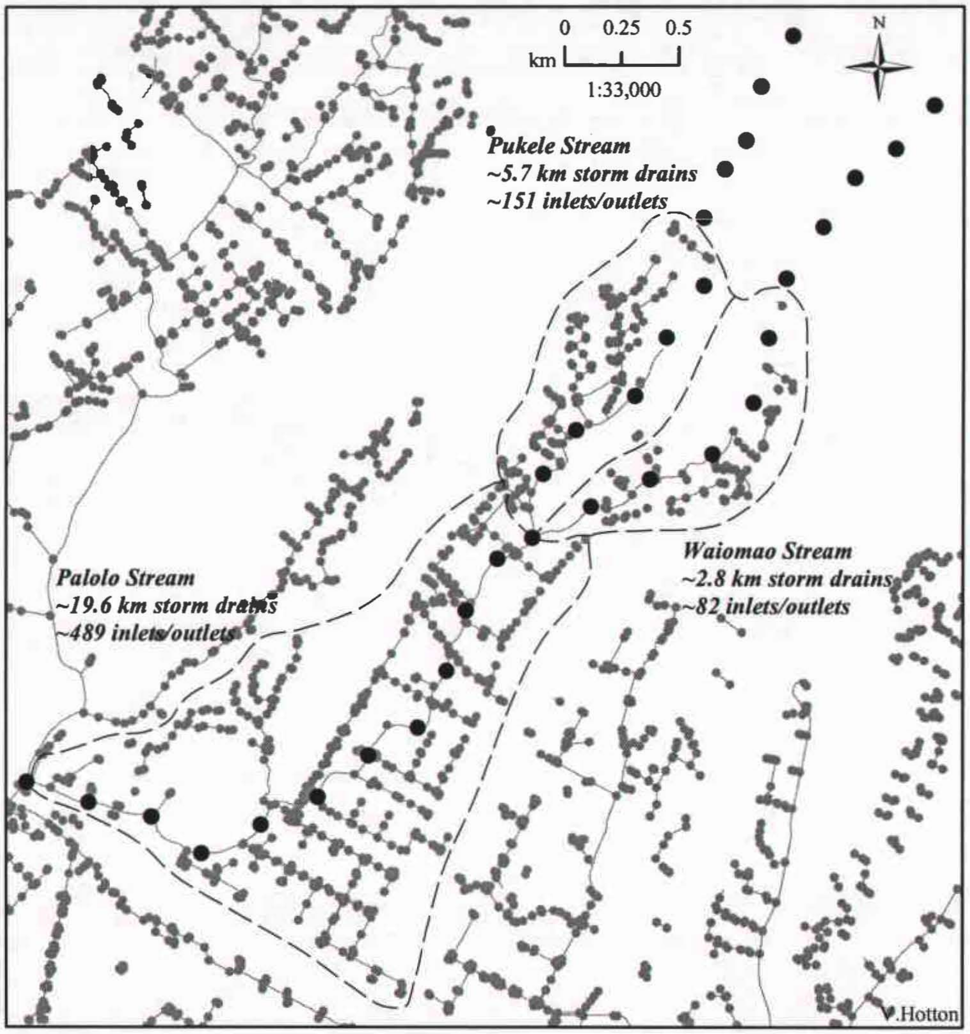


Figure 3.12. Storm drain lines (dark gray lines) and storm drain inlets/outlets (dark gray points) of Palolo Valley's streams (dotted outline). Every 6th sampling location (black points, ~300 m apart) is shown

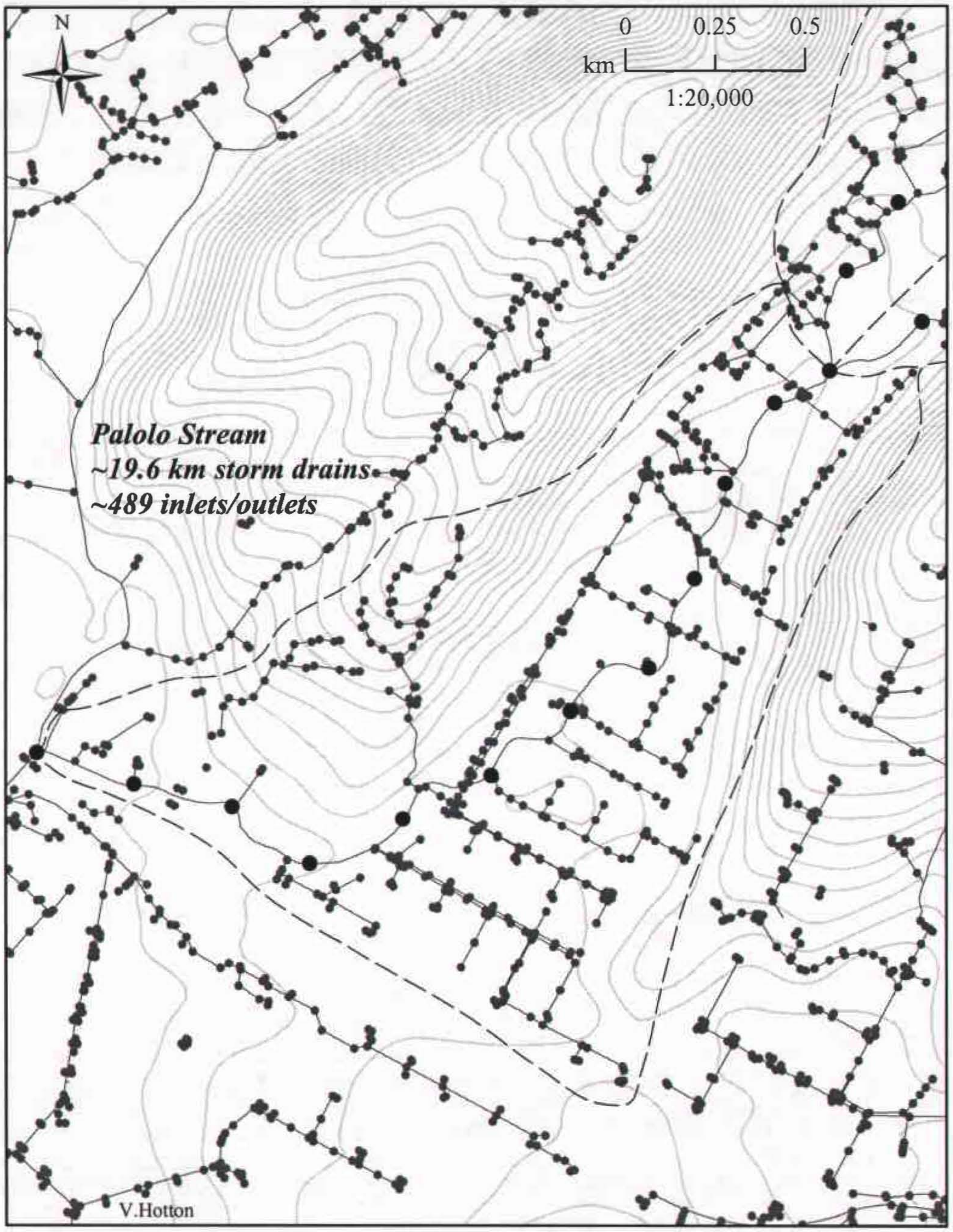


Figure 3.13. Storm drain lines (dark gray lines) and storm drain inlets/outlets (dark gray points) of Palolo Stream (dotted outline). Every 6th sampling location (black points, ~300 m apart) and 12.2 m contours (40 ft, light gray lines) is shown

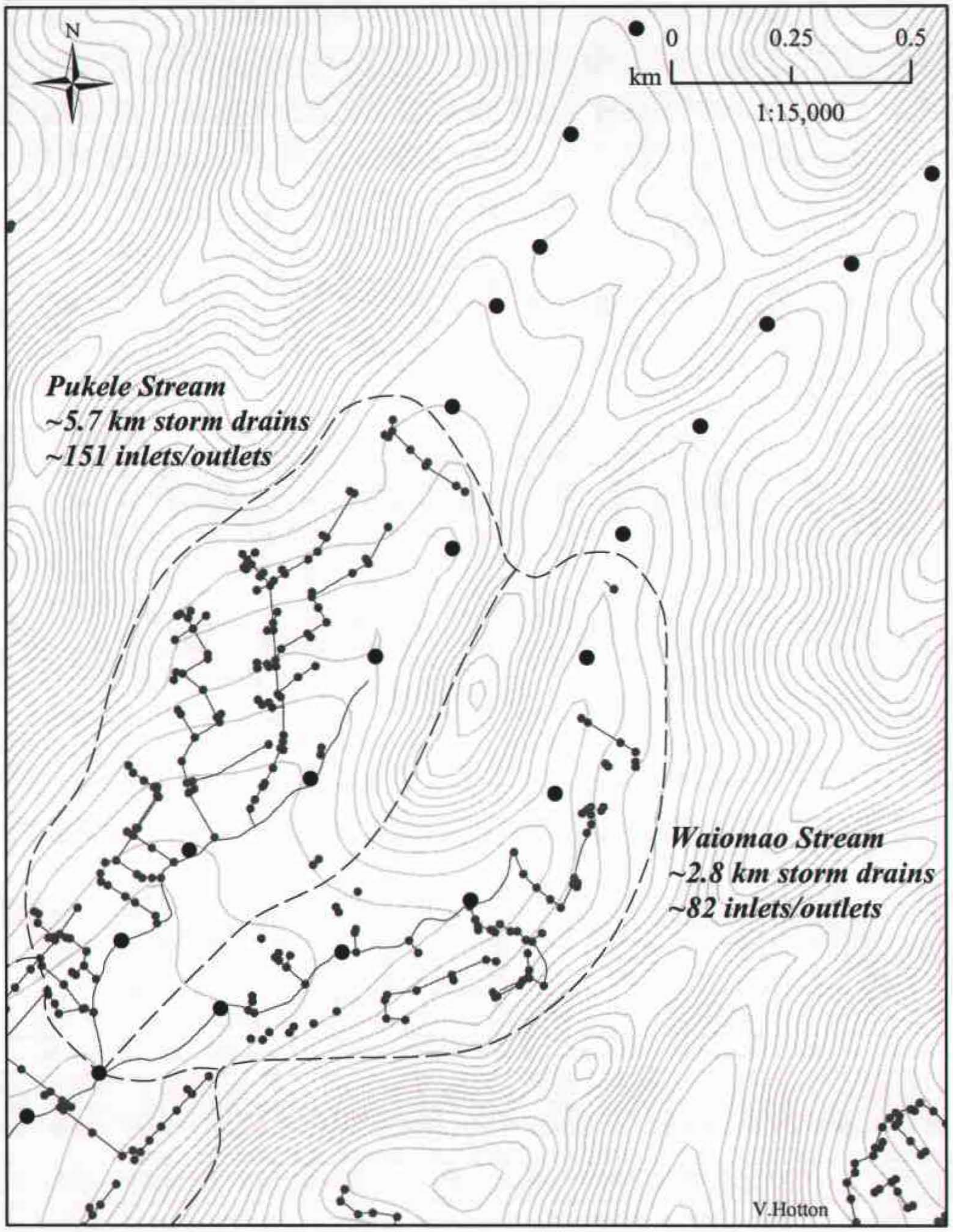


Figure 3.14. Storm drain lines (dark gray lines) and storm drain inlets/outlets (dark gray points) of Pukele Stream and Waiomao Stream (dotted outline). Every 6th sampling location (black points, ~300 m apart) and 12.2 m contours (40 ft, light gray lines) is shown

3.4. Sampling of Streambed Sediment and Water

All three streams of Palolo Valley (Palolo, Pukele and Waiomao) were sampled between April 19 and May 3 of 2000 during baseflow conditions. Although photographs were not available for the sampling period, photographs from March 8, 2005 are presented in **Appendix B** to **S**, which includes a map indicating the locations where photographs were taken (**Appendix A**). Systematic sampling was employed with 50 m intervals between sites starting at Palolo Stream and progressing upstream into Pukele Stream and Waiomao Streams (**Figure 3.15**). Palolo Stream sampling began several meters above the mouth (above the Manoa Stream junction, **Appendix B** - **F**) to 3100 m upstream (at the Pukele Stream and Waiomao Stream junction, **Appendix L**). Pukele Stream heads towards the west and was sampled from its mouth to 2950 m (**Appendix L** - **O**). Waiomao Stream heads toward the east and was sampled from its mouth to 2900 m (**Appendix P** - **S**). There were 57, 53, and 59 locations sampled in Palolo, Pukele, and Waiomao Streams respectively that had streambed sediment present (total = 169). Palolo and Pukele each had six locations that were not sampled because of a lack of bed sediment. At each sample site, six streambed sediment samples were taken. A 5 cm Plexiglas corer was used when enough sediment was present. In channelized sections where less sediment was present, a nylon brush and plastic pan were used. The six samples were combined, double bagged, and returned to the laboratory for further processing.

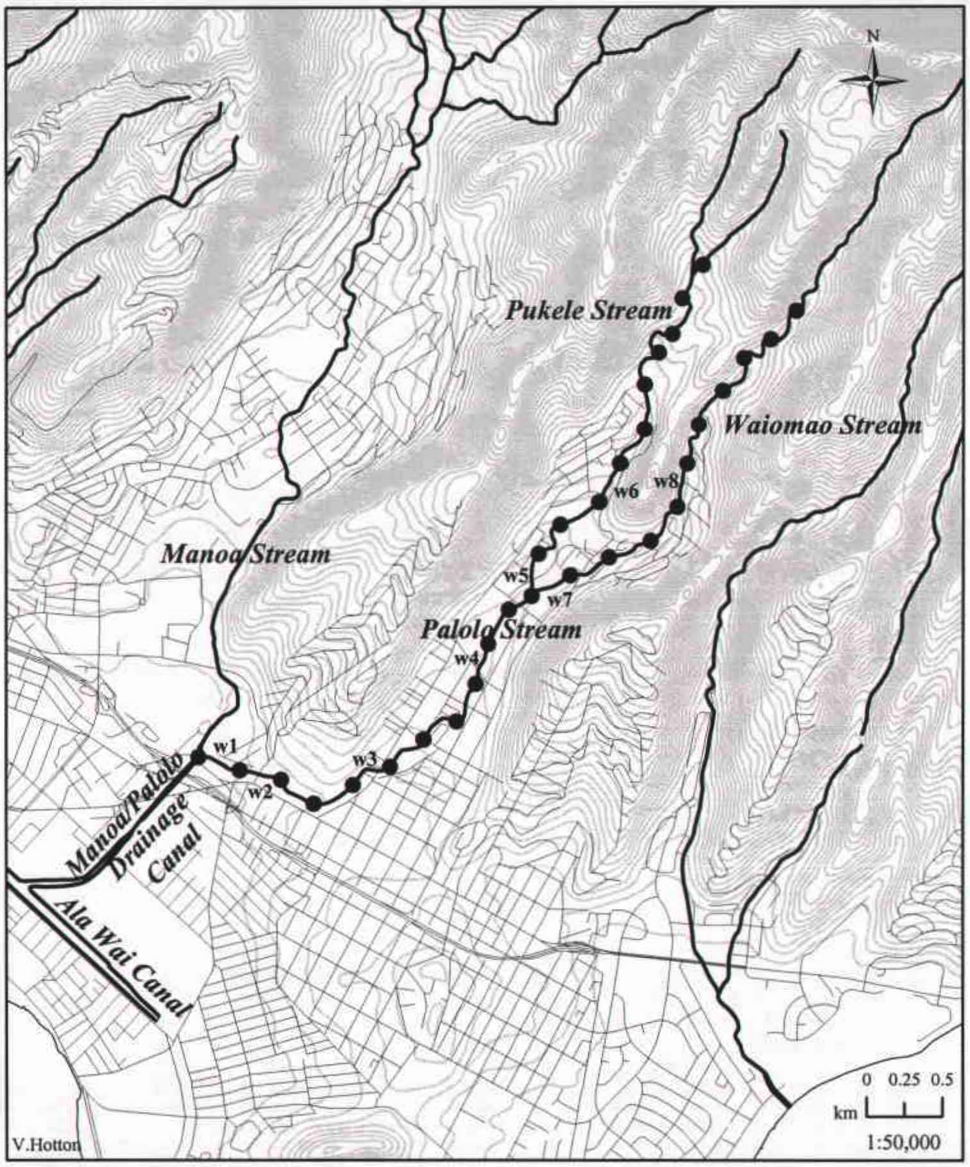


Figure 3.15. Map of every 6th bed sediment sampling location ~300 m apart (black points). Individual samples were 50 m apart. Map includes streams (bold black lines), streets (thin black lines), 12.2 m contours (40 ft, gray lines), and water sample locations (w1-w8)

On May 12, 2000, eight unfiltered water samples were collected for chemical analysis in acidified pre-cleaned 60 mL bottles (**Figure 3.15**). Several drops of HNO_3 were added to bottles to acidify them. In the stream channel, pH, temperature and electrical conductivity (EC) were also measured (**Table 3.3**). Electrical conductivity was used as a proxy for total dissolved solids. Water samples were returned to the laboratory for further processing.

Table 3.3. Temperature, pH, and EC of water in Palolo Valley's streams

Location	Stream	Temp (°C)	pH	EC (µS/cm)
w1	Palolo	31.7	9.53	259
w2	Palolo	25.9	7.75	261
w3	Palolo	34.2	10.05	220
w4	Palolo	32.3	9.84	234
w5	Pukele	27.9	9.17	210
w6	Pukele	22.7	7.07	195
w7	Waiomao	32.3	8.27	677
w8	Waiomao	23.1	6.95	153

3.5. Grain Size Partitioning of Streambed Sediment

In the laboratory, bed sediment samples were weighed and then oven-dried for 48 hours. Dried samples were gently sieved through a 2 mm stainless steel sieve to disaggregate sediment. All bed sediment samples had the <63 µm fraction isolated through sieving (stainless steel sieves) for ~10 min using a Ro-Tap sieve shaker. Additionally, 10 randomly selected samples from Palolo Stream (P2, P7, P17, P24, P30, P33, P35, P41, P54, and P57) had six-grain size classes isolated (< 63, 63-125, 125-250, 250-500, 500-1000, and 1000-2000 µm). All grain size fractions were weighed prior to grinding with a Pica Blender Mill (model 2601, Cianflone Scientific Instruments Corp., Pittsburgh, PA) for 5 min in 30 mL tungsten carbide vials with tungsten carbide balls.

Grinding enhances homogeneity and the precision of sediment digestion (Sutherland 2003).

3.6. Digestion of Streambed Sediment

Three different digestion procedures were employed: a sequential extraction, a weak "bioavailable" one-acid leach, and a total 4-acid digestion. For the sequential extraction, the BCR optimized procedure was employed (**Table 3.4**), which isolates three operationally defined phases: acid-extractable, reducible, and oxidizable. A final aqua regia digestion step was also added to determine the residual component. The procedure was applied to the <63 μm grain size of 20 Palolo Stream samples (P2, P5, P7, P9, P10, P17, P24, P25, P26, P29, P30, P33, P34, P35, P38, P39, P41, P54, P57, and P58).

Table 3.4. Chemical reagents and analytical conditions for the optimized BCR sequential extraction procedure and aqua regia digestion

Step	Operational Definition	Chemical Reagents and Conditions [a]
1	Acid-extractable	To a 1 g aliquot add 40 mL of 0.11 M HOAc, shake for 16 h at 22±5 °C; separate extract from the solid residue by centrifugation at 3000X*g* for 20 min.
2	Reducible	To Step 1 residue add 40 mL of 0.5 M $NH_2OH \cdot HCl$ from a 1 L solution containing 25 mL of 2 M HNO_3 (pH 1.5), shake for 16 h at 22 ±5 °C; centrifuge at 3000X*g* for 20 min.
3	Oxidizable	To Step 2 residue add 10 mL of H_2O_2 (pH 2-3), 1 h at room temperature; heat to 85±2 °C for 1 h; add a further 10 mL of H_2O_2 and heat to 85±2 °C for 1 h; add 50 mL of 1 M NH_4OAc (pH 2) and shake for 16 h at 22±5 °C; centrifuge at 3000X*g* for 20 min.
4	Residual	To Step 3 residue add 3 mL of distilled H_2O, 7.5 mL of 6 M HCl, and 2.5 mL of 14 M HNO_3; leave overnight at 20 °C, boil under reflux for 2 h, cool and filter.

after Rauret et al. (1999), Sutherland and Tack (2003).
[a] HOAc is acetic acid; $NH_2OH \cdot HCl$ is hydroxylamine hydrochloride; H_2O_2 is hydrogen peroxide; and NH_4OAc is ammonium acetate.

The weak one-acid leach involved shaking 1 g samples with 10 mL of room temperature 0.5 M HCl acid for 1 h (Sutherland and Tolosa 2001). Streambed sediments from Palolo Stream, Pukele Stream, and Waiomao Stream had the one-acid weak leach applied to the <63 μm grain size fraction (57, 53, and 59 samples respectively, 169 total).

A total 4-acid digestion was applied to 0.5 g samples with concentrated HNO_3, HF, and $HClO_4$, which was taken to dryness overnight on a hot plate (Sutherland and Tolosa 2000). The residue was solubilized with HCl and diluted to volume to prepare for element analysis. This digestion procedure was applied to the 10 Palolo samples (P2, P7, P17, P24, P30, P33, P35, P41, P54, and P57) that were isolated into the six-grain size classes.

3.7. Concentration Measurement of Elements in Sediment and Water

All streambed sediment samples were analyzed with ICP-AES to measure element concentrations. Element concentrations in water samples were analyzed by ICP-MS. When element concentrations were below the detection limits of ICP-AES, half the detection limit was applied to the data to allow analysis with all samples. For example, the detection limits of As, Cd, Pb, and Zn in ICP-AES are <1, <0.2, <2, and <1 mg/kg respectively. In these cases, the concentrations of 0.5, 0.1, 1.0, and 0.5 mg/kg were applied to As, Cd, Pb, and Zn samples respectively.

To enhance comparability between streambed sediment studies that exclusively used a total digestion procedure, recovery ratios were developed for this study. Recovery ratios allowed the small total digestion sample size (10) to be expanded to the full data set of all three Palolo Valley streams that were digested in weak HCl. Recovery ratios were calculated for the 10 samples of Palolo Stream that had both weak HCl and 4-acid total digestions completed (P2, P7, P17, P24, P30, P33, P35, P41, P54, and P57). The percent recovery ratio was calculated as:

$$[\ [HCl_{Pb}]i \div [Total_{Pb}]i\ ] * 100 \qquad \textbf{[3.1]}$$

where i is a particular sample location, HCl_{Pb} is the weak HCl digestion concentration of Pb at location i, and $Total_{Pb}$ is the 4-acid total digestion concentration of Pb. **Table 3.5** presents descriptive statistics of the recovery ratio. A majority of the recovery ratios were normal based on the skewness test ($\alpha = 0.05$). However, since non-parametric tests were used in data analysis, which is discussed in later chapters, the median recovery ratio was used to be consistent in analysis.

Table 3.5. Summary of recovery ratio statistics for 10 samples from Palolo Stream

	% Mean ± SD	CV%	Skew	% Median ± MAD [a]	RCMV% [b]
Al	5 ± 1	21	0.09	5 ± 1	11
As	45 ± 29	66	1.44	45 ± 14	31
Cd	74 ± 21	28	-0.52	78 ± 11	14
Cr	2 ± 1	48	0.58	2 ± 1	33
Cu	28 ± 7	24	0.81	27 ± 4	13
Fe	4 ± 1	31	0.61	4 ± 1	14
Mn	48 ± 11	23	-1.01	51 ± 6	11
Ni	8 ± 3	42	0.72	7 ± 2	31
Pb	96 ± 10	10	-0.59	97 ± 6	6
Zn	61 ± 11	18	-0.28	63 ± 8	13

[a] MAD is median absolute deviation from the median, which is a robust measure of dispersion.
[b] RCMV% = Relative coefficient of median variation = (MAD ÷ Median) *100.

The median recovery ratio was first applied to the data from the 10 samples of Palolo Stream to see if the $total_{est}$ concentrations were similar to the true 4-acid total concentrations. To calculate $total_{est}$ from the recovery ratio the following equation was used, with Pb as an example:

$$Total_{est} = [HCl_{Pb}]i \div MedianRR_{Pb} \qquad \textbf{[3.2]}$$

where i and HCl_{Pb} are as before, and $MedianRR_{Pb}$ is the median recovery ratio of Pb. The results of the paired Wilcoxon Signed Rank test indicated that there was no statistical difference between the true 4-acid concentration and the $total_{est}$ for Cu, Ni, Pb, and Zn (**Table 3.6**).

Table 3.6. Summary of Wilcoxon Signed Rank test with total digestion and $total_{est}$ of Palolo Stream samples

Method	Median ± MAD (mg/kg) [z]			
	Cu	**Ni**	**Pb**	**Zn**
Total	221 ± 28 [a]	225 ± 11 [a]	273 ± 111 [a]	422 ± 70 [a]
$Total_{est}$	212 ± 72 [a]	216 ± 62 [a]	285 ± 121 [a]	455 ± 131 [a]
Tied p-value	*0.65*	*0.48*	*0.96*	*0.96*

[z] Sample Size of 10. For a given element (column-wise) concentration values with the same letter are not significantly different at $\alpha = 0.05$.

Additionally, no differences were found for Al, As, Cd, and Cr (tied p-values: 0.96, 0.88, 0.88, and 0.88 respectively).

3.8. Quality Control

Certified reference materials (CRM) were used to assess precision and accuracy of the digestions. The CRMs used were stream sediment (GSD 11, CRM 320), soil (SRM 2710, SRM 2711), road dust (CW7), and water (SRM 1643d) (**Table 3.7**). The BCR sequential extraction was used on SRM 2710 and CW 7, while the weak HCl leach was used on GSD 11 and SRM 2711, and the 4-acid total digestion was applied to GSD 11 and CRM 320. The SRM 1643d was used for quality control assessment of water samples.

Table 3.7. Certified reference material (CRM) utilized

CRM Name	Description and Sampling Location	Certifying Body or Reference
CW 7	Road dust material collected from the ceiling of the Tanzenberg tunnel, located 50 km north of Graz, Austria. Sampling was carried out in the ventilation shaft of the tunnel with small brooms and vacuum cleaner. Ground to <90 μm.	Schramel et al. (2000), Sutherland and Tack (2002)
CRM 320	Toce River sediment (<90 μm)	Community Bureau of Reference - BCR
GSD 11	Stream sediment.	China National Analysis Center for Iron and Steel
SRM 1643d	Trace elements in fresh water.	National Institute of Standards and Technology (NIST) (1999)
SRM 2710	Soil collected from upper 10 cm of pasture along Silver Bow Creek in Butte, MT. Site contaminated by Cu, Mn, Pb, and Zn from inputs to the creek from settling ponds of the Anaconda processing plant. During overbank events, contaminated sediment is deposited. Sample ground to <74 μm.	NIST (1997), Sutherland and Tack (2002)
SRM 2711	Soil collected from the upper 15 cm of a wheat field developed over a till layer. Sample ground to <74 μm.	NIST (1993), Sutherland and Tack (2002)

Precision is assessed through the coefficient of variation (CV), which is defined as:

$$CV\% = (\text{Standard Deviation} / \text{Mean}) * 100 \qquad \textbf{[3.3]}$$

While accuracy is assessed through the following equation:

$$\text{Accuracy } \% = [(\text{Mean}_{study} - \text{Mean}_{certified}) / \text{Mean}_{certified}] * 100 \qquad \textbf{[3.4]}$$

where Mean_{study} is the mean element concentration of the CRM when measured in the current study, and $\text{Mean}_{certified}$ is the certified mean for the CRM. **Table 3.8** provides a summary of the sample numbers and media used to assess precision and accuracy in this study.

Table 3.8. Quality control summary of sample numbers and media used

Digestion Method and Media	CRM or Palolo (P) Stream Sample	Precision Replicates	Accuracy Replicates
BCR Sequential of Sediment	SRM 2710 CW 7	5 5	N/A [a]
HCl Weak Leach of Sediment	GSD 11 SRM 2711 P41 (63-125 μm)	5 21 5	N/A [a]
Total Digestion of Sediment	GSD 11 CRM 320 P57 (63-125 μm)	5 5 6	5 5 N/A [a]
Water	SRM 1643d	3	3

[a] Accuracy was unable to be assessed because no CRM was available for weak leach, sequential extractions, or Palolo Stream samples.

The accuracy and precision of SRM 1643d (water) is presented in **Table 3.9**. The CV% were all within an acceptable range (<10%), while most Acc% were within acceptable ranges (±10%).

Table 3.9. Measurement precision (CV%) and accuracy (Acc%) of ICP-MS analysis of water samples with SRM 1643d (3 replicates)

	CV%	*Acc%*		*CV%*	*Acc%*		*CV%*	*Acc%*
Al	3.5	28.0	**Cu**	3.8	8.8	**Ni**	1.0	-11.6
Cd	0.3	-3.8	**Fe**	9.2	4.5	**Pb**	2.9	8.4
Cr	2.5	0.4	**Mn**	0.5	-16.9	**Zn**	0.7	7.0

The element concentrations in the three streams were low (**Table 3.10**), with one location along Waiomao Stream (Location 4), which had elevated major element concentrations of Al (445 μg/L), Fe (740 μg/L), and Mn (379 μg/L). All concentrations of Cd were below detection limits (0.05 μg/L) and are not shown in **Table 3.10**.

Table 3.10. Element concentrations (µg/L) in water of Palolo Valley's streams through ICP-MS analysis

Location	Stream	Al	Cr	Cu	Fe	Mn	Ni	Pb	Zn
w1	Palolo	123	2.1	4.1	220	30	0.3	2	6.5
w2	Palolo	140	2.6	3.5	247	47	0.4	3	8.6
w3	Palolo	153	1.3	7.7	327	33	0.6	2	8.5
w4	Palolo	176	1.9	7.5	388	50	0.3	2	7.5
w5	Pukele	146	2.1	9.2	331	29	0.2	< 2	4.5
w6	Pukele	18	2	2.3	65	9	0.5	< 2	1.4
w7	Waiomao	455	3.6	3.8	740	379	< .2	< 2	3.9
w8	Waiomao	23	1.6	2.3	380	220	< .2	< 2	< 0.5

3.9. Analysis

Streambed sediment analysis will be controlled by grain size and digestion procedure to compare element concentrations among the three streams within Palolo Valley (Palolo, Pukele, and Waiomao). Palolo Valley concentrations will also be compared with established SQGs (TEL and PEL) and element concentration data of other rivers. In addition, element concentrations will be used to calculate ERs with Al used as the conservative element.

Analysis will be aided through the use of statistical computer software by SAS Institute (StatView). The statistical methods utilized will include descriptive statistics, normality testing, data transformations as needed, nonparametric one sample sign tests, nonparametric two-group paired Wilcoxon Signed Rank test, and nonparametric ≥ three-sample Friedman test. Computer generated maps with GIS data will be created to show spatial distribution of landuse data and to assess possible linkages with element concentrations.

4.0. RESULTS: BCR SEQUENTIAL EXTRACTION

This section presents results from 20 random samples along Palolo Stream that were separated into <63 μm grain size (P2, P5, P7, P9, P10, P17, P24, P25, P26, P29, P30, P33, P34, P35, P38, P39, P41, P54, P57, and P58). These samples were processed with the optimized BCR sequential extraction (BCR) technique. See **Table 3.3** for reagents and conditions of the sequential procedure.

4.1. Precision for BCR Sequential Extraction (BCR)

Precision of the optimized BCR procedure was assessed by CV% (**Equation 3.3**) using two certified reference materials (**Table 4.1**).

Table 4.1. Measurement precision of the sequential procedure as assessed by CV%

CRM (n) [a]	Sequential Step	Al	Cu	Fe	Mn	Ni	Pb	Zn
SRM 2710 (5)	Acid-extractable	5.1	3.6	4.6	1.6	[b]	2.3	1.9
	Reducible	3.4	1.8	6.9	2.4	[b]	1.8	0.9
	Oxidizable	5.9	5.4	4.5	50.1	[b]	5.0	4.3
	Residual	8.8	1.5	2.8	2.5	[b]	6.3	1.7
CW 7 (5)	Acid-extractable	3.1	0.9	1.8	1.5	2.3	1.9	0.9
	Reducible	2.0	1.2	1.0	2.3	1.9	5.9	0.9
	Oxidizable	1.7	1.1	1.5	0.5	1.7	2.5	1.0
	Residual	3.8	1.1	3.9	2.7	3.4	6.8	0.9

[a] Number of replicates in parentheses.
[b] Below detection limits.

For the majority of elements, precision was acceptable, i.e. ≤10%. The $CV\%_{Mn}$ in the oxidizable step of SRM 2710 was substantial (50%), while all other $CV\%_{Mn}$ were within acceptable ranges. A few CV% values could not be determined because concentrations were below the detection limits of ICP-AES. Since a majority of CV% values were within acceptable limits, the optimized BCR sequential extraction procedure was conducted effectively.

4.2. Descriptive Statistics for BCR

Descriptive statistics of several elements are given in **Table 4.2**. Skewness was used to evaluate normality ($\alpha = 0.05$) and element distributions were determined to be non-normal (see **Appendix T** for skewness values, including additional descriptive statistics and additional elements). Further statistical analysis was based on medians and ranks of data (non-parametric).

Table 4.2. Descriptive statistics of elements (mg/kg) in Palolo Stream sediment (<63 μm) with a sequential extraction

	Sequential Step [ab]	Mean ± SD	Median ± MAD [c]	Min	Max
Cu	Acid-extractable	5.0 ± 3.7	3.8 ± 1.6	1	14
	Reducible	33 ± 21	28 ± 11	4.2	94
	Oxidizable	31 ± 14	28 ± 9.1	11	67
	Residual	123 ± 16	122 ± 8.0	82	152
Ni	Acid-extractable	5.6 ± 2.6	4.9 ± 1.1	1.6	11
	Reducible	16 ± 5.6	15 ± 3.8	1.2	26
	Oxidizable	14 ± 3.1	14 ± 2.7	9.5	19
	Residual	168 ± 34	165 ± 18	110	242
Pb	Acid-extractable	3.4 ± 2.5	2.0 ± 0.0	2	9.4
	Reducible	178 ± 132	138 ± 38	2	472
	Oxidizable	26 ± 14	20 ± 5.1	14	70
	Residual	23 ± 17	19 ± 8.3	2.5	68
Zn	Acid-extractable	105 ± 47	95 ± 27	43	225
	Reducible	219 ± 198	149 ± 38	71	975
	Oxidizable	42 ± 19	35 ± 7.8	25	104
	Residual	160 ± 42	143 ± 18	115	288

[a] Additional descriptive statistics and elements (Al, Fe, and Mn) are provided in **Appendix T**.
[b] Sample size of 20 per step.
[c] MAD is median absolute deviation from the median, which is a robust measure of dispersion.

The acid-extractible (step 1) median concentrations of Cu, Ni, and Pb were low (2%, 2%, and 1% of total respectively) while substantial amounts of Zn were released (23% = [95/(95+149+35+142)]*100), with a maximum $Zn_{acid\text{-}extractible}$ concentration of 225 mg/kg (sample P33 at 1600 m above the Palolo Stream outlet). The reducible phase (step 2) had several median concentration values that were the highest (Pb and Zn, 178 and 219 mg/kg respectively) or second highest (Ni 16 mg/kg). Some notable maximum values from the reducible phases were $Cu_{reducible}$ (94 mg/kg, P7 at 300 m), $Ni_{reducible}$ (27 mg/kg, P7 at 300 m), $Pb_{reducible}$ (472 mg/kg, P7 at 300 m), and $Zn_{reducible}$ (975 mg/kg, P38 at 1850 m). The oxidizable phase (step 3) had a limited number of elevated concentrations, including: $Cu_{oxidizable}$ (67 mg/kg, P17 at 800 m), $Ni_{oxidizable}$ (19 mg/kg, P10 at 450 m), $Pb_{oxidizable}$ (70 mg/kg, P7 at 300 m), and $Zn_{oxidizable}$ (104 mg/kg, P38 at 1850 m). The residual concentrations (step 4) generally had the highest median, minimum, and maximum values for all elements (Cu, Ni, and Zn), which were expected since it is a pseudo total digestion. However $Pb_{residual}$ had the second lowest median (19 mg/kg). The maximum residual values of elements from the residual phase were $Cu_{residual}$ (152 mg/kg, P57 at 2800 m), $Ni_{residual}$ (242 mg/kg, P33 at 1600 m), $Pb_{residual}$ (68 mg/kg, P7 at 300 m), and $Zn_{residual}$ (288 mg/kg, P38 at 1850 m).

4.3. BCR Phase Comparisons

For individual elements, the non-parametric paired Friedman test was used to test for differences between concentrations among the four steps. Tied p-values for each element (Al, Cu, Fe, Pb, Mn, Ni, and Zn) indicated that at least one pairwise phase comparison was significantly different (all tied p-values <0.0001, $\alpha = 0.05$). To discern which pairwise comparison was significant, the non-parametric paired Wilcoxon Signed Rank test was applied (**Table 4.3**) to compare the BCR steps for each element. The tied p-values of the Wilcoxon Signed Rank test are listed in **Appendix U**.

Table 4.3. Summary of statistical differences among sequential extraction steps based on Wilcoxon Signed Rank test

	Sequential Step Median ± MAD (mg/kg) [z]			
	Acid-Extractable	**Reducible**	**Oxidizable**	**Residual**
Al	126 ± 39 [a]	3281 ± 561 [c]	1935 ± 331 [b]	54275 ± 2890 [d]
Cu	3.8 ± 1.6 [a]	28 ± 11 [b]	28 ± 9.1 [b]	122 ± 8.0 [c]
Fe	5.9 ± 2.5 [a]	4430 ± 527 [c]	1250 ± 339 [b]	102860 ± 6765 [d]
Mn	432 ± 63 [b]	552 ± 132 [b]	61 ± 6.7 [a]	397 ± 80 [b]
Ni	4.9 ± 1.1 [a]	15 ± 3.8 [b]	14 ± 2.7 [b]	165 ± 18 [c]
Pb	2.0 ± 0.0 [a]	138 ± 38 [c]	20 ± 5.1 [b]	19 ± 8.3 [b]
Zn	95 ± 27 [b]	149 ± 38 [c]	35 ± 7.8 [a]	143 ± 18 [c]

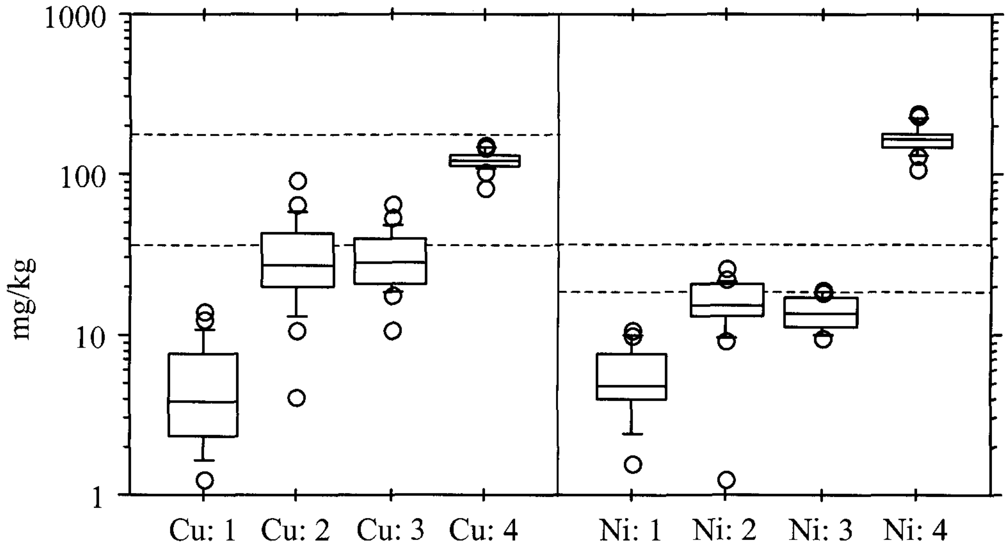
[z] Sample size of 20 per step. For a given element (row-wise) concentration values with the same letter are not significantly different at $\alpha_{adj} = 0.0083$. $\alpha_{adj} = 0.05 \div 6$ pairwise comparisons. For tied p-values see **Appendix U**.

From **Table 4.3**, the statistical phase ordering for each element was:

- $Al_{residual} > Al_{reducible} = Al_{oxidizable} > Al_{acid\text{-}extractable}$
- $Cu_{residual} > Cu_{oxidizable} = Cu_{reducible} > Cu_{acid\text{-}extractable}$
- $Fe_{residual} > Fe_{reducible} > Fe_{oxidizable} > Fe_{acid\text{-}extractable}$
- $Mn_{reducible} = Mn_{acid\text{-}extractable} = Mn_{residual} > Mn_{oxidizable}$
- $Ni_{residual} > Ni_{reducible} = Ni_{oxidizable} > Ni_{acid\text{-}extractable}$
- $Pb_{reducible} > Pb_{oxidizable} = Pb_{residual} > Pb_{acid\text{-}extractable}$
- $Zn_{reducible} = Zn_{residual} > Zn_{acid\text{-}extractable} > Zn_{oxidizable}$

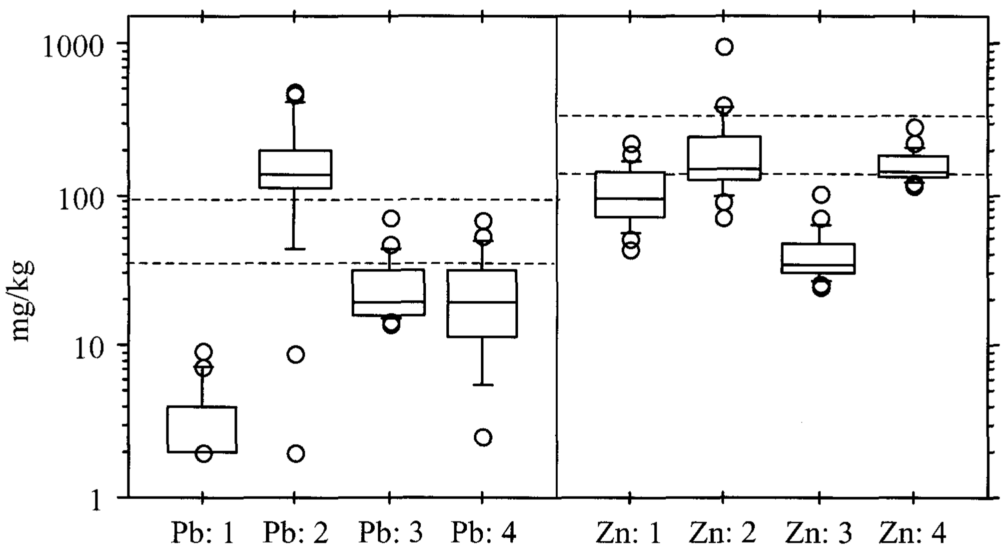
4.4. SQGs compared with BCR

Although SQGs are based on total digestions, a comparison to concentrations from each of the sequential steps can be useful. **Figures 4.1** and **4.2** present box and whisker plots of Cu, Ni, Pb, and Zn with TEL and PEL guidelines (**Table 1.6**) superimposed.



BCR Steps: 1 acid-extractable, 2 reducible, 3 oxidizable, and 4 residual.
Box plot centerline indicates 50th percentile (median), bottom box line is 25th percentile, top box line is 75th percentile, and whiskers are the 10th and 90th percentiles.
The dotted horizontal lines represent the location of TEL and PEL guidelines.
TEL_{Cu} 35.7, PEL_{Cu} 197, TEL_{Ni} 18, and PEL_{Ni} 36 mg/kg.

Figure 4.1. Box plots of Cu and Ni concentrations separated by BCR sequential extraction step



TEL_{Pb} 35, PEL_{Pb} 91.3, TEL_{Zn} 123, and PEL_{Zn} 315 mg/kg.

Figure 4.2. Box plots of Pb and Zn concentrations separated by BCR sequential extraction step

A summary of trace element fraction partitioning relative to TEL and PEL guidelines is presented in **Table 4.4**. The TEL and PEL guidelines were based on a total digestion of freshwater aquatic sediments (**Table 1.6**).

Table 4.4. Summary of element fraction partitioning relative to PEL and TEL

Element and Sequential Step	< TEL	≥ TEL to < PEL	≥ PEL
Cu [a]	*< 35.7*	*≥ 35.7 to < 197*	*≥ 197*
Acid-extractable	100 (20) [b]		
Reducible	65 (13)	35 (7)	
Oxidizable	65 (13)	35 (7)	
Residual		100 (20)	
Ni	*< 18*	*≥ 18 to < 36*	*≥ 36*
Acid-extractable	100 (20)		
Reducible	55 (11)	45 (9)	
Oxidizable	85 (17)	15 (3)	
Residual			100 (20)
Pb	*< 35*	*≥ 35 to < 91.3*	*≥ 91.3*
Acid-extractable	100 (20)		
Reducible	10 (2)	5 (1)	85 (17)
Oxidizable	80 (16)	20 (4)	
Residual	75 (15)	25 (5)	
Zn	*< 123*	*≥ 123 to < 315*	*≥ 315*
Acid-extractable	70 (14)	30 (6)	
Reducible	20 (4)	65 (13)	15 (3)
Oxidizable	100 (20)		
Residual	15 (3)	85 (17)	

[a] Sample size of 20 per step. TEL and PEL concentrations are in mg/kg.
[b] %(n): sample percent (sample number).

Element concentrations released by the acid-extractable step were all <TEL, with the exception of $Zn_{Acid\text{-}extractable}$, which had 30% of the samples between TEL and PEL. The reducible step was spread throughout the three SQG divisions, with $Pb_{reducible}$ and $Zn_{reducible}$ having a great majority of concentrations ≥TEL (90% and 80% respectively) and a smaller percentage ≥PEL (85% and 15% respectively). All elements in the oxidizable step were <PEL. In the residual step there was a greater variation, with all

$Cu_{residual}$ between TEL and PEL, and all $Ni_{residual} \geq$ PEL. All $Pb_{residual}$ and $Zn_{residual}$ concentrations were < PEL.

The non-parametric One Sample Sign test was used to compare TEL and PEL concentration guidelines to each of the four steps in the sequential procedure for Cu, Ni, Pb, and Zn (**Table 4.5** and **Table 4.6** respectively). In **Table 4.5**, $Cu_{residual}$, $Pb_{reducible}$, $Ni_{residual}$, $Zn_{reducible}$, and $Zn_{residual}$ were significantly greater than the TEL guidelines (boldface p-values, $\alpha = 0.05$), while $Cu_{reducible}$, $Cu_{oxidizable}$, $Ni_{reducible}$, and $Zn_{acid\text{-}extractable}$ were no different than the TEL guideline (italicized p-values).

Table 4.5. One Sample Sign test compared to TEL guidelines of Cu, Ni, Pb, and Zn

Element (TEL) [a]	p-value	Element (TEL)	p-value
Cu (35.7 mg/kg)		***Pb (35 mg/kg)***	
Acid-extractable	< 0.0001 [b]	Acid-extractable	< 0.0001 [b]
Reducible	*0.2632* [c]	Reducible	**0.0004** [d]
Oxidizable	*0.2632* [c]	Oxidizable	0.0118 [b]
Residual	**< 0.0001** [d]	Residual	0.0414 [b]
Ni (18 mg/kg)		***Zn (123 mg/kg)***	
Acid-extractable	< 0.0001 [b]	Acid-extractable	*0.1153* [c]
Reducible	*0.2632* [c]	Reducible	**0.0118** [d]
Oxidizable	0.0026 [b]	Oxidizable	< 0.0001 [b]
Residual	**< 0.0001** [d]	Residual	**0.0026** [d]

[a] Sample size: All Streams (169), Palolo (57), Pukele (53), and Waiomao (59).
[b] Plainface p-values indicate the step was statistically < than TEL ($\alpha = 0.05$).
[c] Italicized p-values indicate the step is statistically = to TEL ($\alpha = 0.05$).
[d] Boldface p-values indicate the step is statistically > than TEL ($\alpha = 0.05$).

In **Table 4.6**, only $Pb_{reducible}$ and $Ni_{residual}$ were found to be significantly greater than PEL guidelines (boldface p-values, $\alpha = 0.05$). All other sequential steps and trace elements (Cu and Zn) were significantly less than PEL guidelines (PEL_{Cu} 197 mg/kg, PEL_{Zn} 315 mg/kg).

Table 4.6. One Sample Sign test compared to PEL guidelines of Ni and Pb

Element (PEL)	p-value	Element (PEL)	p-value
Ni (36 mg/kg)		***Pb (91.3 mg/kg)***	
Acid-extractable	< 0.0001 [a]	Acid-extractable	< 0.0001 [a]
Reducible	< 0.0001 [a]	Reducible	**0.0026** [b]
Oxidizable	< 0.0001 [a]	Oxidizable	< 0.0001 [a]
Residual	**< 0.0001** [b]	Residual	< 0.0001 [a]

[a] Plainface p-values indicate the step was statistically < than PEL ($\alpha = 0.05$).

[b] Boldface p-values indicate the step is statistically > than PEL ($\alpha = 0.05$).

5.0. RESULTS: WEAK HCl DIGESTION

This section presents results from the <63 μm grain size fraction of samples digested with weak HCl. This digestion was applied to streambed sediment from Palolo, Pukele, and Waiomao Streams (57, 53, and 59 samples respectively).

5.1. Precision for Weak HCl Digestion (HCl)

Precision of HCl digestion was assessed by CV% (**Equation 3.3**) using two CRMs and sediment from a location along Palolo Stream (**Table 5.1**).

Table 5.1. Precision of the weak HCl digestion (CV%)

	GSD-11 (5) [a]	SRM 2711 (21)	P41 63-125 μm (5)
Al	7.3	6.7	7.2
As	6.2	4.4	BDL
Cd	10.2	2.2	5.1
Cr	BDL [b]	BDL	BDL
Cu	9.4	6.6	3.1
Fe	10.1	9.4	9.5
Mn	7.6	6.6	5.5
Ni	37.3	BDL	6.4
Pb	6.8	4.2	3.5
Zn	7.0	6.5	2.7

[a] Number of replicates in parentheses.
[b] Below detection limits of ICP-AES.

Almost all CV% values were within an acceptable range (≤10%). The $CV\%_{Ni}$ in GSD11 (37%) was anomalous, as the mean concentration of Ni (1.2 mg/kg), was near the detection limits of ICP-AES. However, since the $CV\%_{Ni}$ in sediment from Palolo Stream (P41) was acceptable (6%), the Ni concentrations throughout the valley were deemed satisfactory.

5.2. Descriptive Statistics for HCl

Descriptive statistics for several elements in Palolo, Pukele, and Waiomao Streams are given in **Table 5.2**. Element concentrations were non-normal ($\alpha = 0.05$, see

Appendix V for skewness values, additional descriptive statistics, and additional elements).

Table 5.2. Descriptive statistics of selected elements (mg/kg) in streambed sediment (<63 µm) with weak HCl digestion

Element [a]	Location [b]	Mean ± SD	Median ± MAD	Min	Max
Cr	Palolo Stream	7.9 ± 4.6	7.0 ± 1.0	3	38
	Pukele Stream	2.8 ± 1.0	3.0 ± 1.0	2	6
	Waiomao Stream	2.4 ± 0.8	2.0 ± 0.0	1	6
Cu	Palolo Stream	132 ± 443	57 ± 17	25	3373
	Pukele Stream	33 ± 22	28 ± 6.0	15	149
	Waiomao Stream	20 ± 15	13 ± 4.0	6	57
Ni	Palolo Stream	19 ± 8.3	18 ± 3.0	10	59
	Pukele Stream	7.8 ± 3.6	7.0 ± 2.0	3	22
	Waiomao Stream	2.4 ± 2.9	1.0 ± 0.0	0.5	15
Pb	Palolo Stream	245 ± 596	134 ± 30	21	4588
	Pukele Stream	34 ± 47	24 ± 9.0	7	323
	Waiomao Stream	19 ± 29	7.0 ± 6.0	1	120
Zn	Palolo Stream	402 ± 587	223 ± 40	126	3737
	Pukele Stream	143 ± 408	71 ± 26	23	3019
	Waiomao Stream	47 ± 70	25 ± 11	10	498

[a] Additional descriptive statistics and elements (Al, As, and Cd) are provided in **Appendix V**.
[b] Sample size: Palolo (57), Pukele (53), and Waiomao (59).

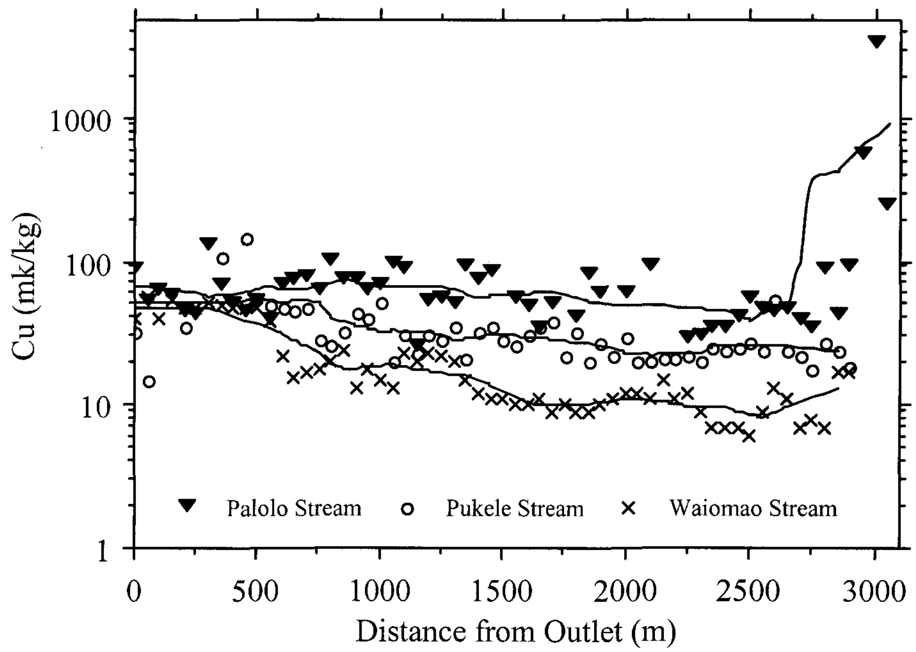
Median concentrations for Cr, Cu, Ni, Pb, and Zn from Palolo Stream were higher than those of its two tributary streams. Additionally, Pukele Stream had higher median values than Waiomao Stream. There were some extremely high concentrations of Cu (3373 mg/kg, sample P61 at 3000 m above starting point), Pb (4588 mg/kg, P60 at 2950 m), and Zn (3737 mg/kg, P51 at 2500 m) within Palolo Stream. Pukele Stream also had a very high maximum Zn value of 3019 mg/kg (P126 at 3350 m above Palolo watershed outlet).

A large number of As and Cd concentrations were below ICP-AES detection limits (<1 and <0.2 mg/kg respectively) at sampling sites along Palolo, Pukele, and Waiomao Streams (As: 15, 41, 57; Cd: 0, 29, 51 samples respectively). Waiomao Stream also had sample locations where Ni and Pb were below ICP-AES detection limits (<1 and <2 mg/kg respectively; 3 and 20 samples respectively).

5.3. Stream Comparisons with HCl

Bivariate scattergrams with "supersmoother" lines (StatView) are provided to show spatial variation in Cu, Ni, Pb, and Zn in bed sediment of Palolo Valley's streams (**Figure 5.1 - 5.4**). The concentrations of Cu (**Figure 5.1**) were about the same throughout Palolo Stream, although there was an increase in the last 500 m where Palolo Stream meets Pukele and Waiomao Stream. The concentrations of Cu in Pukele Stream and Waiomao Stream tended to decrease with increasing distance upstream. The concentration pattern of Ni (**Figure 5.2**) in Palolo Stream was similar to Cu, with an increase in Ni in the last 500 m of the stream. Pukele Stream and Waiomao Stream both decreased in Ni concentrations with increasing distance upstream. The smoothed concentration pattern of Pb (**Figure 5.3**) in Palolo Stream was similar over the lower 2600 m, with an increase in the upper 400 m. Pukele Stream and Waiomao Stream both decreased in Pb concentrations with increasing distance upstream. The Zn concentrations (**Figure 5.4**) in Palolo Stream had a greater variability in the upper 1000 m, while Pukele Stream and Waiomao Stream decreased in Zn concentration when progressing upstream.

Sediment in Palolo Stream tended to have higher Cu, Ni, Pb, and Zn concentrations than those in Pukele Stream and Waiomao Stream (**Figure 5.1 - 5.4**). Also, Pukele Stream tended to have higher concentrations of these four elements than Waiomao Stream. It is also interesting to note that while Palolo Stream concentrations either remained constant or had increasing trace element concentrations upstream, the tributary streams generally decreased in concentration with distance upstream.



Lines were fit with the "supersmoother" algorithm (StatView)

Figure 5.1. Spatial variation in Cu concentration with distance from individual stream outlets for the weak HCl digestion

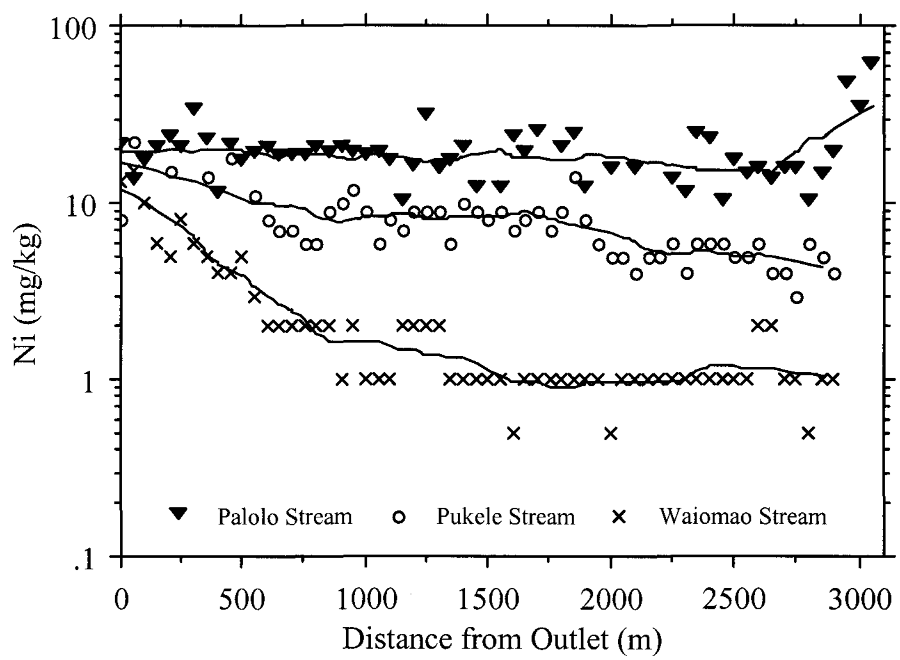


Figure 5.2. Spatial variation in Ni concentration with distance from individual stream outlets for the weak HCl digestion

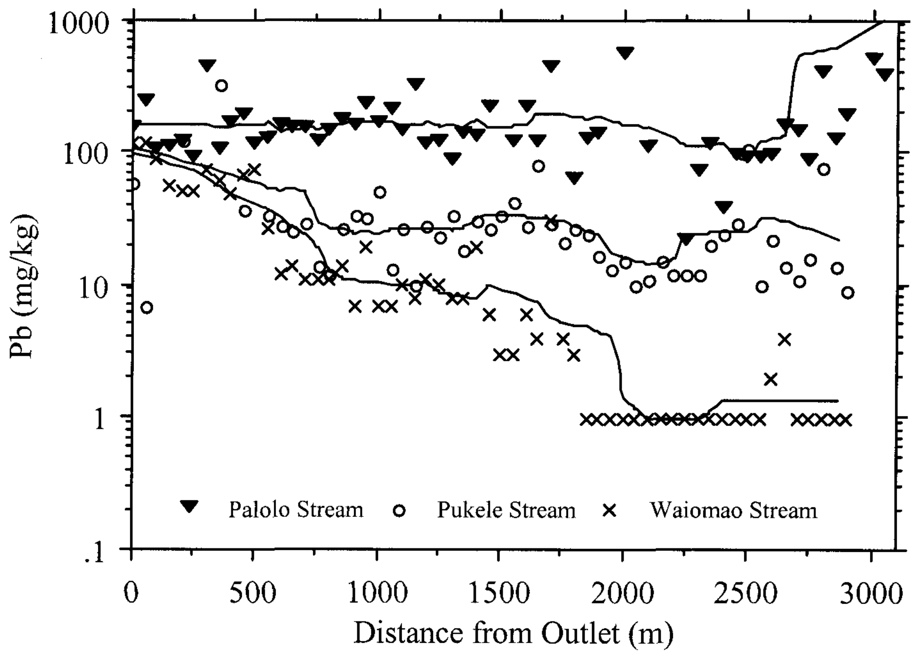


Figure 5.3. Spatial variation in Pb concentration with distance from individual stream outlets for the weak HCl digestion

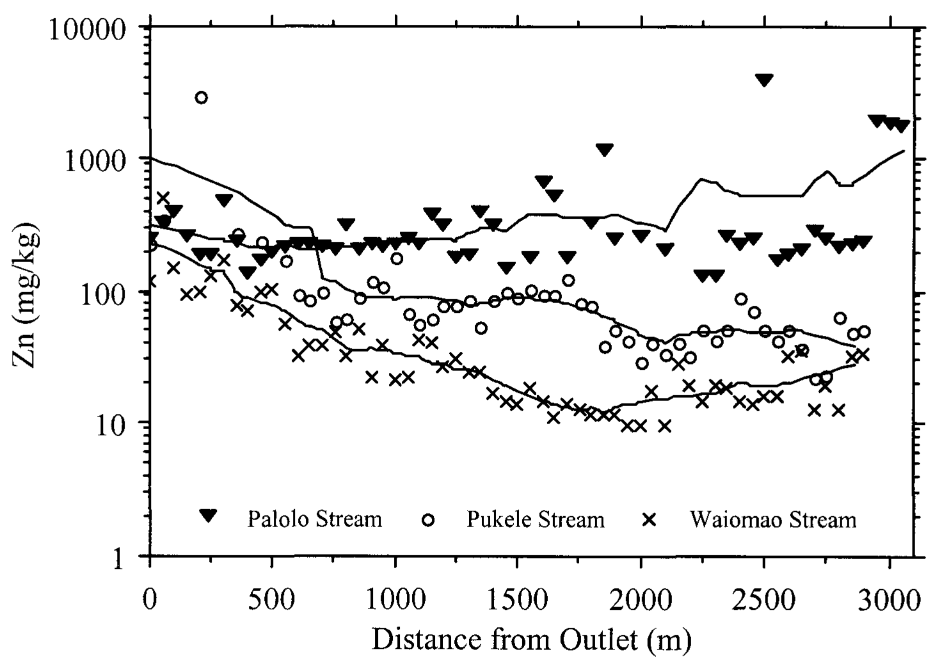


Figure 5.4. Spatial variation in Zn concentration with distance from individual stream outlets for the weak HCl digestion

Since it was possible to match the three streams from their individual outlets and progress 50 m upstream to each sampling site, the non-parametric matched Friedman test for spatial variation was applied to compare the three streams. The tied p-values for Cu, Pb, Ni, and Zn had at least one pairwise stream comparison that was significantly different (tied p-values <0.0001), which was also the case for As, Cd, and Cr. To discern which pairwise comparisons were significant, the non-parametric paired Wilcoxon Signed Rank test was applied (**Table 5.3**).

Table 5.3. Summary of statistical differences among streams based on Wilcoxon Signed Rank test

Stream [y]	Median ± MAD (mg/kg) [z]			
	Cu	**Ni**	**Pb**	**Zn**
Palolo Stream	57 ± 17 [c]	18 ± 3.0 [c]	134 ± 30 [c]	223 ± 40 [c]
Pukele Stream	28 ± 6.0 [b]	7.0 ± 2.0 [b]	24 ± 9.0 [b]	71 ± 26 [b]
Waiomao Stream	13 ± 4.0 [a]	1.0 ± 0.0 [a]	7.0 ± 6.0 [a]	25 ± 11 [a]

[y] Sample Size: Palolo (57), Pukele (53), and Waiomao (59).
[z] For a given element (column-wise) concentration values with the same letter are not significantly different at $\alpha_{adj} = 0.0167$. $\alpha_{adj} = 0.05 \div 3$ pairwise comparisons.

Based on Wilcoxon Signed Rank testing, Palolo Stream had significantly greater median concentrations than Pukele and Waiomao for all elements tested (As, Cd, Cr, Cu, Ni, Pb, and Zn, $\alpha_{adj} = 0.0167$), while Pukele was significantly greater than Waiomao for all elements (Palolo > Pukele > Waiomao).

5.4. SQGs compared with HCl

A summary of element partitioning in the three streams relative to TEL and PEL guidelines is presented in **Table 5.4**. It is important to restate that TEL and PEL guidelines are based on total digestions of freshwater aquatic sediments **(Table 1.6)**. Because weak HCl digestions underestimate the total concentrations of elements in streambed sediment (**Table 3.5**), the stream element partitioning in **Table 5.4** is considered conservative.

Table 5.4. Summary of stream element partitioning relative to PEL and TEL

	< TEL	≥ TEL to < PEL	≥ PEL
Cr	***< 37.3***	***≥ 37.3 to < 90***	***≥ 90***
Palolo Stream [a]	98.2 (56)	1.8 (1)	0 (0)
Pukele Stream	100 (53)	0 (0)	0 (0)
Waiomao Stream	100 (59)	0 (0)	0 (0)
Cu	***< 35.7***	***≥ 35.7 to < 197***	***≥ 197***
Palolo Stream	12 (7) [b]	81 (46)	7 (4)
Pukele Stream	74 (39)	26 (14)	0
Waiomao Stream	80 (47)	20 (12)	0
Ni	***< 18***	***≥ 18 to < 36***	***≥ 36***
Palolo Stream	46 (26)	51 (29)	3 (2)
Pukele Stream	96 (51)	4 (2)	0
Waiomao Stream	100 (59)	0	0
Pb	***< 35***	***≥ 35 to < 91.3***	***≥ 91.3***
Palolo Stream	4 (2)	12 (7)	84 (48)
Pukele Stream	85 (45)	9 (5)	6 (3)
Waiomao Stream	82 (48)	15 (9)	3 (2)
Zn	***< 123***	***≥ 123 to < 315***	***≥ 315***
Palolo Stream	0	77 (44)	23 (13)
Pukele Stream	85 (45)	11 (6)	4 (2)
Waiomao Stream	92 (54)	7 (4)	1 (1)

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59). TEL and PEL concentrations are in mg/kg.
[b] %(n): sample percent (sample number).

In general, Palolo Stream had the greatest number of samples exceeding SQG concentrations, followed by Pukele Stream, and finally Waiomao Stream. More than 50% of samples from Palolo Stream had concentrations ≥TEL for one or more elements. In addition, Palolo had the greatest number of samples that exceeded PEL values. In contrast, nearly 80% of Waiomao's samples were <TEL values for each element.

Table 5.5 shows the results of non-parametric One Sample Sign tests of all streams compared to the TEL guidelines, which is the lower SQG concentration level. Palolo Stream's bed sediment HCl concentrations were significantly higher than TEL_{Cu},

TEL_{Pb}, and TEL_{Zn}, and no different than TEL_{Ni}; while Pukele Stream and Waiomao Stream were significantly lower than TEL guidelines for all four elements.

Table 5.5. One Sample Sign test results of bed sediment HCl concentrations compared to TEL guidelines for Cu, Ni, Pb, and Zn (<63 μm)

Element (TEL) [a]	**p-value**	**Element (TEL)**	**p-value**
Cu (35.7 mg/kg)		***Pb (35 mg/kg)***	
Palolo Stream	**< 0.0001** [b]	Palolo Stream	**< 0.0001** [b]
Pukele Stream	0.0008 [c]	Pukele Stream	< 0.0001 [c]
Waiomao Stream	< 0.0001 [c]	Waiomao Stream	< 0.0001 [c]
Ni (18 mg/kg)		***Zn (123 mg/kg)***	
Palolo Stream	*> 0.9999* [d]	Palolo Stream	**< 0.0001** [b]
Pukele Stream	< 0.0001 [c]	Pukele Stream	< 0.0001 [c]
Waiomao Stream	< 0.0001 [c]	Waiomao Stream	< 0.0001 [c]

[a] Sample size: Palolo (57), Pukele, (53), Waiomao (59).
[b] Boldface p-values indicate the location is statistically > than TEL ($\alpha = 0.05$).
[c] Plainface p-values indicate the location is statistically < than TEL ($\alpha = 0.05$).
[d] Italicized p-values indicate the location is statistically = to TEL ($\alpha = 0.05$).

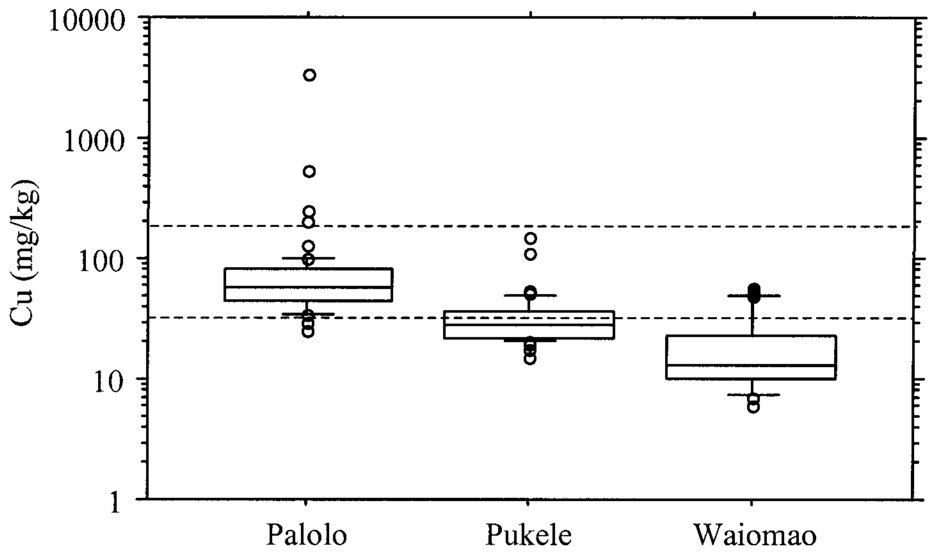
Although not shown here, the three streams were all significantly lower than TEL_{As}, TEL_{Cd}, and TEL_{Cr} (p-value <0.0001), except Palolo Stream, which was no different than TEL_{Cd} (p-value = 0.60). A second set of One Sample Sign tests was completed to determine if Palolo Stream had trace element concentrations that were different than PEL values (**Table 5.6**). Results indicated Pb concentrations in Palolo Stream bed sediment were significantly higher than the PEL_{Pb} (p-value <0.0001). All other elements in Palolo Stream bed sediment were significantly lower than PEL guidelines (As, Cd, Cr, Cu, Ni, and Zn: p-value <0.0001).

Table 5.6. One Sample Sign test results of Palolo Stream HCl concentrations compared to PEL guidelines for Cu, Ni, Pb, and Zn (<63 μm)

Element (PEL) [a]	p-value
Cu (197 mg/kg)	< 0.0001 [b]
Ni (36 mg/kg)	< 0.0001 [b]
Pb (91.3 mg/kg)	**< 0.0001** [c]
Zn (315 mg/kg)	< 0.0001 [b]

[a] Sample size of 57.
[b] Plainface p-values indicate the Palolo Stream is statistically < than PEL ($\alpha = 0.05$).
[c] Boldface p-values indicate the Palolo Stream is statistically > than PEL ($\alpha = 0.05$).

Figures 5.5 - 5.8 present box and whisker plots of Cu, Ni, Pb, and Zn concentrations with the TEL and PEL guidelines superimposed. From the box plots, it can be seen that Palolo Stream generally had a greater spread of data compared to Pukele and Waiomao Stream. Spread was measured by the interquartile range (IQR = 75th percentile - 25th percentile) for concentration of Cu, Ni, Pb, and Zn in Palolo Stream (38, 5, 80, 155 mg/kg respectively). Pukele and had smaller IQRs for Cu, Ni, Pb, and Zn (14, 3, 19, 46 mg/kg respectively) compared to Palolo Stream, while Waiomao Stream had IQRs less than both Palolo and Pukele Stream (13, 1, 17, 28 mg/kg respectively).



Box plot centerline indicates 50th percentile (median), bottom box line is 25th percentile, top box line is 75th percentile, and whiskers are the 10th and 90th percentiles. Notches indicate 95% confidence bands about the median. The dotted horizontal lines represent the location of TEL and PEL guidelines

Figure 5.5. Box plots of Cu in Palolo Valley streams for the weak HCl digestion ($TEL_{35.7}$ and PEL_{197} mg/kg)

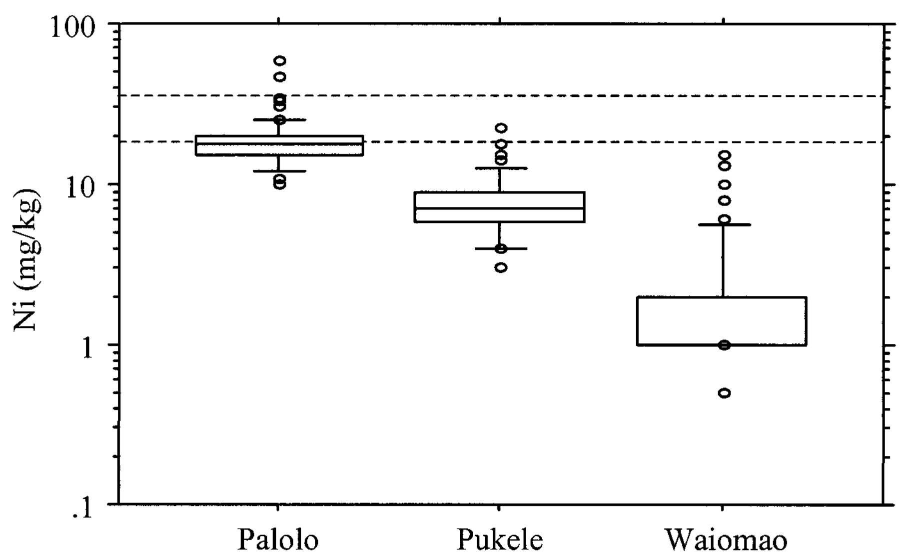


Figure 5.6. Box plots of Ni in Palolo Valley streams for the weak HCl digestion (TEL_{18} and PEL_{36} mg/kg)

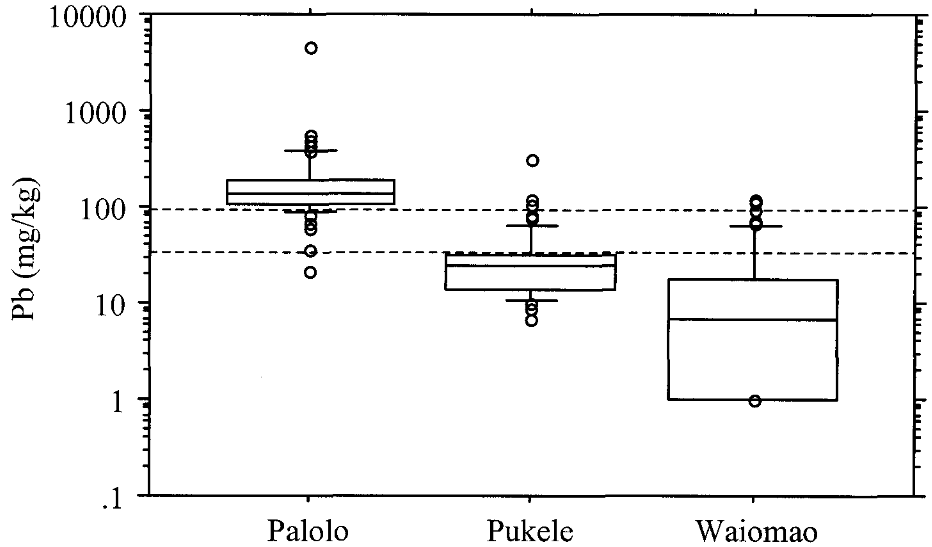


Figure 5.7. Box plots of Pb in Palolo Valley streams for the weak HCl digestion (TEL_{35} and $PEL_{91.3}$ mg/kg)

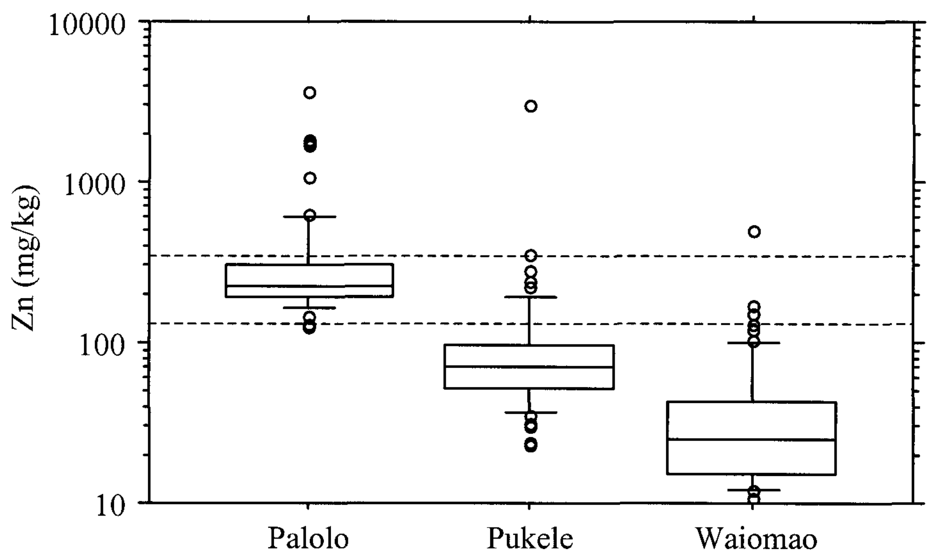


Figure 5.8. Box plots of Zn in Palolo Valley streams for the weak HCl digestion (TEL_{123} and PEL_{315} mg/kg)

5.5. ERs of HCl

Enrichment ratios for several elements were calculated utilizing Sutherland's (2000b) equation (**Equation 1.2**), which is expressed below for Pb:

$$ER_{Pb} = [(C_{Pb}/C_{Al})_{\text{Streambed Sediment}}] / [(BE_{Pb}/BE_{Al})_{\text{Upper Waiomao Stream}}] \quad \textbf{[5.1]}$$

where C_{Pb} is the concentration of Pb in streambed sediment samples, C_{Al} is the concentration of the conservative element Al in streambed sediment samples, BE_{Pb} is the best estimate of Pb's baseline median concentration in upper Waiomao Stream bed sediment samples, and BE_{Al} is the best estimate of conservative Al's baseline median concentration in upper Waiomao Stream bed sediment samples. Aluminum was used as a conservative element in enrichment calculations because it is less influenced by anthropogenic activities compared to other elements, and Al was precisely measured in this study (CV% range: 6.7 - 7.3%, **Table 5.1**). The median concentration of upper Waiomao Stream was used as the best estimate because concentrations were much lower in the upper section of the stream (sample locations P101- P121). The 21 samples were located between 5000 m and 6000 m above the outlet of Palolo Stream. The median BE concentrations from Waiomao Stream used were Al (1,400 mg/kg), Cd (0.1 mg/kg), Cr (2 mg/kg), Cu (11 mg/kg), Ni (1 mg/kg), Pb (1 mg/kg), and Zn (16 mg/kg).

Table 5.7 presents descriptive statistics of ER_{Cu}, ER_{Ni}, ER_{Pb}, and ER_{Zn}. Although ER_{Cr} was calculated, they were not presented here because central values (median and mean) were no different from 1, with a maximum ER_{Cr} of 3.7 in Palolo, and all other $ER_{Cr} \leq 2$ (**Appendix W**). Bed sediment from Palolo Stream had the highest median and maximum ERs of the four trace elements, followed by Pukele Stream and then Waiomao Stream. This result was expected based on previous statistical testing (Palolo > Pukele >

Waiomao, **Table 5.3**). Lead was the most enriched element investigated in all streams, with median values for Palolo (54) Pukele (15) Waiomao (6), and maximum values of Palolo (1889), Pukele (181), and Waiomao Stream (58).

Table 5.7. Descriptive statistics of HCl enrichment ratios for several elements in Palolo Valley streams

ER*n* [a]	**Location** [b]	**Mean ± SD**	**Median ± MAD**	**Min**	**Max**
	Palolo Stream	1.4 ± 0.5	1.4 ± 0.2	0.5	3.7
ER_{Cr}	Pukele Stream	0.9 ± 0.3	0.8 ± 0.1	0.3	2.0
	Waiomao Stream	1.0 ± 0.2	1.0 ± 0.1	0.5	1.6
	Palolo Stream	4.2 ± 13	2.0 ± 0.5	0.7	98
ER_{Cu}	Pukele Stream	1.9 ± 1.2	1.6 ± 0.5	0.4	7.9
	Waiomao Stream	1.5 ± 0.9	1.2 ± 0.2	0.6	4.6
	Palolo Stream	7.1 ± 2.7	6.5 ± 1.0	2.7	19
ER_{Ni}	Pukele Stream	4.8 ± 2.1	4.9 ± 1.6	1.9	11
	Waiomao Stream	1.8 ± 1.4	1.1 ± 0.3	0.5	7.5
	Palolo Stream	94 ± 245	54 ± 15	11	1889
ER_{Pb}	Pukele Stream	20 ± 26	15 ± 5.9	2.0	181
	Waiomao Stream	14 ± 18	6.0 ± 5.0	0.7	58
	Palolo Stream	9.7 ± 18	5.5 ± 1.4	2.0	131
ER_{Zn}	Pukele Stream	5.8 ± 18	2.7 ± 1.1	1.0	132
	Waiomao Stream	2.2 ± 2.3	1.4 ± 0.6	0.6	16

[a] Additional descriptive statistics and Cd are provided in **Appendix W**.
[b] Sample size: Palolo (57), Pukele, (53), and Waiomao (59).

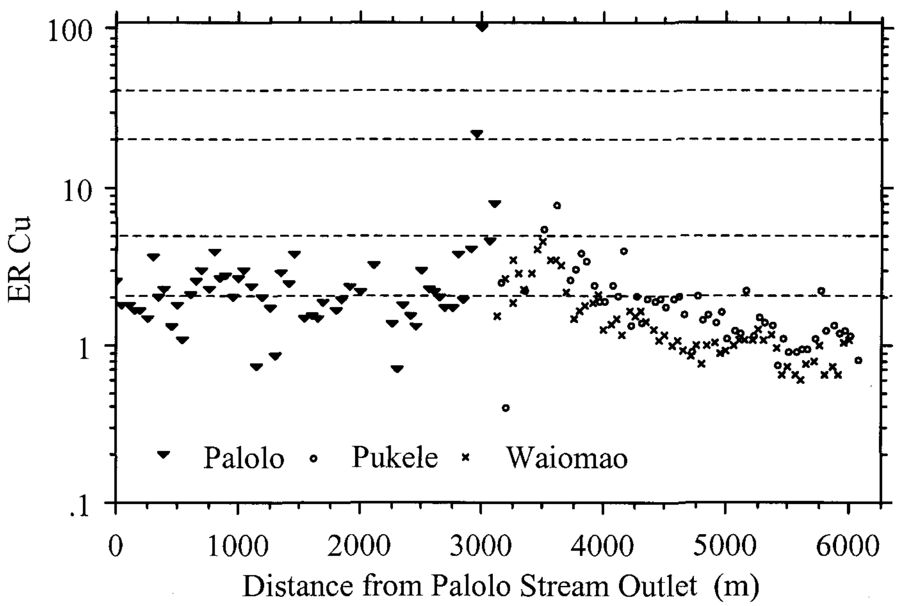
The percentage distributions of ERs in relation to the five categories defined by Sutherland (2000b) are shown in **Table 5.8**. In general, Palolo Stream had a greater percentage of bed sediment samples in the higher ER categories for Cu, Ni, Pb, and Zn, while Waiomao Stream had a greater percentage in the lower ER categories. Pukele Stream was intermediate between Palolo and Waiomao Streams. As an example, Palolo Stream's ER_{Pb} were mostly in the highest category (74%, ER>40). Pukele Stream's ER_{Pb} values were mostly in the third category (68%, ER >5-20), while Waiomao Stream's ER_{Pb} were concentrated in the three lowest ER categories.

Table 5.8. Summary of bed sediment ER_n partitioning relative to five ER categories

ER_n [a]	Stream [b]	ER ≤ 2	ER > 2-5	ER > 5-20	ER > 20-40	ER > 40
	Palolo	98 (56)	2 (1)			
ER_{Cr}	Pukele	100 (53)				
	Waiomao	100 (59)				
	Palolo	70 (40) [c]	24 (14)	2 (1)	2 (1)	2 (1)
ER_{Cu}	Pukele	85 (45)	11 (6)	4 (2)		
	Waiomao	85 (50)	15 (9)			
	Palolo		19 (11)	81 (46)		
ER_{Ni}	Pukele	15 (8)	45 (24)	40 (21)		
	Waiomao	80 (47)	18 (11)	2 (1)		
	Palolo			7 (4)	19 (11)	74 (42)
ER_{Pb}	Pukele	2 (1)	6 (3)	68 (36)	15 (8)	9 (5)
	Waiomao	36 (21)	10 (6)	32(19)	8 (5)	14 (8)
	Palolo	4 (2)	45 (26)	43 (25)	4 (2)	4 (2)
ER_{Zn}	Pukele	42 (22)	45 (24)	11 (6)		2 (1)
	Waiomao	73 (43)	24 (14)	3 (2)		

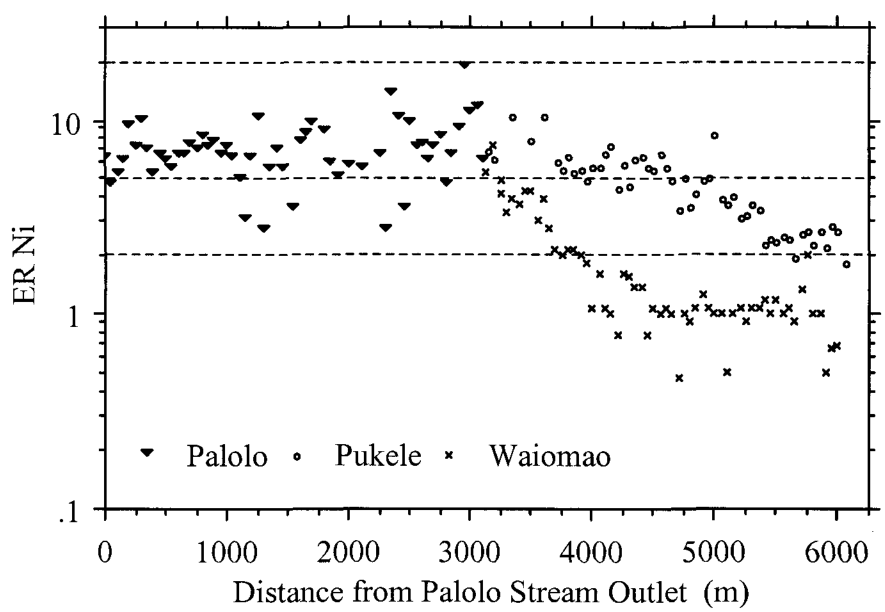
[a] Cadmium is provided in **Appendix X**.
[b] Sample size: Palolo (57), Pukele (53), and Waiomao (59).
[c] %(n): sample percent (sample number).

Bivariate scattergrams are provided to show spatial variation of ER_{Cu}, ER_{Ni}, ER_{Pb}, and ER_{Zn} in the three streams (**Figures 5.9- 5.12**). The figures start at the mouth of Palolo Stream (0 m) and progress upstream. The ER_{Cu} (**Figure 5.9**) and ER_{Zn} (**Figure 5.12**) were spread throughout the lower two categories, with a slight increase up Palolo Stream and ERs decreasing up the two tributaries. There appeared to be a few extremely high and low ER_{Cu} and ER_{Zn} values near the junction of the three streams (~3100 m). A majority of ER_{Ni} (**Figure 5.10**) in Palolo and Pukele Stream were above the second category with little change throughout Palolo Stream and a noticeable decrease up both tributaries, especially for Waiomao Stream. The ER_{Pb} (**Figure 5.11**) of Palolo Stream was spread throughout all five categories, with a slight increase up Palolo Stream, while the tributaries exhibited decreased ER_{Pb} values upstream. Like ER_{Cu} and ER_{Zn}, there appeared to be a few extremely high and low ER_{Pb} values near the tributary junction.



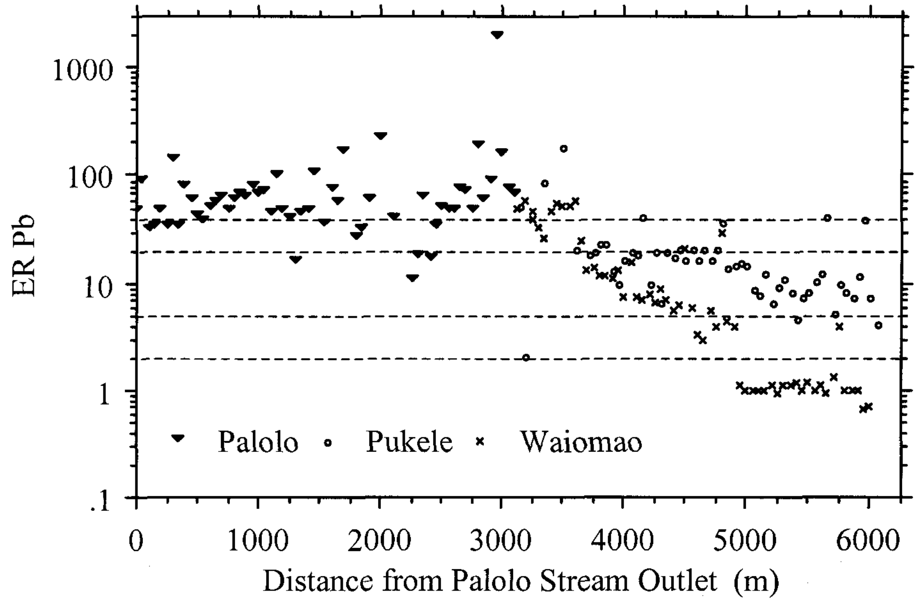
Start distance is at Manoa/Palolo Stream Junction and distances progress upstream. Dotted lines reflect enrichment ratio guidelines (2, 5, 20, and 40).

Figure 5.9. Spatial variation of ER_{Cu} in Palolo Valley streams for the weak HCl digestion



Dotted lines reflect enrichment ratio guidelines (2, 5, and 20).

Figure 5.10. Spatial variation of ER_{Ni} in Palolo Valley streams for the weak HCl digestion



Dotted lines reflect enrichment ratio guidelines (2, 5, 20, and 40).

Figure 5.11. Spatial variation of ER_{Pb} in Palolo Valley streams for the weak HCl digestion

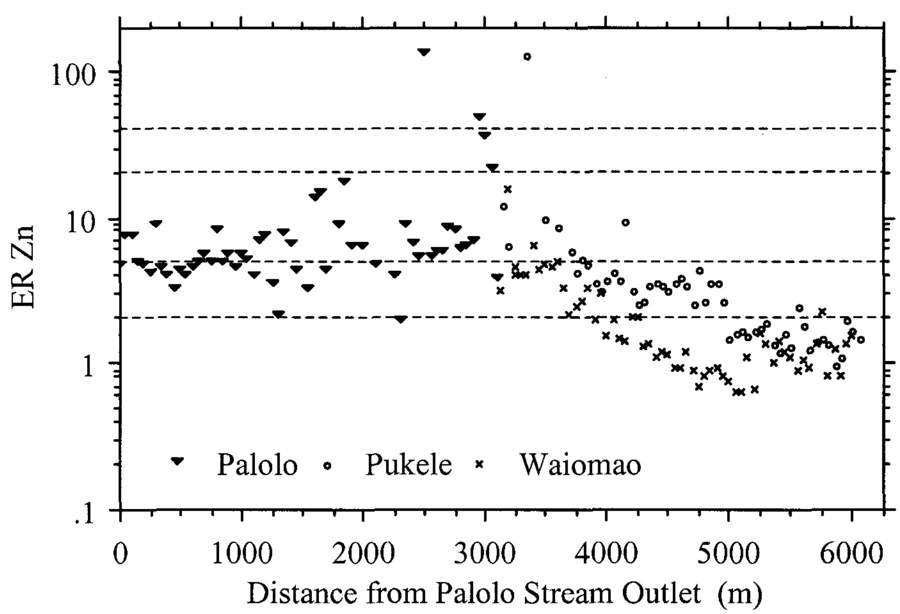


Figure 5.12. Spatial variation of ER_{Zn} in Palolo Valley streams for the weak HCl digestion

6.0. RESULTS: TOTAL DIGESTION & TOTAL ESTIMATION

This section presents results from 10 randomly selected samples from Palolo Stream (P2, P7, P17, P24, P30, P33, P35, P41, P54, and P57) that were isolated into six grain size fractions (<63, 63-125, 125-250, 250-500, 500-1000, 1000-2000 μm). These samples were completely digested with a 4-acid "attack." This digestion dissolves nearly all elements present in the sample, regardless of whether the source is anthropogenic or natural. This digestion will be referred to as "total."

The limited total digestion data set (n=10) will be extended for the <63 μm fraction to derive a total estimate concentration ($total_{est}$) for all sediment samples from Palolo, Pukele, and Waiomao Streams (n = 57, 53, and 59 respectively). The $total_{est}$ concentrations will be calculated from recovery ratios of HCl and total digestions matched samples (n=10, **Equation 3.1**, **Equation 3.2**, and **Table 3.5**).

6.1. Precision and Accuracy for Total Digestion (Total)

Precision (**Equation 3.3**) and Accuracy (**Equation 3.4**) of the total digestion was assessed with two CRMs and sediment from Palolo Stream (**Table 6.1**).

Table 6.1. Measurement precision (CV%) and accuracy (Acc%) of the total digestion

	GSD 11 (5) [a]		CRM 320 (5)		P57 63-125 μm (6)
	CV%	*Acc%*	*CV%*	*Acc%*	*CV%* [b]
Al	0.9	-4.5	2.1	3.8	2.9
As	1.5	8.2	2.4	-11.1	30.6
Cd	6.9	6.1	15.2	35.1	25.6
Cr	2.8	3.5	2.2	-8.1	3.5
Cu	4.8	6.9	2.7	2.0	4.3
Ni	3.2	-3.5	1.1	-2.7	1.9
Pb	1.7	6.9	2.5	2.1	2.2
Zn	1.8	7.9	0.9	-1.3	1.5

[a] Number of replicates in parentheses.
[b] Unable to assess accuracy.

A majority of CV% and Acc% values were within acceptable ranges at ≤10% and ±10% respectively. The Acc%$_{Cd}$ in CRM 320 was high (35%), which was likely because the certified Cd concentration in CRM 320 is very low (0.5 mg/kg) and near the minimum detection limits of ICP-AES (0.2 mg/kg). The CV%$_{As}$ and CV%$_{Cd}$ in Palolo Stream sample P57 was also elevated (31% and 26% respectively), which could have occurred because there was low As and Cd concentrations in the sample (3 and 0.7 mg/kg respectively), which was near the detection limits of ICP-AES (1 and 0.2 mg/kg respectively).

6.2. Descriptive Statistics for Total

Table 6.2 presents descriptive statistics for several elements in two contrasting grain size classes (<63 and 1000-2000 μm). The data was determined to be non-normal ($\alpha = 0.05$, see **Appendix Y** for skewness values, additional descriptive statistics, and all intermediate grain sizes).

Table 6.2. Descriptive statistics of elements (mg/kg) in Palolo Stream sediment of two grain sizes with a total digestion (10 samples per grain size)

Element [a]	Grain Size (μm)	Mean ± SD	Median ± MAD	Min	Max
As	< 63	7.7 ± 7.6	4.5 ± 2.5	2	25
	1000-2000	3.4 ± 2.6	2.0 ± 0.0	2	10
Cd	< 63	1.0 ± 0.7	0.9 ± 0.4	0.3	2.6
	1000-2000	0.8 ± 0.3	0.8 ± 0.1	0.4	1.2
Cr	< 63	511 ± 201	461 ± 11	376	1076
	1000-2000	311 ± 44	309 ± 31	233	375
Cu	< 63	232 ± 59	220 ± 27	121	322
	1000-2000	159 ± 46	158 ± 19	83	262
Ni	< 63	225 ± 23	225 ± 11	191	275
	1000-2000	196 ± 30	192 ± 23	149	239
Pb	< 63	320 ± 140	273 ± 111	145	564
	1000-2000	887 ± 2166	142 ± 67	17	7026
Zn	< 63	487 ± 164	422 ± 70	316	830
	1000-2000	410 ± 118	420 ± 94	223	598

[a] Additional descriptive statistics and all six grain size divisions are provided in **Appendix Y**.

Element concentrations generally increased with decreasing grain size, which was also seen in **Appendix Y** where data for all six grain size fractions were presented. Because the number of samples totally digested for each size fraction was small (n = 10), no further analysis was performed with these data. Alternatively, a $total_{est}$ data set was computed and examined in detail.

6.3. Descriptive Statistics for Total Estimation ($Total_{est}$)

The explanation and calculations of $total_{est}$ was presented earlier when **equations 3.1** and **3.2** were introduced. **Table 6.3** presents descriptive statistics of several elements.

Table 6.3. Descriptive statistics of elements (mg/kg) in Palolo Valley streambed sediment (<63 µm) $total_{est}$ calculation

$Total_{est}$ [a]	Location [b]	Mean ± SD	Median ± MAD	Min	Max
As	Palolo Stream	7.6 ± 9.6	4.4 ± 3.3	1.1	58
	Pukele Stream	1.9 ± 2.4	1.1 ± 0	1.1	16
	Waiomao Stream	1.3 ± 1.0	1.1 ± 0	1.1	9
Cd	Palolo Stream	2.5 ± 9.2	0.6 ± 0.3	0.26	67
	Pukele Stream	0.3 ± 0.4	0.13 ± 0	0.13	2.6
	Waiomao Stream	0.2 ± 0.1	0.13 ± 0	0.13	0.8
Cr	Palolo Stream	526 ± 306	467 ± 67	200	2533
	Pukele Stream	190 ± 70	200 ± 67	133	400
	Waiomao Stream	159 ± 56	133 ± 0	67	400
Cu	Palolo Stream	499 ± 1672	215 ± 64	94	12728
	Pukele Stream	126 ± 82	106 ± 23	57	562
	Waiomao Stream	76 ± 56	49 ± 15	23	215
Ni	Palolo Stream	296 ± 128	277 ± 46	154	908
	Pukele Stream	120 ± 55	108 ± 30	46	338
	Waiomao Stream	37 ± 45	15 ± 0	8	231
Pb	Palolo Stream	253 ± 614	138 ± 31	22	4730
	Pukele Stream	35 ± 48	25 ± 10	7	333
	Waiomao Stream	19 ± 30	7 ± 6	1	124
Zn	Palolo Stream	643 ± 939	357 ± 64	202	5979
	Pukele Stream	229 ± 654	114 ± 41	37	4830
	Waiomao Stream	75 ± 113	40 ± 18	16	797

[a] Additional descriptive statistics are provided in **Appendix Z.**
[b] Sample size: Palolo (57), Pukele (53), and Waiomao (59).

Palolo Stream had the highest median, minimum, and maximum concentrations for all elements examined, and Pukele Stream was higher than Waiomao Stream. Some notable maximum values in Palolo Stream included Cr (2533 mg/kg), Cu (12728 mg/kg), Ni (908 mg/kg), Pb (4730 mg/kg), and Zn (5979 mg/kg). Pukele and Waiomao Streams had elevated maximum concentrations of Zn (4830 and 797 mg/kg respectively).

6.4. SQGs compared with $Total_{est}$

A summary of element partitioning in bed sediment of the three streams relative to the TEL and PEL guidelines is presented in **Table 6.4**. The TEL and PEL guidelines were based on total digestions of freshwater aquatic sediment (**Table 1.6**).

Table 6.4. Summary of stream partitioning relative to PEL and TEL guidelines (mg/kg) for $total_{est}$ concentrations of several elements

	< TEL	**≥ TEL to < PEL**	**≥ PEL**
Cr	**< 37.3**	**≥ 37.3 to < 90**	**≥ 90**
Palolo Stream [a]			100 (57)
Pukele Stream			100 (53)
Waiomao Stream		5 (3) [b]	95 (56)
Cu	**< 35.7**	**≥ 35.7 to < 197**	**≥ 197**
Palolo Stream		42 (24)	58 (33)
Pukele Stream		92 (49)	8 (4)
Waiomao Stream	21 (12)	76 (45)	3 (2)
Ni	**< 18**	**≥ 18 to < 36**	**≥ 36**
Palolo Stream			100 (57)
Pukele Stream			100 (53)
Waiomao Stream	58 (34)	22 (13)	20 (12)
Pb	**< 35**	**≥ 35 to < 91.3**	**≥ 91.3**
Palolo Stream	2 (1)	10 (6)	88 (50)
Pukele Stream	81 (43)	13 (7)	6 (3)
Waiomao Stream	81 (48)	14 (8)	5 (3)
Zn	**< 123**	**≥ 123 to < 315**	**≥ 315**
Palolo Stream			100 (57)
Pukele Stream	51 (27)	40 (21)	9 (5)
Waiomao Stream	83 (49)	15 (9)	2 (1)

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).
[b] %(n): sample percent (sample number).

Palolo Stream had at least 98% of its samples exceeding TEL guidelines for Cr (100%), Cu (100%), Ni (100%), Pb (98%), and Zn (100%). Palolo Stream also had at least 58% of samples exceeding PEL guidelines for Cr (100%), Cu (58%), Ni (100%), Pb (88%), and Zn (100%). It was also interesting to observe that nearly 100% of all samples from Palolo, Pukele, and Waiomao Streams were above the PEL_{Cr} guideline (100%, 100%, and 95% respectively).

Table 6.5 provides the results of non-parametric One Sample Sign tests of all streams compared to the TEL guideline, which is the lower concentration level.

Table 6.5. One Sample Sign test compared to TEL guidelines of several elements for $total_{est}$ concentrations in streambed sediment

Element (TEL) [a]	p-value	Element (TEL)	p-value
As (5.9 mg/kg)		***Ni (18 mg/kg)***	
Palolo	*0.2892* [b]	Palolo	**<0.0001** [d]
Pukele	<0.0001 [c]	Pukele	**<0.0001** [d]
Waiomao	<0.0001 [c]	Waiomao	*0.2976* [b]
Cd (0.596 mg/kg)		***Pb (35 mg/kg)***	
Palolo	**0.0163** [d]	Palolo	**<0.0001** [d]
Pukele	<0.0001 [c]	Pukele	<0.0001 [c]
Waiomao	<0.0001 [c]	Waiomao	<0.0001 [c]
Cr (37.3 mg/kg)		***Zn (123 mg/kg)***	
Palolo	**<0.0001** [d]	Palolo	**<0.0001** [d]
Pukele	**<0.0001** [d]	Pukele	*>0.9999* [b]
Waiomao	**<0.0001** [d]	Waiomao	<0.0001 [c]
Cu (35.7 mg/kg)			
Palolo	**<0.0001** [d]		
Pukele	**<0.0001** [d]		
Waiomao	**<0.0001** [d]		

[a] Sample size: Palolo (57), Pukele, (53), Waiomao (59).
[b] Italicized p-values indicate the location is statistically = to TEL (α = 0.05).
[c] Plainface p-values indicate the location is statistically < than TEL (α = 0.05).
[d] Boldface p-values indicate the location is statistically > than TEL (α = 0.05).

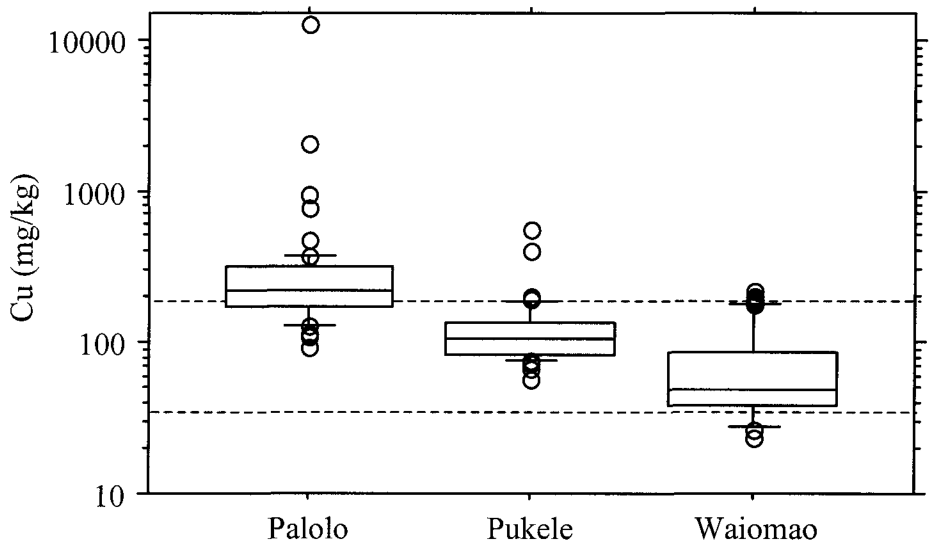
Since there were several cases where the three streams had element concentrations that were statistically greater than the TEL guideline, a second set of non-parametric One Sample Sign tests were conducted comparing the three streams to the higher PEL guideline (**Table 6.6**). As and Cd results were not shown because all streams had concentrations that were significantly lower than the PEL_{As} and PEL_{Cd} guidelines (p-values were <0.0001, $\alpha = 0.05$). It is interesting to observe that Cr in all three streams had concentrations that were statistically greater than PEL_{Cr} in **Table 6.6**. It is also interesting to see that Palolo Stream had element concentrations that statistically exceeded several different PEL guidelines (PEL_{Cr}, PEL_{Ni}, PEL_{Pb}, and PEL_{Zn}) or were statistically no different (PEL_{Cu}). In contrast, all of Waiomao Stream's element concentrations were below TEL and PEL guidelines, except PEL_{Cr}.

Table 6.6 One Sample Sign test compared to PEL guidelines of several elements for $total_{est}$ concentrations in streambed sediment

Element (PEL) [a]	p-value	Element (PEL)	p-value
Cr (90 mg/kg)		***Pb (91.3 mg/kg)***	
Palolo	**<0.0001** [b]	Palolo	**<0.0001** [b]
Pukele	**<0.0001** [b]	Pukele	<0.0001 [d]
Waiomao	**<0.0001** [b]	Waiomao	<0.0001 [d]
Cu (197 mg/kg)		***Zn (315 mg/kg)***	
Palolo	*0.2892* [c]	Palolo	**<0.0001** [b]
Pukele	<0.0001 [d]	Pukele	<0.0001 [d]
Waiomao	<0.0001 [d]	Waiomao	<0.0001 [d]
Ni (36 mg/kg)			
Palolo	**<0.0001** [b]		
Pukele	**<0.0001** [b]		
Waiomao	<0.0001 [d]		

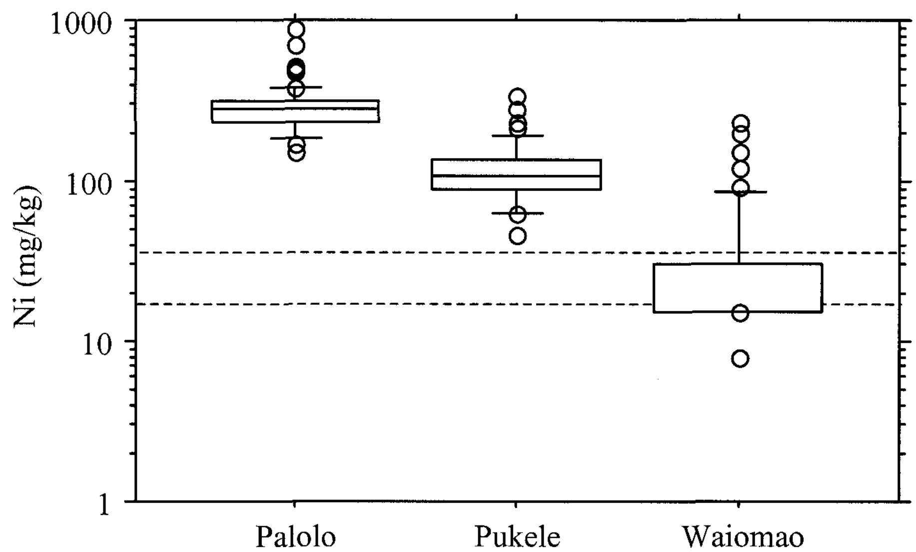
[a] Sample size: Palolo (57), Pukele, (53), Waiomao (59).
[b] Boldface p-values indicate the location is statistically > than TEL ($\alpha = 0.05$).
[c] Italicized p-values indicate the location is statistically = to TEL ($\alpha = 0.05$).
[d] Plainface p-values indicate the location is statistically < than TEL ($\alpha = 0.05$).

In summary, **Figures 6.1 - 6.4** present box and whisker plots of Cu, Ni, Pb, and Zn concentrations with the TEL and PEL guidelines superimposed to allow a visual representation of the results found in SQG partitioning (**Table 6.4**) and One Sample Sign tests (**Table 6.5** and **6.6**).



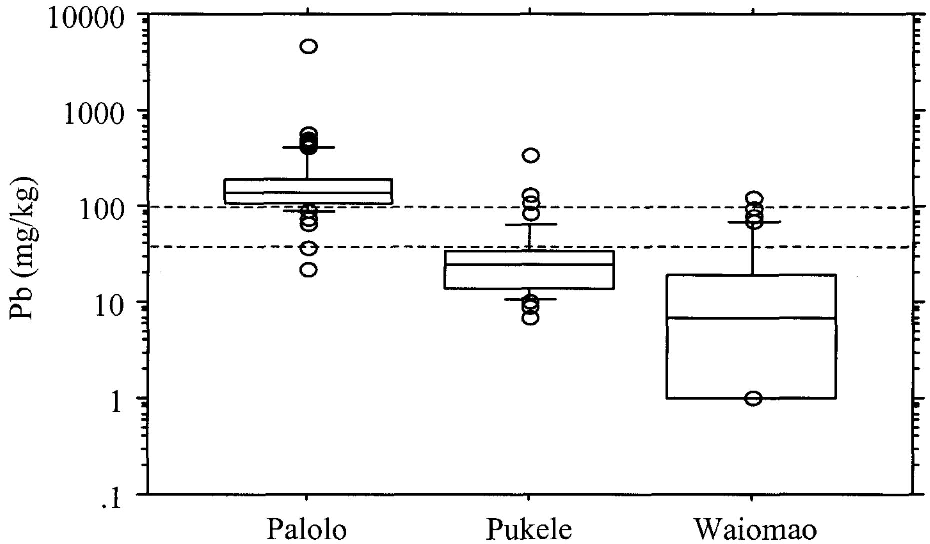
Box plot centerline indicates 50th percentile (median), bottom box line is 25th percentile, top box line is 75th percentile, and whiskers are the 10th and 90th percentiles. Notches indicate 95% confidence bands about the median. The dotted horizontal lines represent the location of TEL and PEL guidelines

Figure 6.1. Box plots of Cu in Palolo Valley streambed sediments for the total$_{est}$ calculation (TEL$_{35.7}$ and PEL$_{197}$ mg/kg)



Waiomao Stream's median (50th), 25th, and 10th percentiles were all 15 mg/kg

Figure 6.2. Box plots of Ni in Palolo Valley streambed sediments for the total$_{est}$ calculation (TEL$_{18}$ and PEL$_{36}$ mg/kg)



Waiomao Stream's 10th and 25th percentiles were all 1 mg/kg.

Figure 6.3. Box plots of Pb in Palolo Valley streambed sediments for the total$_{est}$ calculation (TEL$_{35}$ and PEL$_{91.3}$ mg/kg)

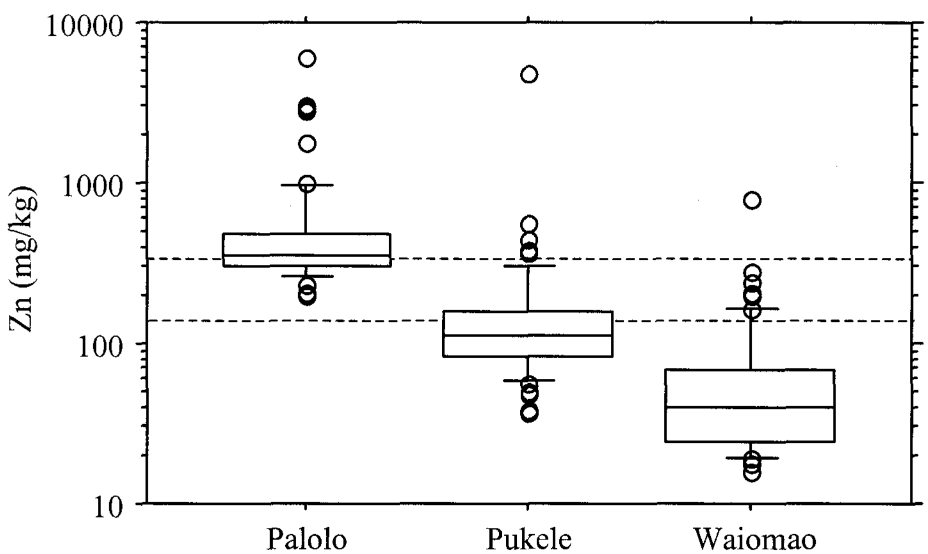


Figure 6.4. Box plots of Zn in Palolo Valley streambed sediments for the total$_{est}$ calculation (TEL$_{123}$ and PEL$_{315}$ mg/kg)

6.5. ERs of $Total_{est}$

Enrichment ratios for Cd, Cr, Cu, Pb, Ni, and Zn were calculated utilizing Sutherland's (2000b) equation (**Equation 1.2**), which is expressed below for Pb:

$$ER_{Pb} = [(C_{Pb}/C_{Al})_{\text{Streambed Sediment}}] / [(BE_{Pb}/BE_{Al})_{\text{Koolau/HVS host geology}}] \quad \textbf{[6.1]}$$

where C_{Pb} is the $total_{est}$ concentration of Pb in streambed sediment samples, C_{Al} is the $total_{est}$ concentration of the conservative element Al in streambed sediment samples, BE_{Pb} is the best estimate of Pb's background total digestion concentration in Koolau and HVS host geology, and BE_{Al} is the best estimate of conservative Al's background total digestion concentration in Koolau and HVS host geology. Aluminum was precisely measured in this study (CV% range: 0.9-2.9%, **Table 6.1**), which allowed Al to be used as the conservative element. The BE of total Al (67,650 mg/kg), Cd (0.27 mg/kg), Cu (100 mg/kg), Ni (215 mg/kg), Pb (6.5 mg/kg), and Zn (145 mg/kg) in the Koolau and HVS host geology were obtained from Sutherland (2000b). The BE of total Cr (315.5 mg/kg) was obtained from Clague and Frey (1982), Wilkinson and Stolz (1983), Roden et al. (1984), Budahn and Schmitt (1985), Frey et al. (1994), and Jackson et al. (1999).

$Total_{est}$ ERs are presented in **Table 6.7** for Cd, Cr, Cu, Ni, Pb, and Zn. The ER_{Pb} was the most elevated in all three streams. The median ER_{Pb} of Palolo Stream was the greatest (18), while Pukele was less (5) and Waiomao Stream was even lower (2). The maximum ER_{Pb} values were also elevated in Palolo, Pukele, and Waiomao Streams (642, 61, and 20 respectively). All other median ERs were generally low and <2, indicating little enrichment of Cd, Cr, Cu, Ni, and Zn. There were a few notable maximum ERs in Palolo Stream (ER_{Cd}: 172, ER_{Cu}: 88, and ER_{Zn}: 50) and Pukele Stream (ER_{Cd}: 15 and ER_{Zn}: 51).

Table 6.7. Descriptive statistics of ER_n for several elements in Palolo Valley streambed sediment ($total_{est}$)

ER_n	Stream [a]	Mean ± SD	Median ± MAD	Min	Max
ER_{Cd}	Palolo	6.4 ± 23	2.1 ± 0.5	0.4	172
	Pukele	1.4 ± 2.0	0.9 ± 0.4	0.4	15
	Waiomao	1.1 ± 0.4	1.0 ± 0.1	0.7	3.1
ER_{Cr}	Palolo	1.3 ± 0.4	1.3 ± 0.2	0.4	3.4
	Pukele	0.8 ± 0.3	0.7 ± 0.1	0.3	1.8
	Waiomao	1.0 ± 0.2	0.9 ± 0.1	0.5	1.5
ER_{Cu}	Palolo	3.8 ± 12	1.8 ± 0.5	0.6	88
	Pukele	1.7 ± 1.1	1.4 ± 0.4	0.4	7.1
	Waiomao	1.4 ± 0.8	1.1 ± 0.3	0.5	4.1
ER_{Ni}	Palolo	1.1 ± 0.4	1.0 ± 0.2	0.4	2.9
	Pukele	0.7 ± 0.3	0.8 ± 0.2	0.3	1.6
	Waiomao	0.3 ± 0.2	0.2 ± 0.1	0.1	1.2
ER_{Pb}	Palolo	32 ± 83	18.3 ± 5.2	3.6	642
	Pukele	6.9 ± 9.0	5.1 ± 1.9	0.7	61
	Waiomao	4.5 ± 6.0	2.0 ± 1.7	0.2	20
ER_{Zn}	Palolo	3.7 ± 6.9	2.1 ± 0.5	0.8	50
	Pukele	2.2 ± 6.8	1.0 ± 0.4	0.4	51
	Waiomao	0.8 ± 0.9	0.5 ± 0.2	0.2	6

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).

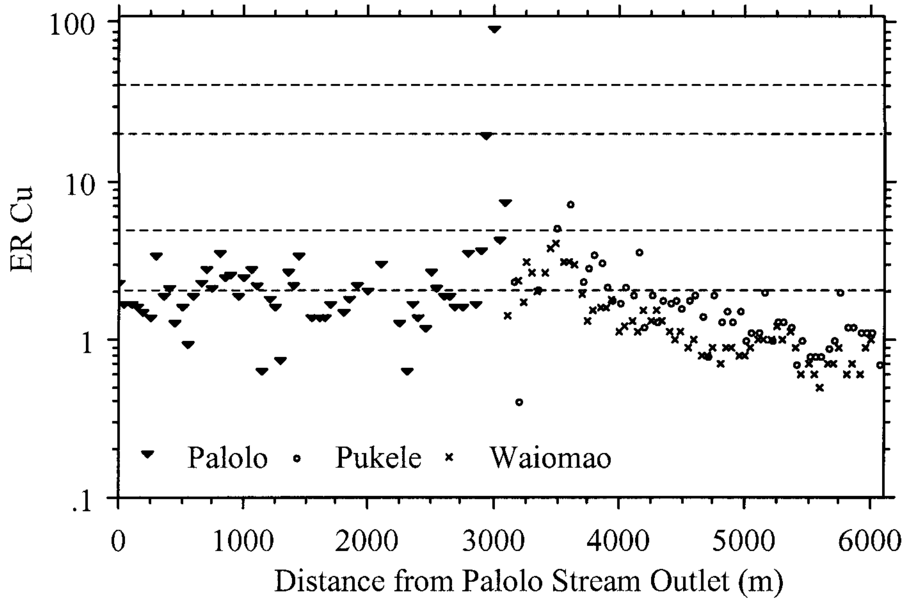
To further illustrate the $total_{est}$ ERs, **Table 6.8** provides a summary of sample percentages throughout the five ER categories. Palolo Stream had a greater proportion of samples that were within the upper ER categories compared to Pukele Stream. Waiomao Stream had the least number of samples that were within the upper ER categories. Lead displayed the most elevated ER, while all other ERs were primarily concentrated in the lower two ER categories (ER_{Cd}, ER_{Cr}, ER_{Cu}, ER_{Ni}, and ER_{Zn}).

Table 6.8. Summary percent of stream partitioning relative to five ER categories ($total_{est}$)

ER_n	Stream [a]	ER ≤ 2	ER > 2-5	ER > 5-20	ER > 20-40	ER > 40
ER_{Cd}	Palolo	63 (36) [b]	24 (14)	7 (4)	4 (2)	2 (1)
	Pukele	91 (48)	8 (4)	2 (1)		
	Waiomao	98 (58)	2 (1)			
ER_{Cu}	Palolo	77 (44)	18 (10)	3 (2)		2 (1)
	Pukele	89 (47)	9 (5)	2 (1)		
	Waiomao	86 (51)	14 (8)			
ER_{Cr} ER_{Ni} [c]	Palolo	98 (56)	2 (1)			
	Pukele	100 (53)				
	Waiomao	100 (59)				
ER_{Pb}	Palolo		4 (2)	56 (32)	30 (17)	10 (6)
	Pukele	17 (9)	36 (19)	43 (23)	2 (1)	2 (1)
	Waiomao	61 (36)	15 (9)	24 (14)		
ER_{Zn}	Palolo	65 (37)	24 (14)	9 (5)		2 (1)
	Pukele	91 (48)	7 (4)			2 (1)
	Waiomao	96 (57)	2 (1)	2 (1)		

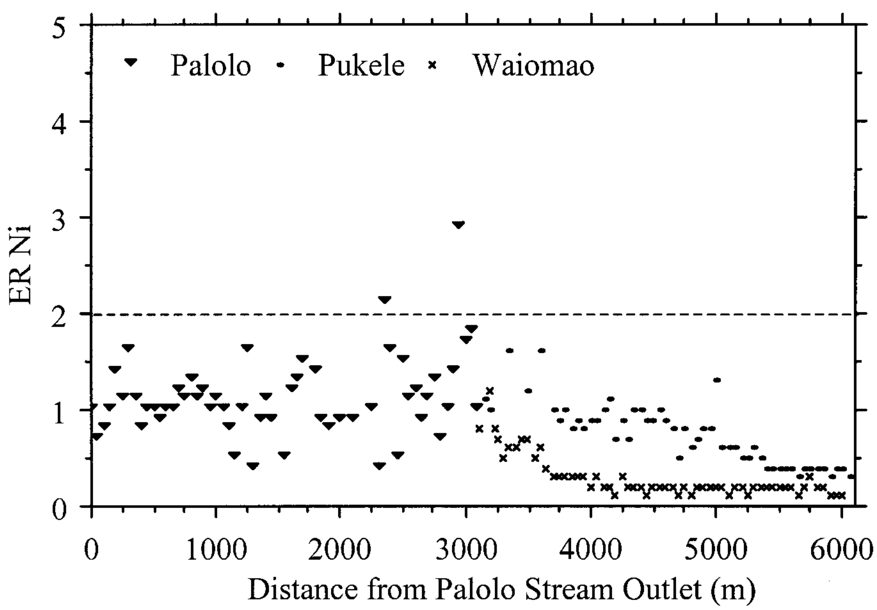
[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).
[b] %(n): sample percent (sample number).
[c] Although the ER_{Cr} and ER_{Ni} had different ER values, the stream partitioning was the same.

Bivariate scattergrams illustrate the spatial variation of ER_{Cu}, ER_{Ni}, ER_{Pb}, and ER_{Zn} in the three streams (**Figures 6.5 - 6.8** respectively). The figures start at the mouth of Palolo Stream (0 m) and progress upstream into the tributaries. The ER_{Cu} (**Figure 6.5**) and ER_{Zn} (**Figure 6.8**) were spread throughout the lower two categories, with a slight increase up Palolo Stream and ERs decreased upstream in the two tributaries. A majority of ER_{Ni} values (**Figure 6.6**) in all three streams were within the lowest ER category with little change throughout Palolo Stream and a noticeable decrease up both tributaries, especially Waiomao Stream. The ER_{Pb} (**Figure 6.7**) of Palolo Stream was spread throughout all five ER categories, with a slight increase up Palolo Stream, while the ER_{Pb} values in both tributaries decreased upstream. There appeared to be a few extremely high and low ER values for each element near the junction of the three streams (~3100 m).



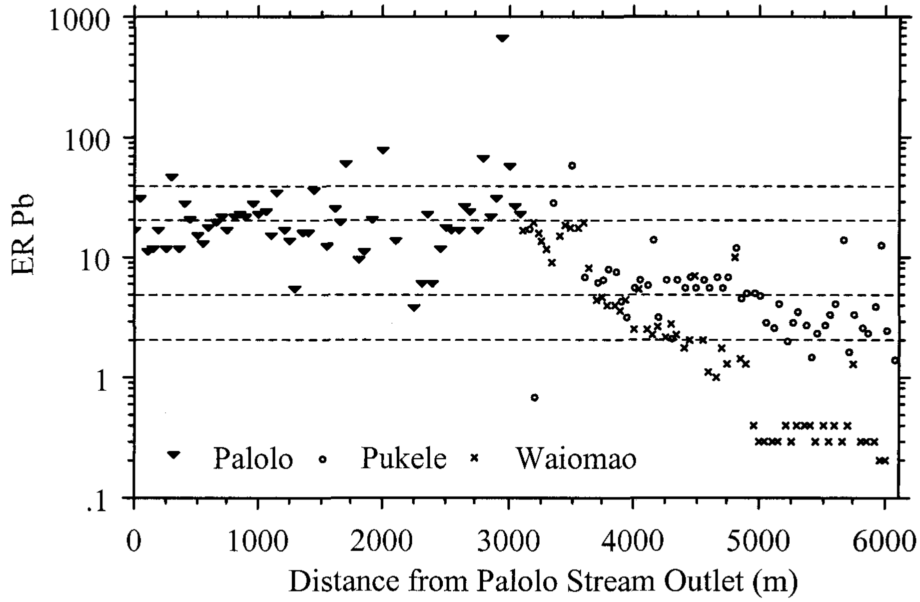
Start distance is at Manoa/Palolo Stream Junction and distances progress upstream.
Dotted lines reflect enrichment ratio guidelines (2, 5, 20, and 40).

Figure 6.5. Spatial variation of ER_{Cu} in Palolo Valley streams for $total_{est}$



Dotted lines reflect enrichment ratio guideline (2).

Figure 6.6. Spatial variation of ER_{Ni} in Palolo Valley streams for $total_{est}$



Dotted lines reflect enrichment ratio guidelines (2, 5, 20, and 40).

Figure 6.7. Spatial variation of ER_{Pb} in Palolo Valley streams for $total_{est}$

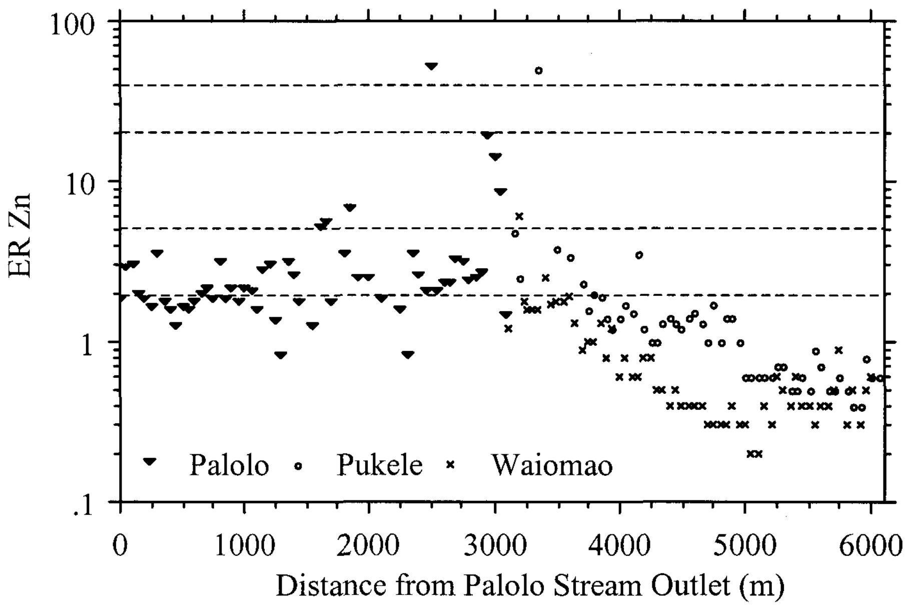


Figure 6.8. Spatial variation of ER_{Zn} in Palolo Valley streams for $total_{est}$

7.0. DISCUSSION

7.1. Digestion Methods and Concentrations

As expected, the digestion methods (BCR, HCl, and total) and estimated totals ($total_{est}$ and BCR_{Sum}) produced variable element concentrations (**Table 7.1.** and **7.2**).

Table 7.1. Median ± MAD (mg/kg) concentration of Cu, Ni, Pb, and Zn in Palolo Valley streams for HCl and $total_{est}$ methods (<63 µm)

	Stream [a]	HCl [b]	$Total_{est}$	Median of Difference ($Total_{est}$ - HCl)
Cu	Palolo	57 ± 17	215 ± 64	158
	Pukele	28 ± 6	106 ± 23	78
	Waiomao	13 ± 4	49 ± 15	36
Ni	Palolo	18 ± 3	277 ± 46	259
	Pukele	7 ± 2	108 ± 30	101
	Waiomao	1 ± 0	15 ± 0	14
Pb	Palolo	134 ± 30	138 ± 31	4
	Pukele	24 ± 9	25 ± 10	1
	Waiomao	7 ± 6	7 ± 6	0
Zn	Palolo	223 ± 40	357 ± 64	134
	Pukele	71 ± 26	114 ± 41	43
	Waiomao	25 ± 11	40 ± 18	15

[a] Matched sample size: Palolo (57), Pukele (53), and Waiomao (59). Median ± MAD for HCl from **Table 5.2** and $total_{est}$ from **Table 6.3**.
[b] For all elements and streams (row-wise) the HCl element concentrations were all significantly lower than the corresponding $total_{est}$ element concentrations (non-parametric Wilcoxon Signed Rank test, $\alpha = 0.05$).

Table 7.2. Median ± MAD (mg/kg) concentration of Cu, Ni, Pb, and Zn in Palolo Stream for HCl, BCR_{Sum}, and $total_{est}$ methods (<63 µm)

	HCl [vw]	$Total_{est}$ [vx]	BCR_{Sum} [vy]	Median of Difference ($Total_{est}$ - BCR_{Sum})
Cu	52 ± 8	198 ± 30	183 ± 19	27
Ni	18 ± 6	269 ± 84	203 ± 19	68
Pb	158 ± 42	164 ± 43	174 ± 41	-15
Zn	248 ± 74	398 ± 118	438 ± 82	-28

[v] Sample size of 20 matched pairs.
[w] The median ± MAD for HCl was extracted from data based on **Table 5.2**.
[x] The median ± MAD for $total_{est}$ was extracted from data based on **Table 6.3**.
[y] The BCR_{Sum} was calculated from the sum of the original BCR results for the four sequential steps. The BCR median ± MAD was similar to adding the steps for each element in **Table 4.2**.

As expected, the HCl digestion had lower element concentrations than the $total_{est}$ element concentrations (**Table 7.1**). However, Pb concentrations were similar for both methods as seen by the small median differences for Palolo, Pukele, and Waiomao Streams (4, 1, 0 mg/kg respectively).

The two estimates of total concentration in **Table 7.2** (BCR_{Sum} and $total_{est}$) were similar as seen by the relatively small median differences for Cu, Ni, Pb, and Zn (27, 68, -15, and -28 mg/kg respectively).

The element-to-element difference associated with different digestion procedures is evident from **Table 7.1** and **7.2**. This demonstrates the potential difficulty in comparing across studies that utilize different sampling designs and analytical methods. The application of a standardized approach to sediment digestion (weak, total, and/or sequential) would greatly enhance comparisons and reduce the potential uncertainty when comparisons are made between studies.

One standard method is the optimized BCR sequential procedure, which was part of this study (**Table 3.4**, Rauret et al. 1999, Sutherland and Tack 2003). The benefits of using the BCR technique as a standard digestion would be (1) there are three operationally defined phases (acid-extractable, reducible, and oxidizable) that are useful in understanding the geochemistry and potential bioavailability of trace elements in streambed sediment, (2) digestion of the residual fraction with aqua regia allows for a pseudo-total digestion to be estimated by adding the four steps together (BCR_{Sum}), and (3) recently tested CRMs for this method allowed standardization of precision and direct comparability between BCR studies (Sutherland and Tack 2002, 2003). Although the optimized BCR technique can be time consuming and costly, the benefits of the analysis could often be worth the investment.

Another widely applied digestion is the total procedure used by the USGS in their NAQWA projects, which was similar to the 4-acid total digestion (total) used in this study. Total digestions have limitations in environmental and geochemical research because they release all element fractions present in a sample. This does not allow for the separation of natural/anthropogenic sources or non-bioavailable/bioavailable fractions. Projects that use total digestion methods could be greatly improved if a weak or sequential digestion was added to better evaluate contaminant partitioning and the potential bioavailability of elements.

Table 7.3 presents Palolo Stream's recovery ratios of the weak HCl digestion relative to the 4-acid total digestion (total) and the BCR_{Sum} relative to the total digestion.

Table 7.3. Palolo Stream's percent recovery ratio for several elements (<63 μm)

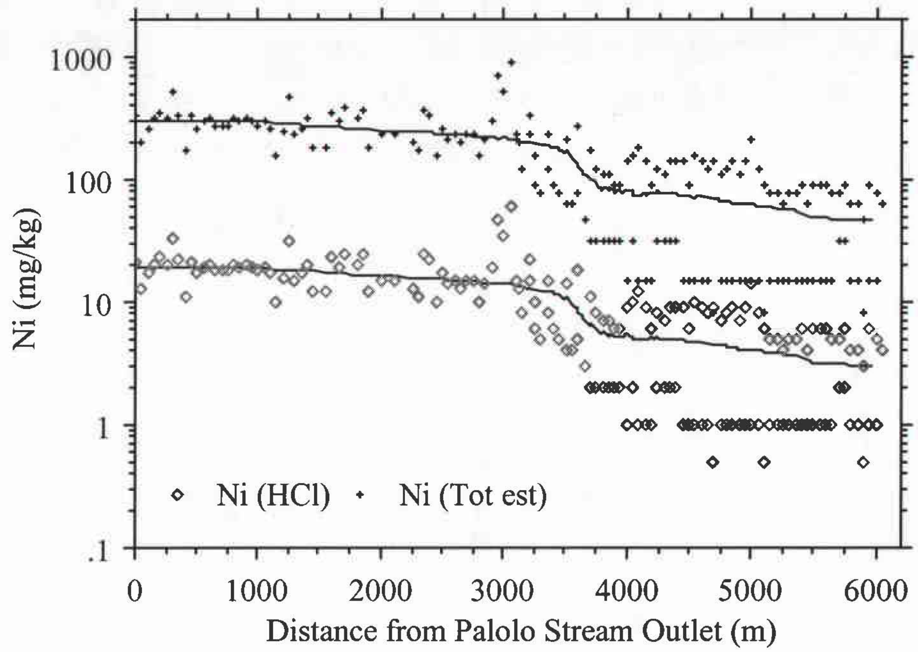
	Median ± MAD	
	% HCl Recovery Ratio [a]	**% BCR_{Sum} Recovery Ratio** [b]
Cr	2 ± 1	-
Cu	27 ± 4	84 ± 4
Ni	7 ± 2	89 ± 8
Pb	97 ± 6	106 ± 6
Zn	63 ± 8	106 ± 4

[a] HCl recovery ratio sample size of 10 from Palolo Stream. Recovery ratio based on **Equation 3.1**: HCl ÷ Total * 100. Median ± MAD from **Table 3.5**.
[b] BCR_{Sum} recovery ratio sample size of 10 from Palolo Stream. Recovery ratio based on **Equation 3.1** adapted to: BCR_{Sum} ÷ Total * 100. Chromium was not available.

It was interesting that 97% of the Pb and 63% of Zn were recovered in the HCl digestion, while less was recovered of Cr, Cu, and Ni (2%, 27%, and 7% respectively). **Figure 7.1** and **7.2** present bivariate scattergrams of the HCl digestion and $total_{est}$ calculation to illustrate low (Ni) and high (Pb) recoveries as seen in **Table 7.3** for Ni and Pb.

Because a weak HCl leach is commonly used as an indicator of trace element bioavailability from aquatic sediment (Campbell et al. 1988, Sutherland et al. 2001), the 97% median recovery ratio of Pb in Palolo Stream's bed sediment indicates that a substantial percentage of Pb could be bioavailable to aquatic organisms. The high Pb bioavailability could be a considerable threat to the aquatic health of plants in Palolo Stream, especially since Pb also had high median and maximum HCl concentrations in sediment samples (134 and 4588 mg/kg respectively, **Table 5.2**). Since Pb recovery was quantitative (97%) with the HCl leach, most Pb would be expected to be of anthropogenic origins rather than a geologic source, which is difficult to extract with a weak HCl leach. An analysis of Pb isotopes in streambed sediment would be needed to further refine the understanding of Pb source(s). Recent isotopic analysis of Pb in RDSs of Palolo Valley found leaded gasoline was the major contributor (Sutherland et al. 2003). It would be predicted that a majority of Pb in Palolo Valley's streambed sediment would also be from leaded gasoline since RDS flush directly into the streams through the storm drain system.

High recovery ratios for Zn (median 63%, **Table 7.3**) suggest contamination by anthropogenic sources. Additionally, since Zn concentrations were high when digested with weak HCl (median 223 mg/kg, maximum 3737 mg/kg, **Table 5.2**), this added further concern for the biotic environment of Palolo Stream.



Lines were fit with the "supersmoother" algorithm (StatView)

Figure 7.1. Spatial variation of Ni concentrations in Palolo Valley stream sediments with distance from outlet (weak HCl and total$_{est}$).

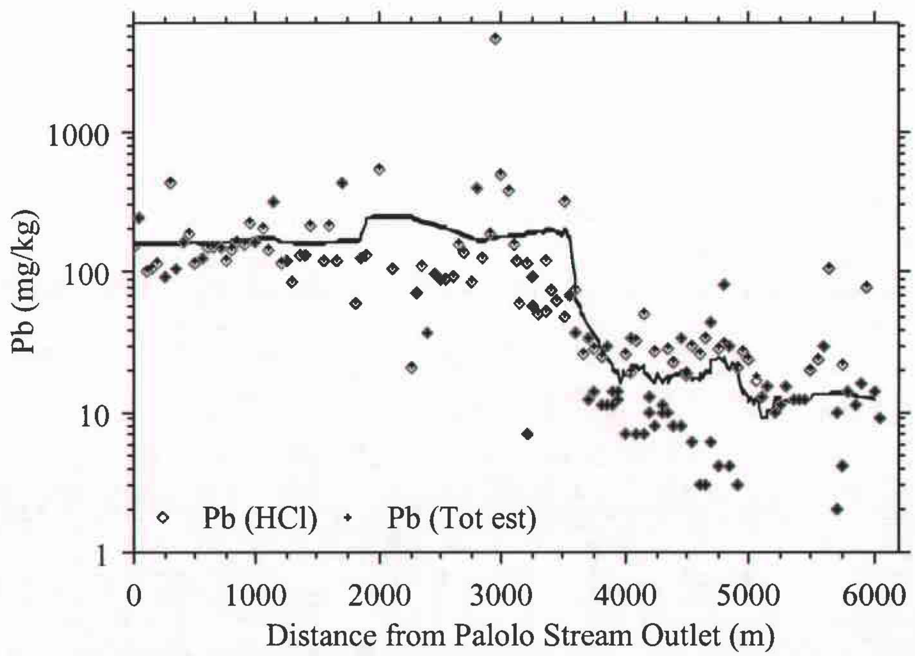


Figure 7.2. Spatial variation of Pb concentrations in Palolo Valley stream sediments with distance from outlet (weak HCl and total$_{est}$)

Chromium, Cu and Ni had low median recovery ratios (2%, 7%, and 27% respectively). This would indicate that the elements were primarily from host geology and would have limited bioavailability unlike Pb and Zn. The BCR_{Sum} median recovery ratios for Cu, Ni, Pb, and Zn were nearly quantitative (~100%, **Table 7.3**) indicating BCR_{Sum} is similar to a total digestion.

Figure 7.3 depicts the sample location (P#) of maximum element concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn (mg/kg) in Palolo Valley's streambed sediment (weak HCl digestion). The maximum element concentrations in Palolo Stream were almost all within three sampling locations, which were near the junction of the three streams (P60, P61, and P62, 100 m apart). The maximum element concentrations in Pukele Stream were spread throughout six sample locations (P123 - P156, 1650 m apart), although several locations were near the junction of the three streams (P123, P126, and P129, 300 m apart, **Appendix L** and **M** photographs). The maximum element concentrations in Waiomao Stream were all within the first three sampling locations of the junction (P64, P65, and P66, 100m apart). A majority of maximum concentrations were near the junction of the three streams. **Appendix L** presents a photograph taken from the Ahe Street Bridge looking down Pukele Stream with the junction in the background. The sample numbers can be referenced in **Table 7.4** for the distance from the Palolo Stream outlet and the concentration of other trace elements associated with the maximum element concentrations.

It was found that where one element was at a maximum concentration, several other elements tended to be elevated or also at their maximum concentration.

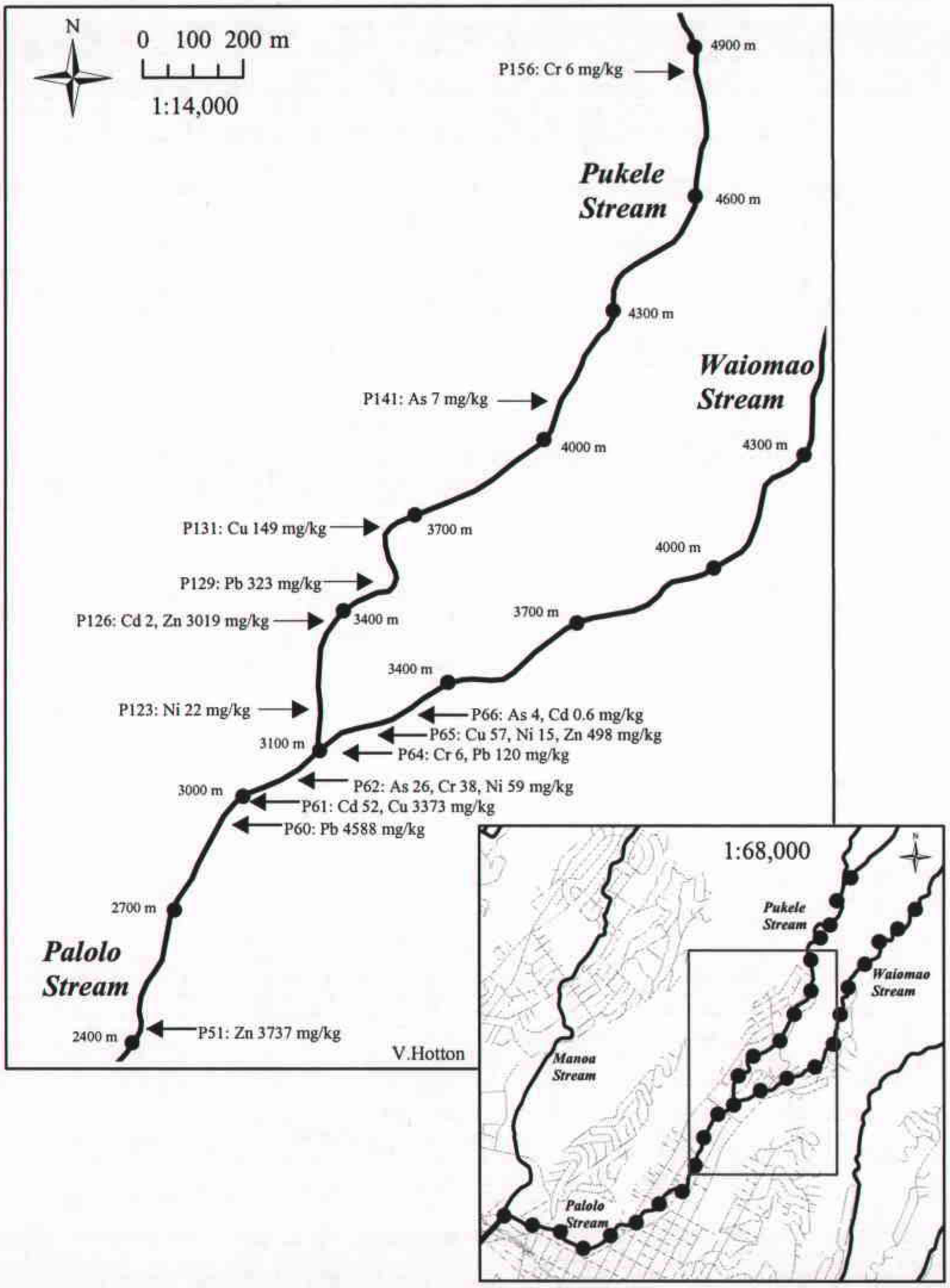


Figure 7.3. Location of maximum element concentrations in streambed sediment digested with weak HCl. Enlarged map includes sample number (P#) and estimated location (arrow) in stream (bold black lines). Every 6th sampling location (~300 m apart) is marked (black points) and distance from Palolo Stream outlet is listed (meters). Smaller map includes streets (thin black lines)

Table 7.4. Maximum concentration (mg/kg) and location (P#, meters) of elements in Palolo Valley streambed sediment (<63 μm weak HCl digestion)

	Stream [a]	Sample Number (P#) and Distance from Palolo Stream Outlet	Maximum Concentration	Associated Elements
As	Palolo	P62 (3050 m)	26	Cd 18, Cr 38, Cu 250, Ni 59, Pb 378, Zn 1734
	Pukele	P141 (4100 m)	7	Cd 0.2, Cr 4, Cu 41, Ni 12, Pb 32, Zn 108
	Waiomao	P66 (3250 m)	4	Cd 0.6, Cr 3, Cu 41, Ni 10, Pb 91, Zn 150
Cd	Palolo	P61 (3000 m)	52	As 11, Cr 15, Cu 3373, Ni 34, Pb 491, Zn 1804
	Pukele	P126 (3350 m)	2	As 4, Cr 5, Cu 36, Ni 15, Pb 122, Zn 3019
	Waiomao	P66 (3250 m)	0.6	As 4, Cr 3, Cu 41, Ni 10, Pb 91, Zn 150
Cr	Palolo	P62 (3050 m)	38	As 26, Cd 18, Cu 250, Ni 59, Pb 378, Zn 1734
	Pukele	P156 (4850 m)	6	As 2, Cd 0.4, Cu 38, Ni 9, Pb 29, Zn 126
	Waiomao	P64 (3124 m)	6	As <1, Cd 0.3, Cu 40, Ni 13, Pb 120, Zn 123
Cu	Palolo	P61 (3000 m)	3373	As 11, Cd 52, Cr 15, Ni 34, Pb 491, Zn 1804
	Pukele	P131 (3600 m)	149	As <1, Cd 0.5, Cr 4, Ni 18, Pb 36, Zn 241
	Waiomao	P65 (3200 m)	57	As 1, Cd 0.3, Cr 4, Ni 15, Pb 115, Zn 498
Ni	Palolo	P62 (3050 m)	59	As 26, Cd 18, Cr 38, Cu 250, Pb 378, Zn 1734
	Pukele	P123 (3200 m)	22	As <1, Cd 0.3, Cr 2, Cu 15, Pb 7, Zn 352
	Waiomao	P65 (3200 m)	15	As 1, Cd 0.3, Cr 4, Cu 57, Pb 115, Zn 498
Pb	Palolo	P60 (2950 m)	4588	As 5, Cd 2, Cr 9, Cu 550, Ni 46, Zn 1879
	Pukele	P129 (3500 m)	323	As 2, Cd 0.5, Cr 5, Cu 108, Ni 14, Zn 283
	Waiomao	P64 (3124 m)	120	As <1, Cd 0.3, Cr 6, Cu 40, Ni 13, Zn 123
Zn	Palolo	P51 (2500 m)	3737	As 3, Cd 4, Cr 7, Cu 55, Ni 17, Pb 87
	Pukele	P126 (3350 m)	3019	As 4, Cd 2, Cr 5, Cu 36, Ni 15, Pb 122
	Waiomao	P65 (3200 m)	498	As 1, Cd 0.3, Cr 4, Cu 57, Ni 15, Pb 115

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).

Figure 7.3 and **Table 7.4** indicate there was a high occurrence of maximum element concentrations near the junction of the three streams (~3100 m from Palolo Stream outlet). This junction is worthy of further investigation to identify anthropogenic sources contributing to elevated element concentrations in streambed sediment. Since this area was an active location of dumping during the year 2000 sampling period (R. Sutherland, personal communication and photographs, 2005) and litter was found when photographs were re-taken in 2005 (**Appendix L** and **M**), this area could continue to be a source of contamination. Additional anthropogenic causes could be related to the density of storm sewers and streets of the Pukele and Waiomao Stream sub-basin joining at Palolo Stream. However, the maximum concentrations could also be a product of one sampling period in time. During the sampling in 2000, the junction of the three streams could have been a sink of elevated trace elements, which would eventually be flushed further downstream. Future streambed sediment re-sampling could help identify continual or momentary streambed contamination.

7.2. SQGs

Based on statistical tests with streambed sediment concentrations compared to TEL and PEL guidelines, Palolo Stream had a considerable number of element concentrations that exceeded these thresholds, while Pukele Stream had less and Waiomao Stream had very little (BCR: **Table 4.5 - 4.6**, HCl: **Table 5.5 - 5.6**, $total_{est}$: **Table 6.5 - 6.6**).

Palolo Stream had concentrations that were statistically greater than TEL and PEL guidelines in BCR's reducible phase (TEL: Zn; PEL: Pb) or statistically no different than the reducible phase (TEL: Cu and Ni). Changes in the redox potential of the water-bed sediment system could release trace elements from the Fe/Mn oxides and become available to plants and through bioaccumulation move up trophic levels into the streams aquatic animals.

The weak HCl digestion's statistical tests indicated that Palolo Stream had concentrations that were statistically greater than TEL and PEL guidelines for several trace elements (TEL: Cu and Zn; PEL: Pb) or statistically no different (TEL: Ni and Cd). The trace element concentrations in Pukele and Waiomao Streams were all statistically lower than the TEL and PEL thresholds of all elements tested (As, Cd, Cr, Cu, Ni, Pb, and Zn). Based on the summary of stream partitioning relative to TEL and PEL values (**Table 5.4**), Palolo Stream had at least one or more samples that were ≥PEL in all elements examined (Pb 84%, Zn 23%, Cu 7%, Cd 5%, Ni 4%, and As 2%). Pukele had fewer samples that were ≥PEL (Pb 6%, Ni 4%, and Zn 4%), while Waiomao had the least number of samples that were ≥PEL (Pb 3% and Zn 2%). All three streams had one or more samples that exceeded the PEL guideline of Pb and Zn. Statistical tests and stream partitioning of element concentrations indicate that there is a potential threat to the biotic integrity of Palolo Stream, while Pukele Stream and Waiomao Stream appear to be safe. Additionally, a weak HCl digestion was used as an indicator of bioavailable trace elements, there is concern for the aquatic health of Palolo Stream since several elements (Cu, Ni, Pb, and Zn) could be readily bioavailable and in concentrations exceeding TEL and PEL values. There would also be concern that these trace elements could bioaccumulate and move up to higher trophic levels affecting aquatic animals. To address these concerns, biological and toxicological testing would be necessary to assess the health of plants and aquatic animals present in Palolo Valley streams, with an emphasis in Pb in Palolo Stream.

Additionally, if there is contamination in Palolo Valley, there could be a greater concern for sediment contamination and biological impacts in the Manoa/Palolo Drainage Canal (**Figure 3.2** and **Appendix B**) and Ala Wai Canal (**Figure 3.2**), which are the primary sinks of elements flushed through Manoa Valley and Palolo Valley. The two canals could have long-term and chronic contamination problems. In contrast, Palolo Valley could have short-term and acute contamination throughout the three streams because the sediment is flushed regularly by flashy precipitation events common through the winter months. Future research should also examine the Manoa/Palolo Drainage Canal and Ala Wai Canal bed sediments.

The $total_{est}$ statistical tests indicated that Palolo Valley streams had concentrations that were statistically greater or no different than TEL and PEL guidelines for the elements examined (**Table 7.5**). Since $total_{est}$ concentrations could be both bioavailable and non-bioavailable, the statistical tests for the $total_{est}$ may not be a great concern for certain elements in contrast to the HCl digestion's results discussed in the previous paragraph. However, there could be concern if $total_{est}$ concentrations were above guidelines and were also found to have high ERs, which will be discussed in the next section.

Table 7.5. Summary of One Sample Sign tests with $total_{est}$ element concentrations compared to TEL and PEL guidelines [a]

As ($TEL_{5.9}$, PEL_{17} mg/kg)		**Ni** (TEL_{18}, PEL_{36} mg/kg)	
Palolo	≈ TEL	Palolo	> **PEL**
Pukele		Pukele	> **PEL**
Waiomao		Waiomao	≈ TEL
Cd ($TEL_{0.596}$, $PEL_{3.53}$ mg/kg)		**Pb** (TEL_{35}, $PEL_{91.3}$ mg/kg)	
Palolo	>TEL	Palolo	> **PEL**
Pukele		Pukele	
Waiomao		Waiomao	
Cr ($TEL_{37.3}$, PEL_{90} mg/kg)		**Zn** (TEL_{123}, PEL_{315} mg/kg)	
Palolo	> **PEL**	Palolo	> **PEL**
Pukele	> **PEL**	Pukele	≈ TEL
Waiomao	> **PEL**	Waiomao	
Cu ($TEL_{35.7}$, PEL_{197} mg/kg)			
Palolo	≈ PEL		
Pukele	> TEL		
Waiomao	> TEL		

[a] Empty cells indicate element concentrations were significantly <TEL. All data was summarized from **Table 6.5** and **6.6**, $\alpha = 0.05$. Bold values (>PEL) indicate element concentrations were statistically greater than the respective PEL concentration.

7.3. ERs

A summary of the HCl and $total_{est}$ ERs for Cr, Cu, Ni, Pb, and Zn are presented in **Table 7.6**. The median ER_{Cr} values were extremely low for all three streams ($ER \leq 2$). The maximum ER_{Cr} values of Palolo Stream were also relatively low (HCl: 3.7 and $total_{est}$: 3.6, **Table 5.7** and **Table 6.7** respectively). Additionally, nearly 100% of all ER_{Cr} values in all digestion methods were $ER \leq 2$ (**Table 6.8**), which is the lowest ER category described by Sutherland (2000b):

- $ER_n \leq 2$ Depletion to minimal enrichment, suggestive of no or minimal contamination.

Although Palolo Stream's $total_{est}$ Cr concentrations (median 467 mg/kg, **Table 6.3**) were significantly higher than the PEL_{Cr} value of 90 mg/kg (**Table 7.5**), the low ER_{Cr} for both HCl and $total_{est}$ in all streams (**Table 7.6**) indicates that elevated $total_{est}$ Cr concentrations in Palolo Valley are likely to be of geologic origin (**Table 6.3**). Additionally, since the weak HCl median/maximum Cr concentrations were low in Palolo, Pukele, and Waiomao Streams (7/38, 3/6, and 2/6 mg/kg respectively, **Table 5.7**), this indicates that very little Cr is bioavailable and is natural (i.e., geogenic).

Table 7.6. Summary of ER_n values for HCl and $total_{est}$ methods

ER_n	Stream	Median ± MAD [a]	
		HCl	$Total_{est}$
ER_{Cr}	Palolo	1.4 ± 0.2	1.3 ± 0.2
	Pukele	0.8 ± 0.1	0.7 ± 0.1
	Waiomao	1.0 ± 0.1	0.9 ± 0.1
ER_{Cu}	Palolo	2.0 ± 0.5	1.8 ± 0.5
	Pukele	1.6 ± 0.5	1.4 ± 0.4
	Waiomao	1.2 ± 0.2	1.1 ± 0.3
ER_{Ni}	Palolo	6.5 ± 1.0	1.0 ± 0.2
	Pukele	4.9 ± 1.6	0.8 ± 0.2
	Waiomao	1.1 ± 0.3	0.2 ± 0.1
ER_{Pb}	Palolo	54 ± 15	18 ± 5.2
	Pukele	15 ± 5.9	5.1 ± 1.9
	Waiomao	6.0 ± 5.0	2.0 ± 1.7
ER_{Zn}	Palolo	5.5 ± 1.4	2.1 ± 0.5
	Pukele	2.7 ± 1.1	1.0 ± 0.4
	Waiomao	1.4 ± 0.6	0.5 ± 0.2

[a] Matched sample size: Palolo (57), Pukele (53), and Waiomao (59).
HCl data from **Table 5.7**. $Total_{est}$ data from **Table 6.7**.

Because Cr had a high $total_{est}$ concentration and low $total_{est}$ ER_{Cr} value, the TEL_{Cr} and PEL_{Cr} guidelines are not appropriate for Palolo Valley since Cr was naturally elevated in total digestions. The baseline total concentration of Cr used in this study for the ER calculation was 315.5 mg/kg (BE_{Cr}, **Equation 6.1**), which was well above the TEL and PEL guidelines for Cr (37.3 and 90 mg/kg respectively). The TEL and PEL guidelines were developed from North American streams, which have different host geologies (Smith et al. 1996). The host geology differences between North America (typically granite) and Hawaii (primarily basalt) make the TEL and PEL guidelines for Cr in

Hawaii inappropriate. It would be beneficial to develop a set of Cr guidelines that reflect the dominant basalt geology of Hawaii.

The median ER_{Cu} values were generally low for all three streams (ER<5). There were a few elevated maximum ER_{Cu} values in Palolo Stream for HCl and $total_{est}$ digestion methods (98 and 88 respectively; **Table 5.7** and **Table 6.7** respectively). Nearly 95% of all ER_{Cu} were ER<5 (**Table 5.8** for HCl and **Table 6.8** for $total_{est}$), which encompasses the two lower ER categories described by Sutherland (2000b):

- $ER_n \leq 2$ Depletion to minimal enrichment, suggestive of no or minimal contamination
- ER_n >2-5 Moderate enrichment, suggestive of moderate contamination.

These slightly elevated ER_{Cu} values suggest little to moderate enrichment of Cu in streambed sediment of Palolo Valley. The baseline total concentration of Cu used in this study for the ER calculation was 100 mg/kg (BE_{Cu}, **Equation 6.1**), which was between the TEL and PEL guidelines for Cu (35.7 and 197 mg/kg respectively). This made the TEL and PEL guideline for Cu less appropriate in Hawaii. Like Cr, it would be beneficial to develop a set of Cu guidelines that reflect the basalt geology of Hawaii.

The median ER_{Ni} values were generally low, with the HCl digestion having moderately higher median ER_{Ni} values (**Table 7.6**). In Palolo Stream, Pukele Stream, and Waiomao Stream, respectively 100%, 85%, and 20% of ER_{Ni} values in the weak HCl digestion were between ER>2 and ER≤20 (**Table 5.8**). This encompasses the lower second and third ER categories by Sutherland (2000b):

- ER_n >2-5 Moderate enrichment, suggestive of moderate contamination
- ER_n >5-20 Significant enrichment, suggestive of a significant contamination signal.

Waiomao Stream's remaining 80% of samples were ≤2, which suggests that Ni was not enriched in Waiomao Stream, while Palolo Stream and Pukele Stream were moderately to significantly enriched with nickel. The baseline total concentration of Ni used in this study for the ER calculation was 215 mg/kg (BE_{Ni}, **Equation 6.1**), which was well above the TEL and PEL guidelines for Ni (18 and 36 mg/kg respectively). This made the TEL and PEL guideline for Ni inappropriate in Hawaii. Like Cr and Cu, it would be beneficial to develop a set of Ni guidelines that reflect basalt geology.

Lead was the most enriched trace element throughout the three streams using various concentration methods (**Table 7.6**). Although there was a relatively large range of median ER_{Pb} for Palolo Stream, it suggests that Palolo Stream is significantly to extremely enriched in Pb because median ER_{Pb} values (HCl: 54 and $total_{est}$: 18) encompass the upper three ER categories by Sutherland 2000b:

- ER_n >5-20 Significant enrichment, suggestive of a significant contamination signal
- ER_n >20-40 Highly enriched, indicating a strong contamination signal
- ER_n >40 Extremely enriched, indicating an extreme contamination signal.

Pukele Stream was less enriched in Pb than Palolo Stream, although Pukele Stream did have enriched ER_{Pb} median values (HCl: 15, $total_{est}$: 5.1). Waiomao Stream's median ER_{Pb} values were the least enriched (HCl: 6.0, $total_{est}$: 2.0). Since Palolo Stream had high ER_{Pb} values, high median HCl and $total_{est}$ concentrations (134 and 138 mg/kg respectively in **Table 7.1**), and the Pb concentrations were significantly greater than the PEL_{Pb} guidelines (HCl and $total_{est}$), there could be great concern for Pb contamination in Palolo Stream. Although Pukele and Waiomao Stream had moderate ER_{Pb} values, their lower Pb concentrations (**Table 7.1**) were significantly lower compared to the TEL_{Pb} and PEL_{Pb} guidelines. This indicates that Pukele and Waiomao Stream are relatively uncontaminated in Pb compared to Palolo Stream. The baseline total concentration of Pb used in this study for the ER calculation was 6.5 mg/kg (BE_{Pb}, **Equation 6.1**), which was well below the TEL and PEL guidelines for Pb (35 and 91.3 mg/kg respectively). This makes the TEL and PEL guideline for Pb appropriate in Hawaii. Future research in Palolo Valley related to Pb in Palolo Stream would be extremely beneficial since Pb appeared to be the most enriched. Additionally, isotope analysis of Pb would allow sourcing (Sutherland et al. 2003). Toxicology assessments could evaluate the biological impact of Pb in sediment.

The median ER_{Zn} values were generally low ($\leq$2) throughout the three streams (**Table 7.6**). The ER_{Zn} values were similar to the results of ER_{Cu} and ER_{Ni}. However, Zn had a higher HCl/total recovery ratio (median 63%, **Table 7.3**). This would indicate that Zn is intermediate between Cu and Ni (lower concentrations, low HCl/total recovery ratio, and low ERs) and Pb (high concentrations, high HCl/total recovery ratio, and high ERs). The baseline total concentration of Zn used in this study for the ER calculation was 145 mg/kg (BE_{Zn}, **Equation 6.1**), which was between the TEL and PEL guidelines for Zn (123 and 315 mg/kg respectively). This made the TEL and PEL guideline for Zn less appropriate in Hawaii. Like Cr, Cu, and Ni, it would be beneficial to develop a set of Zn guidelines that reflect basalt geology. If future research were conducted in Palolo Stream, studying Cr, Cu, Ni, Pb, and Zn would be extremely useful since they had a range of results related to ERs and applicability with SQGs.

The low ERs of Cd (**Appendix W** and **X**, **Table 6.7** and **6.8**) were not summarized in **Table 7.6** because Cd also had low concentrations in HCl and $total_{est}$ (**Appendix V** and **Table 6.3** respectively) with few samples exceeding the TEL and PEL guidelines. This indicates that none or very little enrichment and contamination of Cd in Palolo Valley. The baseline concentration of Cd used in this study for the ER calculation was 0.27 mg/kg (BE_{Cd}, **Equation 6.1**), which was below the TEL and PEL guidelines for Cd (0.596 and 3.53 mg/kg respectively). This made the TEL and PEL guideline for Cd appropriate in Hawaii.

7.4. Palolo Valley Streams Compared to US Streams

7.4.1. *Nuuanu Stream, Honolulu, HI*

Table 7.7 presents weak HCl digestion results from Palolo Valley and Nuuanu Stream. Nuuanu Stream was separated into two sections: streambed sediment from the lower urban sections (n=49) and baseline streambed sediment from the upper reaches (n=10) (Andrews and Sutherland 2004). Nuuanu Valley watershed (11.7 km^2) is west of Palolo Valley watershed (11.4 km^2) separated by Manoa Valley watershed (15 km^2).

Table 7.7. Element concentrations (mg/kg) in streambed sediment of Palolo and Nuuanu Valley watershed streams (<63 µm, weak HCl digestion)

	Watershed	Stream Location/Media	Median ± MAD	Min	Max
Cu	Palolo [a]	Palolo Stream	57 ± 17	25	3373
		Pukele Stream	28 ± 6.0	15	149
		Waiomao Stream	13 ± 4.0	6	57
	Nuuanu [b]	Lower Urban	61 ± 19	34	136
		Baseline Headwater	21 ± 3.2	17	37
Pb	Palolo	Palolo Stream	134 ± 30	21	4588
		Pukele Stream	24 ± 9.0	7	323
		Waiomao Stream	7.0 ± 6.0	1	120
	Nuuanu	Lower Urban	122 ± 27	47	332
		Baseline Headwater	2.4 ± 0.5	1.8	6.8
Zn	Palolo	Palolo Stream	223 ± 40	126	3737
		Pukele Stream	71 ± 26	23	3019
		Waiomao Stream	25 ± 11	10	498
	Nuuanu	Lower Urban	175 ± 77.0	61	380
		Baseline Headwater	19 ± 2.8	16	25

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).
[b] Nuuanu Watershed data from Andrews and Sutherland (2004). Sample size: streambed sediment from Lower Urban areas (49) and Baseline Headwaters streambed sediment (10).

Palolo Stream and urban Nuuanu Stream sediment were similar in concentrations for Cu, Pb, and Zn, with Palolo Stream being higher overall. Pukele Stream and baseline

Nuuanu Stream sediment were similar for Cu. Waiomao Stream and baseline Nuuanu Stream sediment were similar for Pb and Zn. The following summary gives the highest to lowest median concentrations from **Table 7.7** (">"only indicates rank and has no statistical meaning):

Cu: Nuuanu Low > Palolo > Pukele > Nuuanu Base > Waiomao
Pb: Palolo > Nuuanu Low > Pukele > Waiomao > Nuuanu Base
Zn: Palolo > Nuuanu Low > Pukele > Waiomao > Nuuanu Base.

7.4.2. *Manoa Stream, Honolulu, HI*

Table 7.8 presents Palolo Valley's streams ($total_{est}$) compared to Manoa Stream (identical 4-acid total digestion, Sutherland 2000b). Manoa Valley watershed is directly west of Palolo Valley watershed. The following summary gives the highest to lowest median concentrations from **Table 7.8** (">"only indicates rank and has no statistical meaning):

Cu: Palolo > Manoa-Rs > Manoa-CI > Manoa-Low > Manoa-Base > Pukele > Waiomao
Ni: Manoa-Base > Manoa-Rs > Manoa-CI > Manoa-Low > Palolo > Pukele > Waiomao
Pb: Palolo > Manoa-Low > Manoa-Rs > Manoa-CI > Pukele > Manoa-Base > Waiomao
Zn: Palolo > Manoa-Low > Manoa-Rs > Manoa-CI > Manoa-Base > Pukele > Waiomao.

Table 7.8. Element concentrations (mg/kg) in streambed sediment of Palolo and Manoa Valley watershed streams (<63 µm, total$_{est}$ and total respectively)

	Watershed	Palolo Valley Stream and Manoa Stream Zone	Median	Min	Max
Cu	Palolo [a]	Palolo	215	94	12728
		Pukele	106	57	562
		Waiomao	49	23	215
	Manoa [b]	Lower Urban	181	133	258
		Commercial-Industrial	191	170	300
		Residential	199	172	267
		Baseline Headwater	173	150	212
Ni	Palolo	Palolo	277	154	908
		Pukele	108	46	338
		Waiomao	15	8	231
	Manoa	Lower Urban	307	278	439
		Commercial-Industrial	315	216	408
		Residential	323	289	360
		Baseline Headwater	341	302	379
Pb	Palolo	Palolo	138	22	4730
		Pukele	25	7	333
		Waiomao	7	1	124
	Manoa	Lower Urban	95	59	175
		Commercial-Industrial	50	10	175
		Residential	52	17	1078
		Baseline Headwater	10	5	28
Zn	Palolo	Palolo	357	202	5979
		Pukele	114	37	4830
		Waiomao	40	16	797
	Manoa	Lower Urban	276	210	368
		Commercial-Industrial	242	180	444
		Residential	252	208	510
		Baseline Headwater	196	162	268

[a] Palolo Valley from total$_{est}$ (**Table 6.3**), sample size: Palolo (57), Pukele (53), and Waiomao (59).
[b] Manoa based on Sutherland (2000b) 4-acid total digestion of Manoa Stream. Sample size: Lower Urban (17), Commercial-Institutional (42), Residential (49), and Baseline streambed sediment from headwaters (15). The Lower zone is near the stream outlet, upstream is the Commercial-Institutional zone followed by the Residential zone and ending in the Baseline Headwater zone.

7.4.3. *Oahu Island Streams of USGS NAWQA*

Table 7.9 presents Palolo Valley streams (total$_{est}$) compared to Oahu Island streams from the USGS NAWQA study. The following is a summary of the highest to lowest median concentrations from **Table 7.9** (">"only indicates rank and has no statistical meaning):

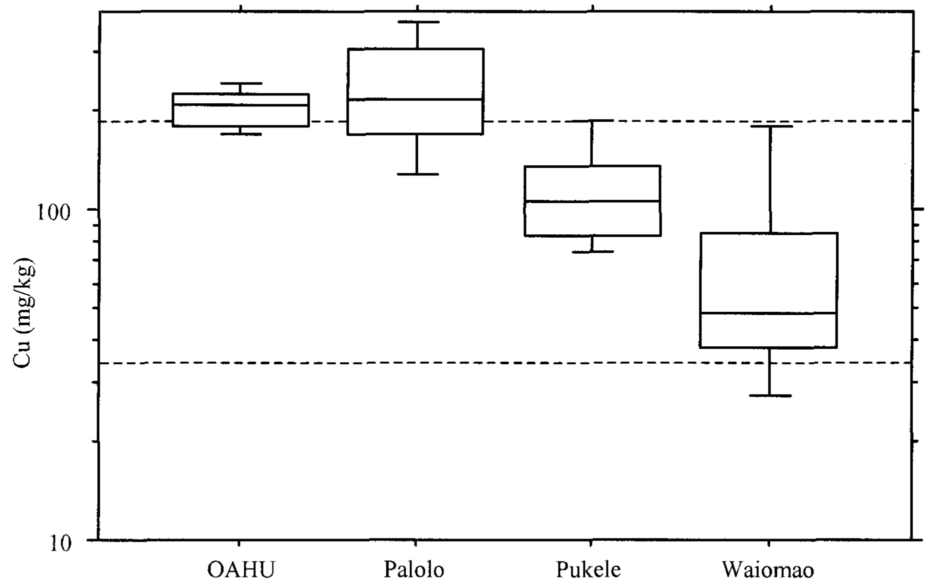
Cu:	Palolo > OAHU > Pukele > Waiomao
Ni:	Palolo > OAHU > Pukele > Waiomao
Pb:	Palolo > Pukele > OAHU > Waiomao
Zn:	Palolo > OAHU > Pukele > Waiomao.

Table 7.9. Element concentrations (mg/kg) in streambed sediment of Palolo Valley watershed and Oahu Island streams of the USGS NAWQA (<63 µm, $total_{est}$ and total respectively)

	Watershed and Island	Stream [a]	Median ± MAD	Min	Max
Cu	Palolo Valley Watershed	Palolo Stream	215 ± 64	94	12728
		Pukele Stream	106 ± 23	57	562
		Waiomao Stream	49 ± 15	23	215
	Oahu [b]	OAHU Streams	210 ± 20	110	270
Ni	Palolo Valley Watershed	Palolo Stream	277 ± 46	154	908
		Pukele Stream	108 ± 30	46	338
		Waiomao Stream	15 ± 0	8	231
	Oahu	OAHU Streams	265 ± 50	150	430
Pb	Palolo Valley Watershed	Palolo Stream	138 ± 31	22	4730
		Pukele Stream	25 ± 10	7	333
		Waiomao Stream	7 ± 6	1	124
	Oahu	OAHU Streams	22 ± 15	3	220
Zn	Palolo Valley Watershed	Palolo Stream	357 ± 64	202	5979
		Pukele Stream	114 ± 41	37	4830
		Waiomao Stream	40 ± 18	16	797
	Oahu	OAHU Streams	245 ± 30	160	640

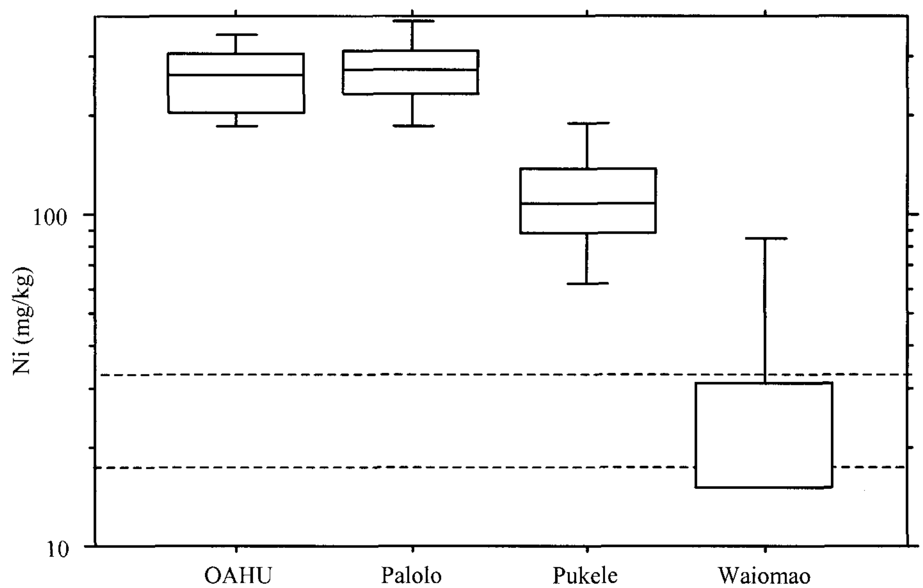
[a] Sample size of Palolo, Pukele, Waiomao, and OAHU: 57, 53, 59, and 24 respectively.
[b] Oahu data based on USGS (2004b).

Figures 7.4 to **7.7** present box and whisker plots of Cu, Ni, Pb, and Zn respectively from Oahu NAWQA streams and the three Palolo Valley streams with TEL and PEL guidelines superimposed. The USGS NAWQA study of Oahu Streams was based on a similar total digestion (USGS 2004a, 2004b, and 2004c).



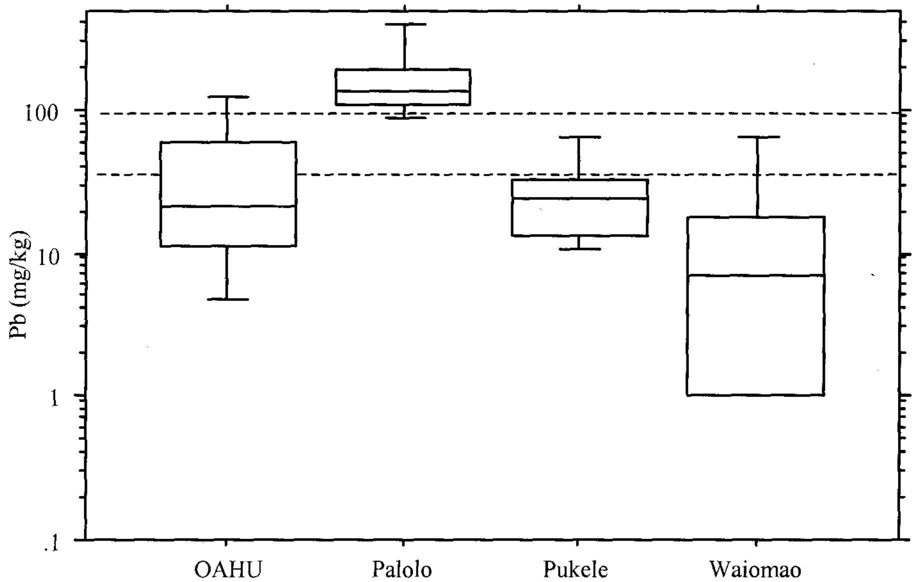
The dotted horizontal lines represent the location of TEL and PEL guidelines.
Digestion: OAHU (total), Palolo, Pukele, and Waiomao ($total_{est}$).

Figure 7.4. Box plots of Cu concentrations in USGS NAWQA Oahu Island streams and Palolo Valley streambed sediment ($TEL_{35.7}$ and PEL_{197} mg/kg)



Waiomao Stream's median (50^{th}), 25^{th}, and 10^{th} percentile values were all 15 mg/kg.

Figure 7.5. Box plots of Ni concentrations in USGS NAWQA Oahu Island streams and Palolo Valley streambed sediment (TEL_{18} and PEL_{36} mg/kg)



Waiomao Stream's 25th and 10th percentile values were both 1 mg/kg.

Figure 7.6. Box plots of Pb concentrations in USGS NAWQA Oahu Island streams and Palolo Valley streambed sediment (TEL_{35} and $PEL_{91.3}$ mg/kg)

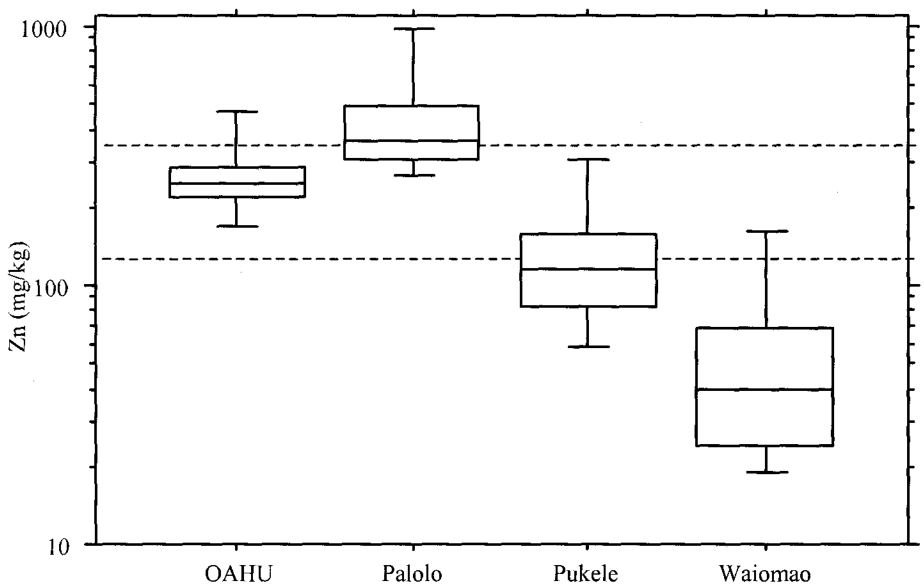


Figure 7.7. Box plots of Zn concentrations in USGS NAWQA Oahu Island streams and Palolo Valley streambed sediment (TEL_{123} and PEL_{315} mg/kg)

The USGS separated the 24 Oahu streams into urban (5), mixed (10), agricultural (3), and forest (6) landuses (USGS 2004b). These landuse divisions were analyzed for statistical differences, although not shown here, and no consistent statistical difference in element concentrations between landuses was apparent. Because of this, the 24 streams were grouped together in **Table 7.9** and the box plots of **Figures 7.4 - 7.7**. The box plots of Cu and Ni concentrations for Oahu streams and Palolo Stream had similar distributions (**Figure 7.4** and **7.5**). The Pb and Zn box plots for Palolo Stream had higher concentrations compared to the Oahu streams (**Figure 7.6** and **7.7**). Concentrations of Cu, Ni, Pb, and Zn in Pukele and Waiomao Stream were lower than the Oahu streams and Palolo Stream. The exception was Pb in Pukele Stream, which was similar to Oahu streams.

7.4.4. *Continental USGS NAWQA Streams and Oahu Island Streams*

Beginning in 1991, the USGS started the NAWQA program throughout the US, which to date has researched over 50 study units (USGS 2004d). Rice (1999) compiled bed sediment trace element data for 20 conterminous US sites that were studied from 1992 to 1996 (**Table 7.10**, excluding OAHU). Analysis of bed sediment at these sites involved a total digestion similar to one of the methods used in this thesis. **Figures 7.8 - 7.12** show median concentrations of Cr, Cu, Ni, Pb, and Zn from streambed sediment of Palolo, Pukele, and Waiomao Streams ($total_{est}$), NAWQA Oahu streams with a total digestion (USGS 2004a, 2004b, and 2004c), and 20 conterminous NAWQA streams with a total digestion (Rice 1999). Some of the figures include two zones of Nuuanu Stream with weak HCl digestion (Cu, Pb, and Zn: Andrews and Sutherland 2004) and four zones of Manoa Streams with a total digestion (Cu, Ni, Pb, and Zn: Sutherland 2000b).

Table 7.10. Abbreviations and locations of 21 USGS NAWQA study sites

Abbr.	USGS NAWQA Study Site (States)	Area (km^2)
ACFB	Apalachicola-Chattahoochee-Flint River (AL, FL, GA)	51,800
ALBE	Albemarle-Pamlico Drainage (NC, VA)	72,520
CCPT	Central Columbia Plateau (ID, WA)	33,929
CNBR	Central Nebraska Basin (NE)	77,700
CONN	Connecticut, Housatonic, and Thames (CT, MA, NH, NY, RI, VT)	40,818
GAFL	Georgia-Florida Coastal Plain (GA, FL)	160,580
HDSN	Hudson River Basin (NY, CT, MA, NJ, VT)	34,447
LSUS	Lower Susquehanna River Basin (PA, MD)	24,217
NVBR	Nevada Basin and Range (NV, CA)	31,186
OAHU	Oahu Island (HI)	1,564
OZRK	Ozark Plateaus (AR, KS, MO, OK)	124,320
POTO	Potomac River Basin (DC, MD, PA, VA, WV)	48,897
REDN	Red River of the North (MN, ND, SD)	233,100
RIOG	Rio Grande Valley (CO, NM, TX)	188,881
SANJ	San Joaquin-Tulare Basins (CA)	80,808
SPLT	South Platte River Basin (CO, NE, WY)	62,937
TRIN	Trinity River Basin (TX)	48,096
USNK	Upper Snake River Basin (ID, MT, NV, UT, WY)	95,312
WHIT	White River Basin (IN)	29,397
WILL	Willamette Basin (OR)	31,080
WMIC	Western Lake Michigan Drainage Basin (MI, WI)	51,800

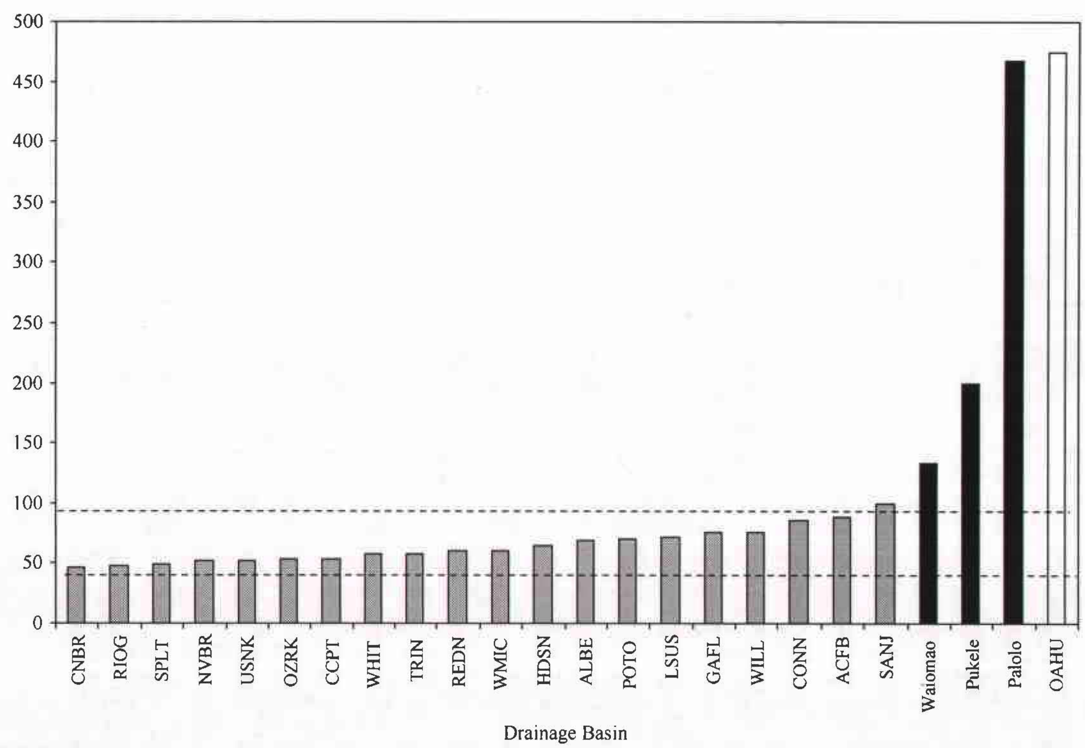


Figure 7.8. Median Cr concentration in streambed sediment of US continental streams and Oahu streams ($TEL_{37.3}$ and PEL_{90} mg/kg)

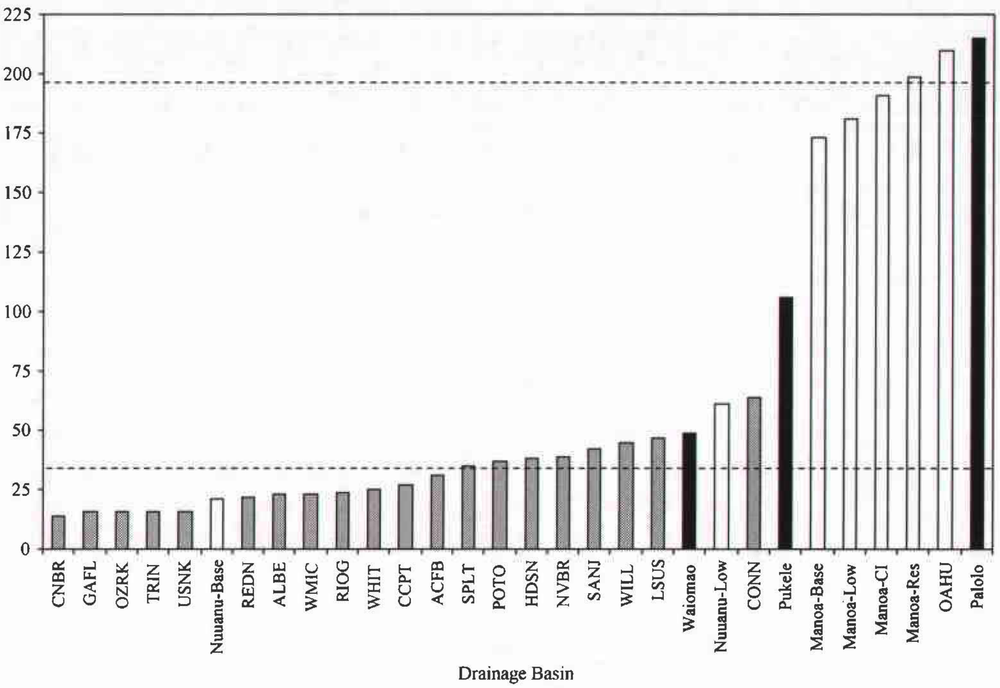


Figure 7.9. Median Cu concentration in streambed sediment of US continental streams and Oahu streams ($TEL_{35.7}$ and PEL_{197} mg/kg)

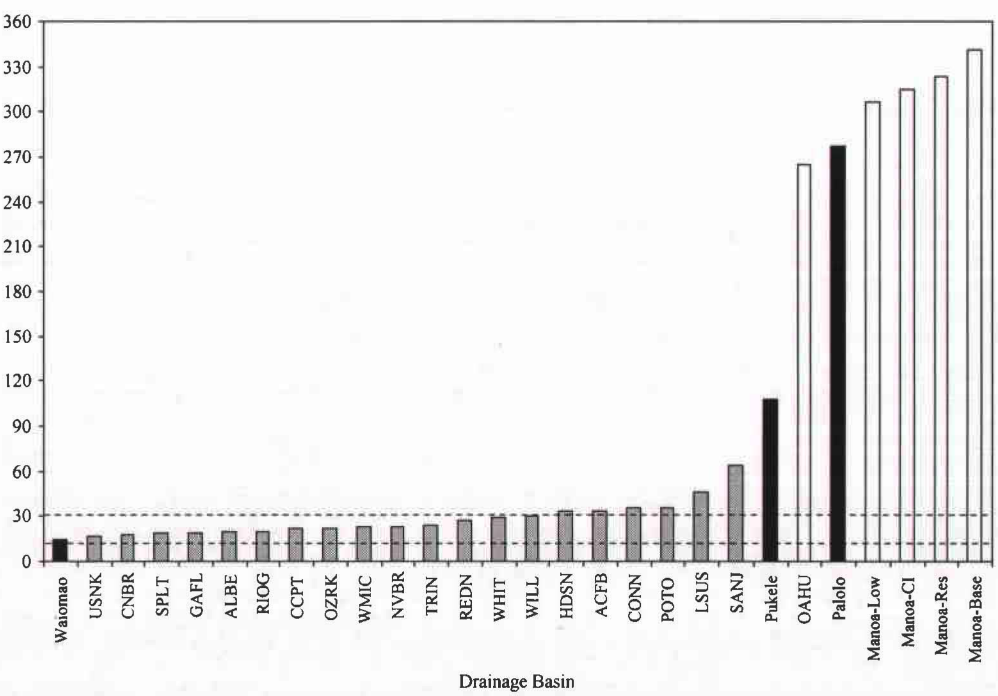


Figure 7.10. Median Ni concentration in streambed sediment of US continental streams and Oahu streams (TEL_{18} and PEL_{36} mg/kg)

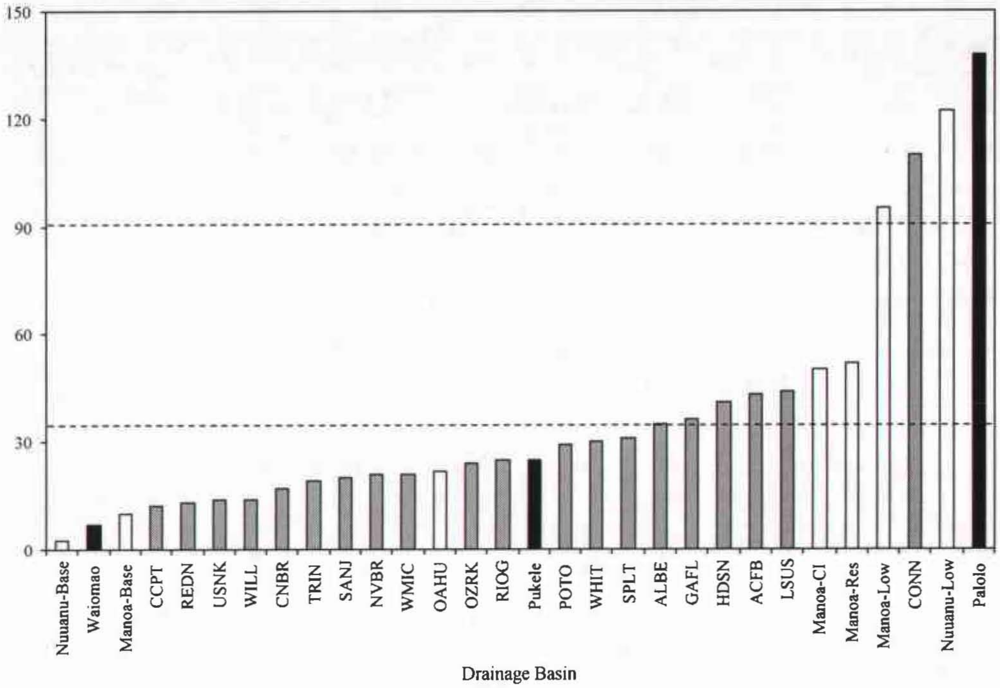


Figure 7.11. Median Pb concentration in streambed sediment of US continental streams and Oahu streams (TEL_{35} and $PEL_{91.3}$ mg/kg)

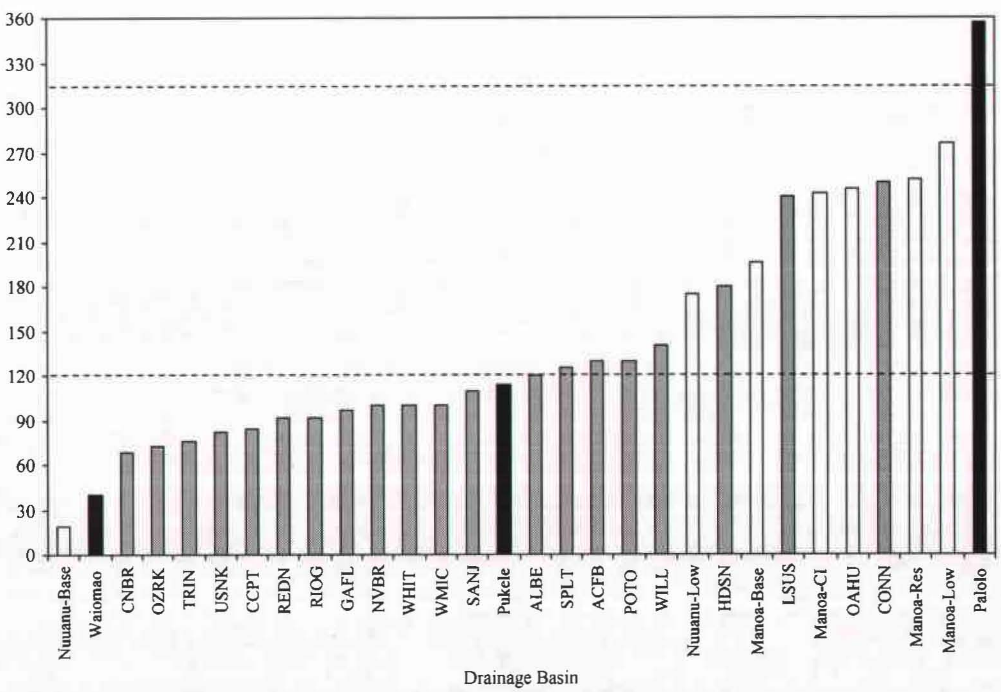


Figure 7.12. Median Zn concentration in streambed sediment of US continental streams and Oahu streams (TEL_{123} and PEL_{315} mg/kg)

While the continental study sites have a considerably large range of basin sizes (24,217 to 233,100 km^2, **Table 7.10**) geologic ages and compositions, the comparisons are useful to show how Palolo Valley (11.4 km^2), Nuuanu Valley (11.7 km^2), Manoa Valley (15 km^2), and the island of Oahu (1,564 km^2) compare to conterminous sites.

Although there were differences among the various streams within Oahu (**Table 7.7 - 7.9** and **Figures 7.4 - 7.7**), the island streams within more urban areas (Palolo Stream, Oahu NAWQA, Nuuanu Stream [lower-urban], and Manoa Stream [lower-urban, commercial-industrial, and residential]) tended to have higher Cr, Cu, Ni, Pb, and Zn median concentrations compared to the 20 NAWQA conterminous streams. The Oahu Island streams within less urban areas (Pukele Stream, Waiomao Stream, Nuuanu Stream Baseline, and Manoa Stream Baseline) tended to have median concentrations below or similar to the 20 NAWQA conterminous streams (**Figures 7.8 - 7.12**). Palolo, Pukele, Waiomao, and Oahu Island NAWQA streams had the highest median concentration of Cr compared to the 20 continental NAWQA sites, which reflected a geogenic control (**Figure 7.8**, Cr concentrations for Nuuanu and Manoa Stream were not available). Palolo Stream had the highest median concentration of Cu, Pb, and Zn compared to all locations (**Figure 7.9**, **7.11**, and **7.12**).

Many streams throughout Oahu (Palolo, Pukele, Manoa-Lower, Nuuanu-Lower, and NAWQA Oahu streams) ranked higher than the 20 USGS NAWQA conterminous streams, supporting previous evidence of significant streambed contamination. Additionally, many Oahu streams in urban areas were well above TEL and PEL guidelines for Cr, Cu, Ni, Pb, and Zn compared to the USGS NAWQA conterminous streams, which may indicate further threats to aquatic organisms in Oahu's streams.

It could be argued that the elevated bed sediment concentrations of Cr, Cu, Ni, Pb, and Zn in Oahu streams compared to SQGs may simply reflect the anomalous basaltic geology of Hawaii. That is, the SQGs were developed for continental aquatic streams dominated by granitic bedrock. As seen in **Table 7.11** the Cr, Cu, Ni, and Zn concentrations in Koolau and Honolulu Volcanic Series host rock exceeded TEL guidelines (Cr, Cu, Ni, and Zn) and/or PEL guidelines (Cr and Ni). Additionally, it is also evident there are differences between the basaltic bedrock of Hawaii compared to the upper continental crust (UCC), which is dominated by granite. This could indicate that the TEL and PEL guidelines are not appropriate in Hawaii's naturally enriched environment of Cr, Cu, Ni, and Zn. This would also indicate similar guidelines presented earlier need to be viewed with extreme caution: TEL and PEC (**Table 1.4**, MacDonald et al. 2000) and ERL and ERM (**Table 1.5**, Long et al. 1995).

Table 7.11. Host geology concentrations of total elements in Koolau and Honolulu Volcanic Series basalt and upper continental crust with TEL and PEL guideline concentrations (mg/kg)

	Koolau Volcanic Basalt [a]	Honolulu Volcanic Series Basalt [a]	Upper Continental Crust Granite [c]	Sediment Quality Guidelines	
				TEL	PEL [d]
Cd	0.22	0.32	0.1	0.596	3.53
Cr	310 [b]	321 [b]	35	37.3	90
Cu	100	100	14-25	35.7	197
Ni	190	240	19-20	18	36
Pb	6	7	17-20	35	91.3
Zn	110	180	52-71	123	315

[a] Cadmium, Cu, Ni, Pb, and Zn in Koolau and Honolulu after Sutherland (2000b).
[b] Chromium in Koolau and Honolulu after Clague and Frey (1982), Wilkinson and Stolz (1983), Roden et al. (1984), Budahn and Schmitt (1985), Frey et al. (1994), and Jackson et al. (1999).
[c] after Wedepohl (1995) and McLennan and Taylor (1999).
[d] after Smith et al. (1996) and MacDonald et al. (2000).

The TEL and PEL guidelines for Cd and Pb would be appropriate for Hawaii since the host geology had relatively low concentrations of these elements compared to the SQGs.

Additionally, geogenic Pb concentrations in basalt are two to three times lower than found in UCC granite. Future research could develop sediment quality guidelines that were specific for volcanic environments, such as Oahu, which has geogenic enrichment of Cr, Cu, Ni and Zn.

Because ERs, median concentrations, and maximum concentrations were elevated for Cu, Ni, Pb, and Zn (**Table 7.6**), a natural geologic enrichment is unlikely to be the only source of these elements to the bed sediment of Oahu streams. It is likely that anthropogenic inputs associated with a high population density and urbanization are adversely impacting Oahu streams.

7.5. Spatial Associations of Trace Elements in Palolo Valley

Urbanization of Honolulu could be a significant influence on the elevated and varying element concentrations in Palolo, Pukele, and Waiomao Streams. Urbanization would also affect Manoa and Nuuanu Streams since they are neighboring watersheds in Honolulu. The NAQWA Oahu streams could also be affected because several of the 24 streams were classified as urban (5) or mixed (10) landuses (USGS 2004b).

As seen in **Table 7.12**, there is a clear difference among landuse characteristics in Palolo Valley's three streams. In street length, storm drain length, and storm drain in/outlets number, Palolo Stream had 65-70%, while Pukele Stream had 20-21%, and Waiomao had 10-15%. This represents a striking difference in the degree of urbanization and corresponds to the statistical ranking of As, Cd, Cr, Cu, Ni, Pb, and Zn in streambed sediments (Palolo > Pukele > Waiomao, $\alpha_{adj} = 0.0167$).

Figure 7.13 provides a visual example of the difference between Palolo Stream, Pukele Stream, and Waiomao Stream for storm drain network density and **Figure 7.14**

shows streets and land parcels. Although vehicle and population numbers were only available for Palolo and Pukele/Waiomao, there was still a similar relationship with >75% in Palolo and <25% in Pukele/Waiomao. **Figure 7.14** provides a qualitative approach for visualizing population density (and vehicle numbers) between sub-watersheds in Palolo Valley. Where there are more land parcels, streets, storm drains, and storm drain in/outlets, there are likely greater numbers of vehicles and population.

Table 7.12. Landuse characteristics of Palolo Valley's streams

Landuse Characteristic	Sub-Valley and Valley	Quantity	%
Street Length [a]	Palolo Stream	22.7 km	65
	Pukele Stream	7.2 km	20
	Waiomao Stream	5.4 km	15
	Total (Palolo Valley)	35.2 km	
Storm Drain Length [a]	Palolo Stream	19.6 km	70
	Pukele Stream	5.7 km	20
	Waiomao Stream	2.8 km	10
	Total (Palolo Valley)	28.1 km	
Storm Drain In/Outlets [a]	Palolo Stream	489	68
	Pukele Stream	151	21
	Waiomao Stream	82	11
	Total (Palolo Valley)	722	
2000 Vehicle Count [b]	Palolo Stream	5,520	76
	Pukele Stream Waiomao Stream	1,786	24
	Total (Palolo Valley)	7,306	
2000 Population [b]	Palolo Stream	10,644	78
	Pukele Stream Waiomao Stream	3,083	22
	Total (Palolo Valley)	13,727	

[a] University of Hawaii at Manoa (UHM) Geography Cartography Lab (2005). See City and County of Honolulu (2005) for online access to similar data files.
[b] US Census Bureau (2004).

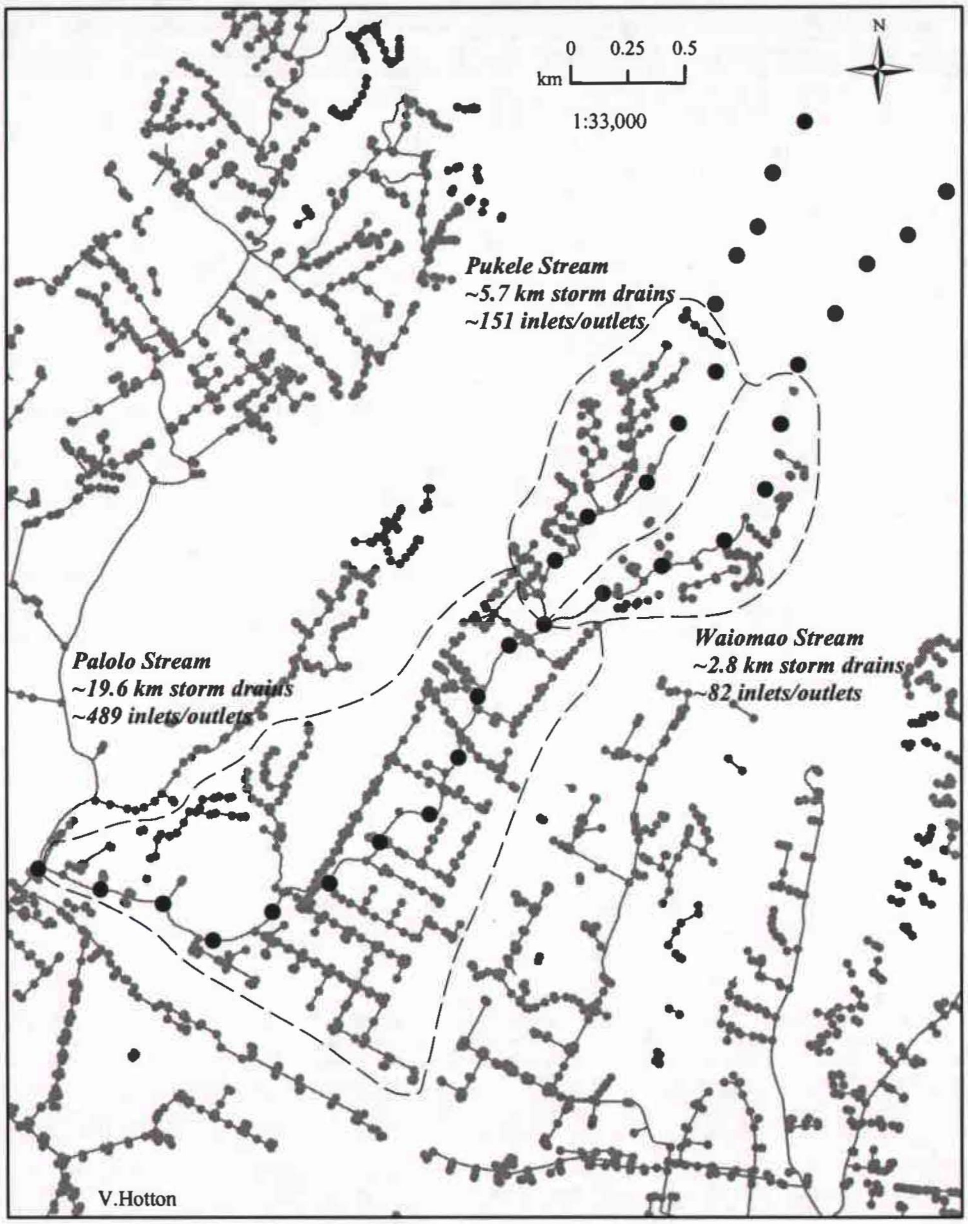


Figure 7.13. Storm drain lines (dark gray lines) and storm drain inlets/outlets (dark gray points) of Palolo Valley streams (dotted outline). Every 6th sampling location (black points, ~300 m apart) is shown

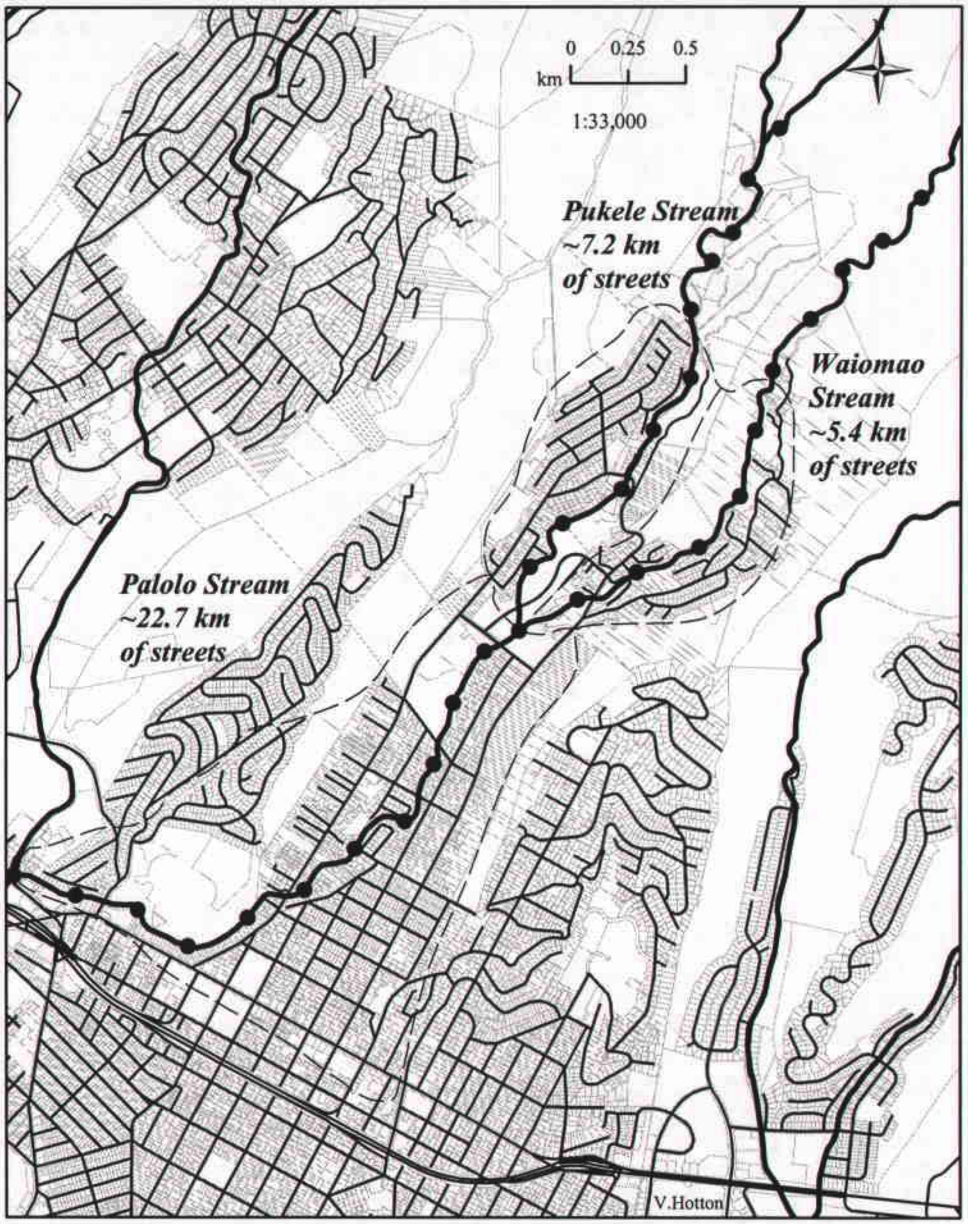


Figure 7.14. Streets (thin black lines) and parcels (light gray polygons) of Palolo Valley streams (dotted outline). Every 6th sampling location (black points, ~300 m apart) is shown along stream (thick black lines)

The possible cascade of elements originating from vehicles and land parcels throughout the valley can be shown in a simple flow of arrows. These arrows start from the potential sources (vehicles, land parcels, population, and streets), which then move through various pathways (vehicles, streets, RDS, storm drain in/outlets, storm drains), and are deposited in sinks (streambed sediment):

Vehicles and/or Land Parcels → Streets → Road Deposited Sediments →
→ Storm Drain Inlets → Storm Drains → Storm Drain Outlets →
→ Streambed Sediment.

The streambed sediment in Palolo Stream would continue to move downstream, reaching Manoa/Palolo Drainage Canal (**Figure 3.2**). The Manoa/Palolo Drainage Canal enters the Ala Wai Canal, which drains into the ocean along the Waikiki area of Honolulu. The residence time of streambed sediment in Palolo Valley would be shorter than the two drainage canals based on differing topography and channel features. Palolo Valley has steep topography and highly channelized sections, such as box channels and drop structures (see photographs in **Appendix B** through **S**), which are able to flush sediments quickly through the channel. This is especially true during the rainy winter season.

Since there appears to be an association between greater urbanization and higher element concentrations, there is a need for further research into the landuse characteristics in Palolo Valley. Such research with the aid of GIS analysis could discern whether different landuses within Palolo Valley influence the different element concentrations found in streambed sediment of Palolo, Pukele, and Waiomao Streams.

8.0. SUMMARY

Based on several methods of measuring element concentrations in Palolo Valley's streambed sediment (BCR, BCR_{Sum}, HCl, total, and $total_{est}$), it was apparent that the three streams of Palolo Valley exhibited different levels of contamination (mg/kg) and enrichment (ERs) of Cu, Ni, Pb, and Zn. Palolo Stream had the greatest element concentrations and ERs, while Waiomao Stream had the lowest, and Pukele Stream was intermediate (Palolo > Pukele > Waiomao).

Palolo Stream exceeded more SQGs (As, Cd, Cr, Cu, Ni, Pb, and Zn) than Pukele Stream, and Pukele Stream exceeded more than Waiomao Stream (HCl and $total_{est}$). Palolo Stream exceeded many TEL and PEL guidelines and the contaminated sediment could be a potential threat to the aquatic health of the stream. Waiomao Stream was generally below all TEL and PEL guidelines, which indicated there was likely no threat to aquatic organisms. For contaminant status, Pukele Stream was intermediate to Palolo Stream and Waiomao Stream (Palolo > Pukele > Waiomao).

Lead concentrations in streambed sediment exceeded more TEL and PEL guidelines than other elements examined (As, Cd, Cu, Ni, and Zn). This indicated that Pb poses the greatest threat to the biotic integrity of Palolo Valley. Copper, Ni, and Zn were intermediate with a notable number of samples exceeding TEL and PEL guidelines. Although nearly all Cr concentrations ($total_{est}$) exceeded the upper PEL guideline, the corresponding low ERs ($total_{est}$) indicated Cr was geologically controlled.

When the streams of Palolo Valley (Palolo, Pukele, and Waiomao), Nuuanu Valley, Manoa Valley, and NAWQA Oahu streams were compared to 20 NAWQA conterminous streams, all Oahu streams tended to have higher element concentrations

(Cr, Cu, Ni, Pb, and Zn). This indicated there could be a geogenic and/or anthropogenic factor(s) causing these differences between Oahu and the conterminous streams. To some extent, the elevated concentrations of Cr, Cu, Ni, and Zn in Palolo Valley Stream bed sediment may reflect a geogenic control from the host basalt. However, an anthropogenic control is expected to be of importance for Pb because of its high concentrations and elevated ERs. Anthropogenic causes may be related to the high degree of urbanization and population density within the small valleys of Honolulu.

The landuse characteristics that were tabulated for the Palolo, Pukele, and Waiomao Streams also had the same ordering as element concentrations for street length, storm drain length, and storm drain in/outlets (Palolo > Pukele > Waiomao). Vehicle numbers and population were similar, although they were not as discriminating since Pukele Stream and Waiomao Stream were grouped together (Palolo > Pukele/Waiomao).

Based on the results of (1) trace element concentrations, (2) trace element ERs, (3) SQG comparisons, (4) national stream comparisons, and (5) landuse characteristics of Palolo Valley, there is a significant concern for Pb contamination of streambed sediment in Palolo Stream and some concern for Cu, Ni, and Zn. There is also concern for the impact the Pb contaminated sediment of Palolo Stream could be having on the aquatic health of the stream and downstream ecosystems. Pukele Stream may have some isolated contamination, while Waiomao Stream is primarily uncontaminated and streambed sediment is not likely to negatively impact aquatic health. The different landuse characteristics may have a direct influence on the degree of element contamination observed between the three streams (Palolo > Pukele > Waiomao).

The following summarizes the key findings of this work:

8.1. Digestion Methods and Concentrations

- Element concentrations from the HCl weak leach were significantly and statistically different with Palolo > Pukele > Waiomao (As, Cd, Cr, Cu, Ni, Pb, and Zn).

- Total and $total_{est}$ concentrations were generally high in all three streams (Cr, Cu, Ni, Pb, and Zn).

- HCl/total recovery ratios were high for Pb and Zn (97% and 63% respectively) indicating a high potential bioavailability. Copper and Ni had low recovery ratios, indicating less bioavailability (27% and 7% respectively).

8.2. SQGs

- The comparisons with TEL and PEL guidelines of several elements (As, Cd, Cr, Cu, Ni, Pb, and Zn) indicated that the three streams were at different levels of streambed sediment contamination (Palolo > Pukele > Waiomao).

- Palolo Stream samples exceeded many TEL and PEL guidelines for several elements (HCl and $total_{est}$) indicating a high level of contamination. Waiomao Stream samples exceeded very few guidelines indicating no contamination. Pukele Stream was intermediate to Palolo and Waiomao Streams.

- Palolo Stream samples analyzed using the BCR sequential extraction indicate that the reducible fraction (step 2) was the phase that had higher element concentrations and some statistically significant results compared to TEL and PEL guidelines (Pb, Zn, Cu, and Ni).

- Koolau and HVS basalt of Oahu are naturally elevated in several elements (Cr, Cu, Ni, and Zn) compared to the UCC (granite), which indicates that the TEL and PEL guidelines formulated for the continental US are not as applicable in Palolo Valley and throughout Hawaii.

8.3. ERs

- The ER values (HCl and $total_{est}$) indicated that Palolo Stream had the greatest enrichment of elements examined (HCl and $total_{est}$: Cd, Cr, Cu, Ni, Pb, and Zn) compared to Pukele and Waiomao Stream (Palolo > Pukele > Waiomao).

- The ER values indicated that Pb was the most enriched element (Palolo > Pukele > Waiomao). The ERs of Cu, Ni, and Zn indicated moderate to significant enrichment (HCl and $total_{est}$).

• Chromium had a very low ER_{Cr} ($total_{est}$), which indicated that the high $total_{est}$ concentrations of Cr were naturally occurring.

8.4. Palolo Valley Streams Compared to US Streams

• Oahu streams within more urban areas (Palolo Stream, Oahu NAWQA, Nuuanu Stream lower-urban, and Manoa Stream [lower-urban, commercial-industrial, and residential]) tended to have higher Cr, Cu, Ni, Pb, and Zn median concentrations compared to the 20 NAWQA conterminous streams.

• The Oahu streams within less urban areas (Pukele Stream, Waiomao Stream, Nuuanu Stream Baseline, and Manoa Stream Baseline) tended to have median concentrations below or similar to the 20 NAWQA conterminous streams.

8.5. Spatial Associations of Trace Elements in Palolo Valley

• There was a clear difference among landuse characteristics in Palolo Valley's three streams. In street length, storm drain length, and storm drain in/outlet number Palolo Stream had 65-70%, while Pukele Stream had 20-21%, and Waiomao had 10-15%. This represented a striking difference in the degree of urbanization and corresponded to the ranking of contaminants (As, Cd, Cr, Cu, Ni, Pb, and Zn) in streambed sediments (Palolo > Pukele > Waiomao).

• Vehicle and population numbers available for Palolo and Pukele/Waiomao showed a similar relationship with >75% in Palolo and <25% in Pukele/Waiomao (Palolo > Pukele/Waiomao).

• Streambed sediment in Palolo Valley is transient because of steep topography, concentrated channelization in the lower reaches, and flashy precipitation events during the winter. There is a longer residence time in the shallow slope channels of Manoa/Palolo Drainage Canal and Ala Wai Canal. The two canals are predicted to have long-term and chronic sediment contamination compared to short-term and acute contamination in Palolo Valley.

8.6. Future Research

Unfortunately, the problem of sediment contamination in Palolo Valley and other urban streams of Honolulu (Nuuanu Stream, Manoa Stream, and several Oahu NAWQA Streams) will continue because trace elements from land parcels, vehicles, and RDS will continue to enter the streams directly through the storm drain system and/or through atmospheric deposition directly into the stream channel. Because these problems are likely to continue or increase in this urban environment, it will be beneficial to conduct future research, which could lead to a better understanding of the problem and provide management options to reduce trace elements entering the stream. Based on the results of this thesis, the following suggestions for future research were made throughout the discussion chapter and are summarized here with a few additional suggestions:

- Resample Palolo, Pukele, and lower portions of Waiomao Stream to document whether trace element hotspots are a chronic or transient occurrence. If hotspots were chronic, further landuse and GIS analysis could identify potential anthropogenic and/or natural sources throughout the watershed.

- Expand sampling to include the downstream systems, Manoa/Palolo Drainage Canal and Ala Wai Canal, which were predicted to have chronic contamination and biological impairments.

- Measure Pb isotope signatures in Palolo Valley to source (anthropogenic and/or natural) the elevated Pb concentrations found in streambed sediment.

- Conduct toxicological studies of biota in Palolo Valley and downstream systems to see if ecosystems integrity is being impaired.

- Develop SQGs for basalt because the current guidelines are inadequate as they are based on granite

- Investigate the management options for reducing the amount of trace elements reaching the streams from land parcels, vehicles, streets, RDS, and storm drains. The options could include filtering RDS before they can enter storm drains or improving the street sweeping schemes.

APPENDICES

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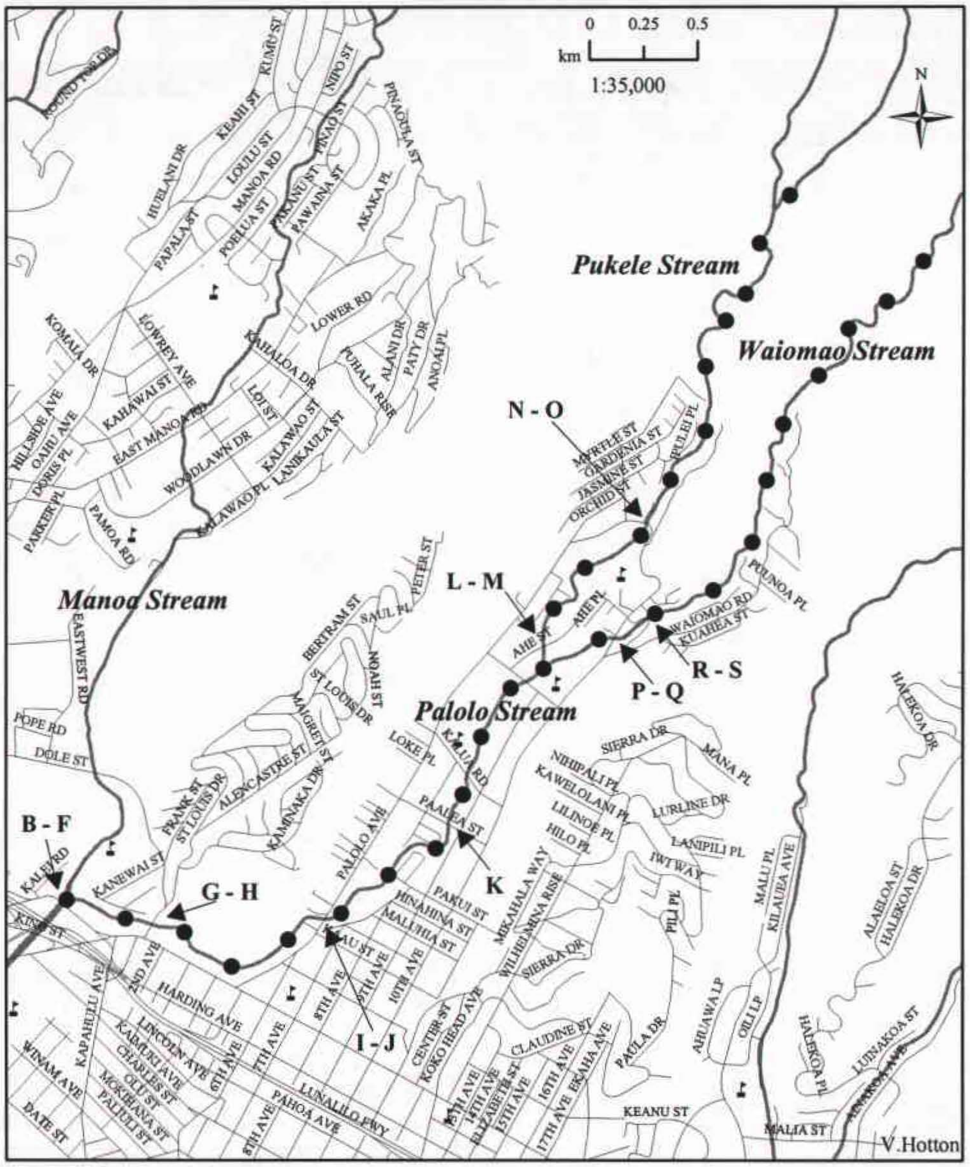
V - X	Weak HCl Digestion Data	142
Y - Z	Total Digestion and Total Estimation Data	144

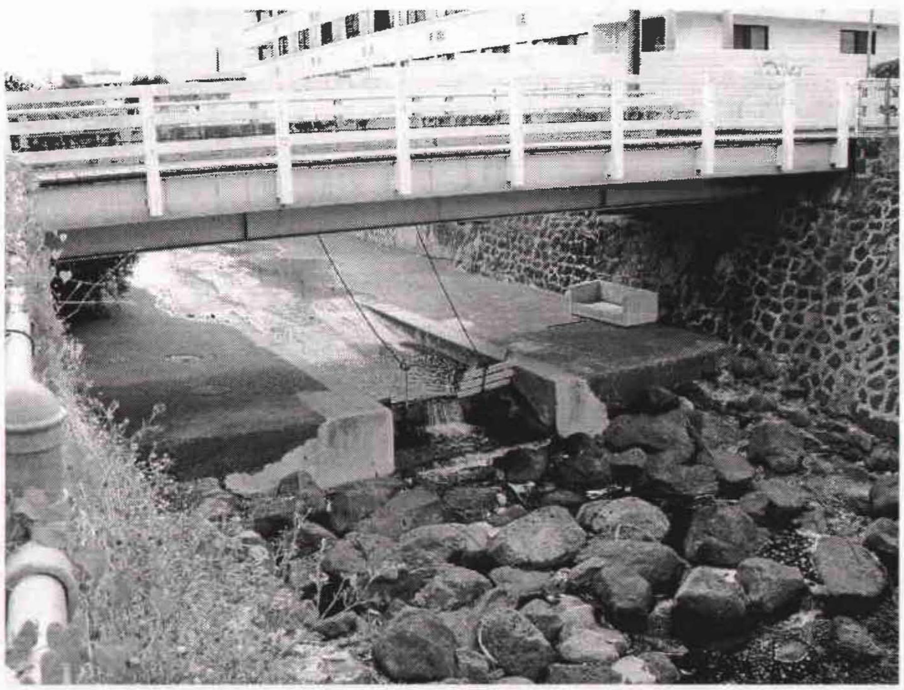


Appendix A. Locations (arrow) of photographs taken on March 8, 2005 (Appendix B through S). Streets (black lines), public schools (flagged building), perennial streams (gray lines), and every 6th sampling location (black points, ~300 m) is shown

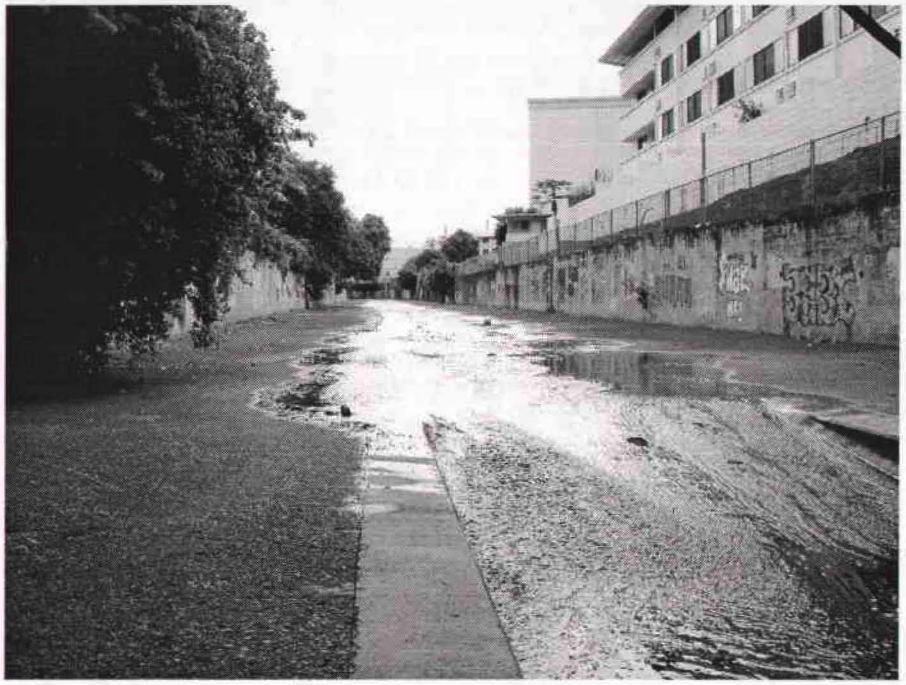
Appendix B. Manoa/Palolo Drainage Canal showing several bridges crossing the canal. View from Palolo Stream bank looking downstream

Appendix C. Palolo Stream and Manoa Stream junction. View from Palolo Stream bank looking downstream

Appendix D. Palolo Stream near outlet with trash debris in center. View from Palolo Stream bank looking downstream



Appendix E. Palolo Stream channel drop structure below the Koali Rd. Bridge. View looking upstream near stream outlet



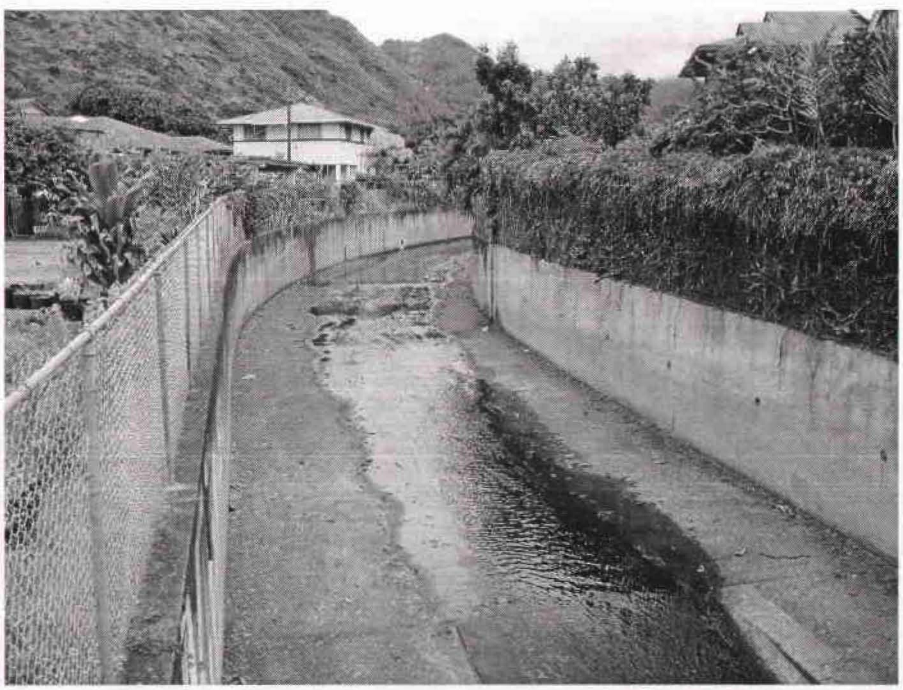
Appendix F. Palolo Stream box channelization at drop structure.
View below Koali Rd. Bridge looking upstream

Appendix G. Palolo Stream semi-natural channel.
View from St. Louis Dr. Bridge looking downstream

Appendix H. Palolo Stream semi-natural channel. View from St. Louis Dr. Bridge looking upstream

Appendix I. Palolo Stream channelization showing some sediment lag deposits along channel sides. View looking downstream from Palolo Ave. Bridge near Kehau Pl.

Appendix J. Palolo Stream channelization showing storm drain outlets and drop structure. View looking upstream from Palolo Ave. Bridge near Kehau Pl.



Appendix K. Palolo Stream box channelization showing storm drains along right side. View looking upstream from Paalea St. Bridge

Appendix L. Palolo, Pukele, and Waiomao Stream junction in distance. View from Pukele Stream on Ahe St. Bridge looking downstream

Appendix M. Pukele Stream channelization with trash debris fanning out from small drains along channel floor. View from Ahe St. Bridge looking downstream

Appendix N. Pukele Stream semi-natural channel.
View looking upstream from 10th Ave. Bridge near Palolo Pl.

Appendix O. Road deposited sediment (RDS) near 10th Ave. Bridge near Palolo Pl. Location south side of 10th Ave. looking downstream

Appendix P. Waiomao Stream semi-natural channel. View from 10th Ave. Bridge near Waiomao Rd. looking downstream

Appendix Q. Waiomao Stream semi-natural channel. View from 10th Ave. Bridge near Waiomao Rd. looking upstream

Appendix R. Waiomao Stream semi-natural channel. View from under 10th Ave. Pl. Bridge looking upstream

Appendix S. Waiomao Stream semi-natural channel. View from 10th Ave. Pl. Bridge looking upstream

Appendix T. Descriptive statistics of elements (mg/kg) in Palolo Stream sediment (<63 μm) with a sequential extraction

	BCR Step	Mean ± SD	CV %	Skew-ness	Median ± MAD	RCMV % [b]	Min	Max
Al [a]	Acid-extract	136 ± 69	50	0.89	126 ± 39	31	14	309
	Reducible	3285 ± 642	20	0.36	3281 ± 561	17	2429	4636
	Oxidizable	2033 ± 511	25	0.33	1935 ± 331	17	1083	3195
	Residual	55099 ± 6712	12	0.64	54275 ± 2890	5.3	42100	73280
Cu	Acid-extract	5.0 ± 3.7	74	1.16	3.8 ± 1.6	42	1	14
	Reducible	33 ± 21	63	1.36	28 ± 11	40	4.2	94
	Oxidizable	31 ± 14	43	0.86	28 ± 9.1	32	11	67
	Residual	123 ± 16	13	-0.18	122 ± 8.0	6.6	82	152
Fe	Acid-extract	6.4 ± 3.8	59	0.59	5.9 ± 2.5	42	0.16	15
	Reducible	4773 ± 1253	26	1.39	4430 ± 527	12	3166	8176
	Oxidizable	1273 ± 399	31	0.32	1250 ± 339	27	601	2128
	Residual	109638 ± 19492	18	1.40	102860 ± 6765	6.6	86624	157900
Mn	Acid-extract	415 ± 105	25	-0.27	432 ± 63	15	226	599
	Reducible	553 ± 187	34	0.04	552 ± 132	24	282	845
	Oxidizable	61 ± 11	18	0.16	61 ± 6.7	11	39	86
	Residual	482 ± 319	66	1.10	397 ± 80	20	23.6	1311
Ni	Acid-extract	5.6 ± 2.6	47	0.55	4.9 ± 1.1	23	1.6	11
	Reducible	16 ± 5.6	36	-0.49	15 ± 3.8	25	1.2	27
	Oxidizable	14 ± 3.1	23	0.25	14 ± 2.7	19	9.5	19
	Residual	168 ± 34	20	0.68	165 ± 18	11	110	242
Pb	Acid-extract	3.4 ± 2.5	74	1.36	2.0 ± 0.0	0.0	2	9.4
	Reducible	178 ± 132	74	1.07	138 ± 38	28	2	472
	Oxidizable	26 ± 14	55	1.70	20 ± 5.1	26	14	70
	Residual	23 ± 17	74	1.11	19 ± 8.3	44	2.5	68
Zn	Acid-extract	105 ± 47	45	0.98	95 ± 27	28	43	225
	Reducible	219 ± 198	90	2.99	149 ± 38	26	71	975
	Oxidizable	42 ± 19	44	2.03	35 ± 7.8	23	25	104
	Residual	160 ± 42	26	1.61	143 ± 18	13	115	288

[a] Sample size: 20.

[b] RCMV% = Relative coefficient of median variation = (MAD ÷ Median) *100.

Appendix U. Palolo Stream's tied p-values of Wilcoxon Signed Rank test for sequential step comparison

Al	Acid-ext.	Reduc.	Oxid.	**Ni**	Acid-ext.	Reduc.	Oxid.
Reduc.	**<0.0001** [a]			Reduc.	**0.0001**		
Oxid.	**<0.0001**	**0.0001**		Oxid.	**<0.0001**	0.1559	
Resid.	**<0.0001**	**<0.0001**	**<0.0001**	Resid.	**<0.0001**	**<0.0001**	**<0.0001**
Cu	Acid-ext.	Reduc.	Oxid.	**Pb**	Acid-ext.	Reduc.	Oxid.
Reduc.	**<0.0001** [a]			Reduc.	**0.0001**		
Oxid.	**<0.0001**	0.9405		Oxid.	**<0.0001**	**0.0001**	
Resid.	**<0.0001**	**<0.0001**	**<0.0001**	Resid.	**0.0001**	**0.0001**	0.1559
Fe	Acid-ext.	Reduc.	Oxid.	**Zn**	Acid-ext.	Reduc.	Oxid.
Reduc.	**<0.0001**			Reduc.	**0.0001**		
Oxid.	**<0.0001**	0.9353		Oxid.	**0.0001**	**<0.0001**	
Resid.	**<0.0001**	**<0.0001**	**<0.0001**	Resid.	**0.0007**	0.0761	**<0.0001**
Mn	Acid-ext.	Reduc.	Oxid.				
Red.	0.0187						
Oxid.	**<0.0001**	**<0.0001**					
Resid.	0.8519	0.1453	**<0.0001**				

[a] Boldface tied p-values are statistically significant at an $\alpha_{adj} = 0.0083$. This indicates that the paired steps are significantly different.

Appendix V. Descriptive statistics of selected elements (mg/kg) in streambed sediment (<63 µm) with weak HCl digestion

	Location [a]	Mean ± SD	CV %	Skew-ness	Median ± MAD	RCMV % [b]	Min	Max
Al	Palolo	3879 ± 1019	26	1.60	3700 ± 700	19	2500	7800
	Pukele	2391 ± 676	28	1.20	2200 ± 300	14	1500	4800
	Waiomao	1619 ± 458	28	1.92	1400 ± 100	7	1100	3400
As	Palolo	3.4 ± 4.3	125	2.97	2.0 ± 1.5	75	0.5	26
	Pukele	0.9 ± 1.1	123	4.38	0.5 ± 0.0	0	0.5	7
	Waiomao	0.6 ± 0.5	81	7.27	0.5 ± 0.0	0	0.5	4
Cd	Palolo	1.9 ± 7.2	375	6.33	0.5 ± 0.2	40	0.2	52
	Pukele	0.2 ± 0.3	131	5.50	0.1 ± 0.0	0	0.1	2
	Waiomao	0.1 ± 0.1	64	4.19	0.1 ± 0.0	0	0.1	0.6
Cr	Palolo	7.9 ± 4.6	58	5.14	7.0 ± 1.0	14	3	38
	Pukele	2.8 ± 1.0	37	1.33	3.0 ± 1.0	33	2	6
	Waiomao	2.4 ± 0.8	35	1.72	2.0 ± 0.0	0	1	6
Cu	Palolo	132 ± 443	335	7.05	57 ± 17	30	25	3373
	Pukele	33 ± 22	65	3.70	28 ± 6.0	21	15	149
	Waiomao	20 ± 15	74	1.27	13 ± 4.0	31	6	57
Ni	Palolo	19 ± 8.3	43	2.64	18 ± 3.0	17	10	59
	Pukele	7.8 ± 3.6	46	1.78	7.0 ± 2.0	29	3	22
	Waiomao	2.4 ± 2.9	120	2.75	1.0 ± 0.0	0	0.5	15
Pb	Palolo	245 ± 596	243	6.98	134 ± 30	22	21	4588
	Pukele	34 ± 47	138	4.85	24 ± 9.0	38	7	323
	Waiomao	19 ± 29	155	1.99	7.0 ± 6.0	86	1	120
Zn	Palolo	402 ± 587	146	4.04	223 ± 40	18	126	3737
	Pukele	143 ± 408	285	6.81	71 ± 26	37	23	3019
	Waiomao	47 ± 70	150	4.75	25 ± 11	44	10	498

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).

[b] RCMV% = Relative coefficient of median variation = (MAD ÷ Median) *100.

Appendix W. Descriptive statistics of enrichment ratios for several elements of weak HCl digestion in Palolo Valley streams

ER_n	Location [a]	Mean ± SD	CV %	Skew-ness	Median ± MAD	RCMV % [b]	Min	Max
ER_{Cd}	Palolo	6.2 ± 22	358	6.76	2.0 ± 0.5	27	0.4	165
	Pukele	1.3 ± 1.9	145	5.63	0.8 ± 0.3	39	0.4	14
	Waiomao	1.1 ± 0.3	33	3.47	1.0 ± 0.1	8	0.7	3
ER_{Cr}	Palolo	1.4 ± 0.5	33	1.91	1.4 ± 0.2	15	0.5	3.7
	Pukele	0.9 ± 0.3	36	1.49	0.8 ± 0.1	18	0.3	2.0
	Waiomao	1.0 ± 0.2	20	0.02	1.0 ± 0.1	8.0	0.5	1.6
ER_{Cu}	Palolo	4.2 ± 13	307	6.92	2.0 ± 0.5	26	0.7	98
	Pukele	1.9 ± 1.2	65	2.74	1.6 ± 0.5	30	0.4	7.9
	Waiomao	1.5 ± 0.9	60	1.60	1.2 ± 0.2	28	0.6	4.6
ER_{Ni}	Palolo	7.1 ± 2.7	37	1.68	6.5 ± 1.0	15	2.7	19
	Pukele	4.8 ± 2.1	43	0.72	4.9 ± 1.6	32	1.9	11
	Waiomao	1.8 ± 1.4	78	1.86	1.1 ± 0.3	28	0.5	7.5
ER_{Pb}	Palolo	94 ± 245	261	7.06	54 ± 15	29	11	1889
	Pukele	20 ± 26	129	4.65	15 ± 5.9	40	2.0	181
	Waiomao	14 ± 18	130	1.45	6.0 ± 5.0	83	0.7	58
ER_{Zn}	Palolo	9.7 ± 18	185	5.72	5.5 ± 1.4	26	2.0	131
	Pukele	5.8 ± 18	310	6.88	2.7 ± 1.1	40	1.0	132
	Waiomao	2.2 ± 2.3	103	3.84	1.4 ± 0.6	41	0.6	16

[a] Sample Size: Palolo (57), Pukele (53), and Waiomao (59).
[b] RCMV% = Relative coefficient of median variation = (MAD/Median) * 100.

Appendix X. Summary of enrichment ratio partitioning relative to five ER categories

ER_n	Stream [a]	ER ≤ 2	ER > 2-5	ER > 5-20	ER > 20-40	ER > 40
ER_{Cd}	Palolo	67 (38) [b]	23 (13)	5 (3)	3 (2)	2 (1)
	Pukele	91 (48)	7 (4)	2 (1)		
	Waiomao	98 (58)	2 (1)			
ER_{Cr}	Palolo	98(56)	2 (1)			
	Pukele	100 (53)				
	Waiomao	100 (53)				
ER_{Cu}	Palolo	70 (40)	24 (14)	2 (1)	2 (1)	2 (1)
	Pukele	85 (45)	11 (6)	4 (2)		
	Waiomao	85 (50)	15 (9)			
ER_{Ni}	Palolo		19 (11)	81 (46)		
	Pukele	15 (8)	45 (24)	40 (21)		
	Waiomao	80 (47)	18 (11)	2 (1)		
ER_{Pb}	Palolo			7 (4)	19 (11)	74 (42)
	Pukele	2 (1)	6 (3)	68 (36)	15 (8)	9 (5)
	Waiomao	36 (21)	10 (6)	32(19)	8 (5)	14 (8)
ER_{Zn}	Palolo	4 (2)	45 (26)	43 (25)	4 (2)	4 (2)
	Pukele	42 (22)	45 (24)	11 (6)		2 (1)
	Waiomao	73 (43)	24 (14)	3 (2)		

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).
[b] %(n): sample percent (sample number).

Appendix Y. Descriptive statistics of elements (mg/kg) in Palolo Stream sediment of multiple grain sizes with a 4-acid total digestion (10 samples per grain size)

	Grain Size (µm) [a]	Mean ± SD	CV %	Skew -ness	Median ± MAD	RCMV % [b]	Min	Max
As	< 63	7.7 ± 7.6	99	1.39	4.5 ± 2.5	56	2	25
	63-125	7.3 ± 6.4	87	1.65	5.5 ± 2.0	36	2	23
	125-250	6.5 ± 4.9	76	0.87	4.5 ± 2.5	56	2	16
	250-500	4.8 ± 2.9	60	0.72	4.5 ± 2.0	44	2	10
	500-1000	3.4 ± 2.7	79	1.75	2.0 ± 0.0	0	2	10
	1000-2000	3.4 ± 2.6	77	1.85	2.0 ± 0.0	0	2	10
Cd	< 63	1.0 ± 0.7	68	1.32	0.9 ± 0.4	41	0.3	2.6
	63-125	1.1 ± 0.7	61	1.57	0.9 ± 0.3	29	0.4	2.7
	125-250	1.0 ± 0.6	61	1.93	0.8 ± 0.2	19	0.5	2.6
	250-500	0.9 ± 0.4	39	1.17	0.8 ± 0.2	19	0.5	1.7
	500-1000	0.9 ± 0.4	48	0.74	0.8 ± 0.2	20	0.3	1.6
	1000-2000	0.8 ± 0.3	30	0.14	0.8 ± 0.1	13	0.4	1.2
Cr	< 63	511 ± 201	39	2.55	461 ± 11	2	376	1076
	63-125	459 ± 174	38	2.46	414 ± 34	8	352	944
	125-250	397 ± 53	13	0.45	387 ± 41	11	325	498
	250-500	370 ± 55	15	-0.04	366 ± 42	11	279	448
	500-1000	342 ± 51	15	0.48	334 ± 34	10	276	427
	1000-2000	311 ± 44	14	-0.18	309 ± 31	10	233	375
Cu	< 63	232 ± 59	25	-0.14	220 ± 28	12	121	322
	63-125	216 ± 54	25	-0.02	215 ± 25	11	117	297
	125-250	210 ± 55	26	-0.02	207 ± 34	16	112	298
	250-500	197 ± 56	28	0.48	194 ± 30	15	106	311
	500-1000	249 ± 207	83	2.21	175 ± 28	16	101	808
	1000-2000	159 ± 46	29	0.77	158 ± 19	12	83	262
Ni	< 63	225 ± 23	10	0.84	225 ± 11	5	191	275
	63-125	242 ± 51	21	2.03	234 ± 18	7	199	376
	125-250	252 ± 40	16	1.15	240 ± 18	8	210	340
	250-500	242 ± 32	13	-0.10	239 ± 33	14	194	282
	500-1000	220 ± 36	17	0.31	211 ± 26	12	167	282
	1000-2000	196 ± 30	15	0.03	192 ± 23	12	149	239
Pb	< 63	320 ± 140	44	0.48	273 ± 111	40	145	564
	63-125	290 ± 119	41	0.77	239 ± 67	28	168	500
	125-250	257 ± 123	48	0.52	221 ± 80	36	134	437
	250-500	250 ± 142	57	0.86	192 ± 65	34	114	501
	500-1000	454 ± 861	190	2.52	146 ± 49	33	51	2863
	1000-2000	887 ± 2166	244	2.63	142 ± 67	47	17	7026
Zn	< 63	487 ± 164	34	1.05	422 ± 70	17	316	830
	63-125	471 ± 129	28	0.55	441 ± 93	21	323	694
	125-250	452 ± 116	26	0.38	424 ± 8	20	309	648
	250-500	427 ± 105	25	0.07	432 ± 113	26	291	577
	500-1000	431 ± 104	24	-0.03	413 ± 71	17	262	573
	1000-2000	410 ± 118	29	-0.06	420 ± 94	22	223	598

[a] 10 samples per grain size.
[b] RCMV% = Relative coefficient of median variation = (MAD ÷ Median) * 100.

Appendix Z. Descriptive statistics of elements (mg/kg) in Palolo Valley streambed sediment (<63 μm) total$_{est}$ calculation

	Location [a]	Mean ± SD	CV %	Skew-ness	Med ± MAD	RCMV % [b]	Min	Max
Al	Palolo	86199 ± 22638	26	1.60	82222 ± 15555	19	55556	173333
	Pukele	53124 ± 15029	28	1.20	48889 ± 6667	14	33333	106667
	Waiomao	35970 ± 10179	28	1.92	31111 ± 2222	7	24444	75556
As	Palolo	7.6 ± 9.6	125	2.97	4.4 ± 3.3	75	1.1	58
	Pukele	1.9 ± 2.4	124	4.40	1.1 ± 0	0	1.1	16
	Waiomao	1.3 ± 1.0	82	7.28	1.1 ± 0	0	1.1	9
Cd	Palolo	2.5 ± 9.2	375	6.33	0.6 ± 0.3	40	0.26	67
	Pukele	0.3 ± 0.4	131	5.50	0.13 ± 0	0	0.13	2.6
	Waiomao	0.2 ± 0.1	64	4.19	0.13 ± 0	0	0.13	0.8
Cr	Palolo	526 ± 306	58	5.14	467 ± 67	14	200	2533
	Pukele	190 ± 70	37	1.32	200 ± 67	34	133	400
	Waiomao	159 ± 56	35	1.72	133 ± 0	0	67	400
Cu	Palolo	499 ± 1672	335	7.05	215 ± 64	30	94	12728
	Pukele	126 ± 82	65	3.69	106 ± 23	22	57	562
	Waiomao	76 ± 56	74	1.27	49 ± 15	31	23	215
Ni	Palolo	296 ± 128	43	2.65	277 ± 46	17	154	908
	Pukele	120 ± 55	46	1.79	108 ± 30	28	46	338
	Waiomao	37 ± 45	121	2.74	15 ± 0	0	8	231
Pb	Palolo	253 ± 614	243	6.98	138 ± 31	22	22	4730
	Pukele	35 ± 48	138	4.84	25 ± 10	40	7	333
	Waiomao	19 ± 30	156	2.00	7 ± 6	86	1	124
Zn	Palolo	643 ± 939	146	4.04	357 ± 64	18	202	5979
	Pukele	229 ± 654	285	6.81	114 ± 41	36	37	4830
	Waiomao	75 ± 113	150	4.75	40 ± 18	45	16	797

[a] Sample size: Palolo (57), Pukele (53), and Waiomao (59).
[b] RCMV% = Relative coefficient of median variation = (MAD ÷ Median) * 100.

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