HEAVY METAL POLLUTION IN THE NU'UANU WATERSHED: AQUATIC AND ROADSIDE SEDIMENTS

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Abstract

Previous research on Honolulu streams indicates that contamination by trace metals from automobile usage is a significant problem, especially Cu (copper), Pb (lead), and Zn (zinc). Therefore, this study was designed to determine the influence of road sediments and storm sewers on bioavailable trace metal concentrations in bed sediments of Nu`uanu Stream, O`ahu. Enrichment ratios (ERs) indicated that the Nu`uanu watershed is significantly polluted in the lower, urbanized reaches, with maximum ER values of 444 (road sediments) and 74 (stream sediments) for Pb. Median ER values for Cu, Pb, and Zn in stream sediments were calculated as 2.0, 28.3, and 4.6, respectively. Considering the lack of industrial centers in the Hawaiian Islands, the Nu`uanu watershed has extremely high levels of Pb, with a maximum value of 332 mg/kg and 3140 mg/kg in stream and road samples.
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CHAPTER 1. INTRODUCTION

The primary focus of this research is to examine the geographic pattern of Cu, Pb, and Zn distribution in an urban stream, particularly in relation to storm sewers. In general, researchers have discovered that anthropogenic Cu, Pb, and Zn in the environment are ubiquitous, inter-linked, and found in materials ranging from rural and urban soils to stream sediments, mosses to trees, and benthic feeders to humans. For the Honolulu area, devoid of a major industrial center, the majority of Pb was most likely anthropogenically produced and released in automobile emissions. Contemporary sources of Cu, Pb, and Zn also include vehicle and tire wear, concrete, paint and battery manufacturing, insecticides, and phosphate fertilizers, to name a few (Sutherland, 2000a).

On O‘ahu, the main sink of environmental Pb appears to be sediments that have adsorbed Pb from automobile emissions from the 1920s to the 1990s (Sutherland, 2000a). This metal is now being re-incorporated into active geomorphic systems as urban development exposes older sediments to erosion processes (Sutherland, 2000a; DeCarlo and Anthony, 2002). In urban areas, environmental Pb is often transported into the roads and then into the storm sewer systems during rainfall events. In addition, Cu and Zn collect in road-deposited sediments (RDS) and are also flushed into the storm sewer system by urban runoff. Unfortunately, these untreated storm sewers debouch directly into O‘ahu streams (Figure 1). Once in the streams, these trace metals can become available to benthic feeders for ingestion and inhalation and then there is the potential for bioaccumulation.

1.1 Trace metals in soils

Hawai‘i does not have any major sources of mining or industrial Pb contamination, and therefore, soils in close proximity to major roads are a particularly important source of Pb. During the leaded gasoline era, the 1920s to the 1990s in the US, Pb from automobile
1920 - 1990: Leaded gas emissions release Pb into air

Soil Sink
Long-term storage

particle erosion and remobilization

Coarse particles to landfills

Street sweeping

RDS
short-term sink

flush of sediment and water via storm sewer

Fluvial System: deposition and storage in bed sediments and bed and suspended sediment transfer downstream

Output to near-shore waters

Figure 1. Anthropogenic Pb in the environment: storage and transport.
emissions accumulated in local soil profiles, and as these local soils are exposed to erosional forces, they re-introduce stored Pb to the modern environment (Sutherland, 2000a).

In general, there appears to be a horizontal distance decay function, describing the distribution of Pb in soil; the majority of Pb from automobile emissions deposits out within the first 2 m of the roadside. Sutherland and Tolosa (2001) reported that both Pb and Zn concentrations in roadside soils had the highest ER values within the first 10 m from the road and that ER values declined as distance from the road increased (Figure 2). The correlation between proximity to major roads and level of Pb contamination can be seen in many studies. Facchinelli et al. (2001) found that the highest ERs in northwestern Italy corresponded to major highways in the region. Sampling from median strips of main roads in Spain, Sánchez-Martin et al. (2000) found that Pb concentrations were much higher in the median strips (highest value of 1480 mg/kg) than in baseline soils of the area (high value of 50.3 mg/kg).

In the Honolulu area, Fu et al. (1988) analyzed soil and grasses in Ala Moana Park and found that Pb levels were highest at either end of the transect near Ala Moana Boulevard and Ala Moana Park Drive as compared to the interior of the park. In addition, Sutherland (2000c) specifically targeted soils in close proximity to Honolulu roads and compared levels of Cu, Pb, and Zn contamination in these soils with background soils. He found that Pb was 4 - 5 times higher in roadside soil profiles, both the topsoil level (0 – 2.5 cm depth) and the subsoil level (7.5 – 10 cm depth), than in the background soil profiles. Finally, DeCarlo and Anthony (2002) found the highest concentration of Pb in a soil core from a Honolulu public park on conservation land, a finding that at first seemed suspect. However, further investigation revealed that this site was a popular tourist destination and idling tour buses and increased traffic in the area could account for the elevated Pb levels.
Figure 2. The relationship between metal concentration and distance from the road (Sutherland and Tolosa, 2001)
Thus, as demonstrated by the above studies, soils near major roads are sinks for Pb and can be considered one of the primary sources of Pb.

1.2 Trace metals in road-deposited sediments

Studies of roadside sediments are also important, especially in urban areas. Road-deposited sediments include weathered particles from the paved road surface and sidewalk, trace metal particles deposited from vehicle wear and tear and particulate emissions, and eroded soil particles that have washed into the road (Dempsey et al. 1993; Sutherland and Tolosa, 2000). Pirrone and Keeler (1993) examined factors affecting atmospheric deposition and resuspension of trace metals and found that surface roughness, wind velocity, and particle growth from humidity and static forces, such as van der Waal’s attraction, all affect the amount of sediment depositing on the road. In general, finer grain sizes, which concentrate trace metals, are potentially more prone to resuspension, and, once deposited, are also easy to entrain in overland runoff. However, Droppo et al. (2002) reported that urban sediments tend to change in their degree of aggregation during transport from the streets to the streams. In their study area, sediments were found primarily in an unaggregated state in the street, were moderately aggregated in surface runoff, and were highly aggregated in the storm sewer system. These results suggest that fine sediments may actually become less prone to transport and suspension as they travel to the stream system.

As RDSs accumulate, they have the potential to be remobilized during precipitation events. Urban streets are designed to funnel runoff into storm drains, and this design facilitates the removal of particulate matter from the road surface. Ellis et al. (1986) found that the two main factors affecting metal and sediment loadings in sediments caught in roadside storm inlets were total runoff volume and storm duration. In their study on metal differentiation into dissolved and suspended solid transport, Morrison et al. (1984) reported
that Pb was most strongly associated with the suspended solid phase in road runoff, with over 95% of Pb loading in particulate form. Since Pb is found mostly in the suspended phase rather than dissolved, it has the potential to be temporarily stored along the transport path, in runoff channels, at the storm sewer inlet, in the storm sewer system, at the storm sewer outlet, and in the stream near the mouth of the outlet (Parker et al., 2000). It is trace metal storage at the mouth of the outlet which will be examined in this study, since previous research on Hawai‘i streams found Cu, Pb, and Zn in high concentrations in bed sediments and stream biota despite the fact that there are no local industrial sources of these metals (DeCarlo and Anthony, 2002; Sutherland 2000a).

1.3 Trace metals in aquatic sediments

1.3.1 Sources

There are three main anthropogenic sources of trace metal contamination in aquatic sediments: mining wastes, industrial discharge, and urban runoff via storm sewer systems. Mining of ores that contain Pb produces contaminated tailings, which exposes the trace metal to leaching and weathering into the surrounding environment. Heiny and Tate (1997) discovered that samples taken downstream from mined sites contained higher concentrations of Pb than samples taken in areas with no mining activities. Similarly, O’Brien (1997), in comparing the distribution of trace elements between physiographic provinces in New Jersey, found that one of the areas with the highest concentrations of trace metals, the New England province, was once extensively mined for magnetite ore.

Industrial discharge and atmospheric deposition into surrounding water bodies is another source of contamination in stream sediments. Mellor and Bevan (1999) attributed elevated levels of Pb in the central and southern parts of a UK catchment to a long history of urban and industrial development. Industries in this area discharged wastes into the sewer system, which flowed into a treatment plant, except in times of high discharge when
the wastes were diverted into the combined sewer overflows and debouched in the streams. Using National Stream Quality Accounting Network (NASQAN) program data, Alexander and Smith (1988) found that municipal sewage treatment plants and industrial point sources contribute a significant amount of Pb into US streams at about half the NASQAN sites. In addition, about 5% of the decrease in Pb in the environment today can be attributed to a decline in industrial Pb discharges. Research on the Ave River basin in Portugal indicated that the sites with the highest enrichment factors for Cd, Cu, Ni, and Pb (40) were located downstream from metal plating industries (Soares et al. 1999).

In this thesis, contamination of aquatic sediments via urban runoff and storm sewer systems is most pertinent, as there is often a direct connection between the roadside environment and the aquatic environment. As discussed in the preceding sections, Pb contamination of soils and sediments is prevalent in urban areas. In the UK, Mellor (2001) reported that both total and acetic acid extractable Pb concentrations were highest in stream sediments adjacent to the main coast road. Flores-Rodríguez et al. (1994) examined the mobility changes that solid particles undergo as they are transported through both separate and combined sewers. Although Cd and Zn became more mobile and therefore more bioavailable during transport, Pb actually became more stable resulting in decreased mobility during transport. However, the authors also found that the sample site near the ring highway did contain a significant amount of Pb in the ion-exchangeable fraction, indicating that Pb in road runoff may be potentially more bioavailable than Pb in sewage.

Further support for the negative influence storm drains have on the aquatic environment can be found in the research of Garban et al. (1996). For the River Seine in France, Pb contamination followed a different pattern than other trace metal contaminants in that Pb levels were highest just downstream of storm drains, which reflected the influence that urban runoff was having on stream sediments. Lottermoser (1998) found that, in coastal river sediments of New South Wales, elevated Pb levels in the sediments were found
within 200 m of sewer outlets, indicating the effect of sewage effluent and road runoff inputs. For Manoa Stream, DeCarlo and Anthony (2002) reported the highest levels of Cu and Zn were not found in the most downstream and heavily urbanized section, but rather just below the University of Hawai`i, where a number of large storm drains conduct urban runoff into the stream from high traffic areas.

A distance decay relationship between point sources of contamination and metal concentrations often exists in fluvial environments. In Manoa Stream, Sutherland (2000a) found that three of five strongly polluted samples came from sites just below storm drain outlets. Similarly, Rhoads and Cahill (1999) reported that metal concentrations were elevated just below storm sewer outfalls compared to samples taken from just above the outfalls in the Kaskaskia River in Illinois. Their data showed that as distance from the outfall increased in the downstream direction, trace metal concentrations declined abruptly.

1.3.2 Contaminated sediments and aquatic health

Although the biotic aspects of metal contamination will not be examined in this thesis, the affects of contaminated sediments on aquatic organisms are in order. Many toxics in the environment have the ability to bioaccumulate. Thus benthic feeding fish, that may ingest large quantities of contaminated sediments, constitute a link, direct or indirect, between the contaminated stream sediments and other organisms, including humans.

According to Streit (1998), bioaccumulation can be defined as “the accumulation of a contaminant into an organism or a biological community, resulting either from a direct uptake from water (i.e., by bioconcentration) or from ingestion (i.e., by biomagnification) (p 357).” Streit also maintains that concentrations of trace metals in benthic invertebrates are usually correlated to concentrations in bed sediments.

In the case of Pb, research by Suedel et al. (1994) indicates that this metal does not bioaccumulate very readily. Actually, Pb levels tended to decrease at the higher trophic
levels. Metals that bioaccumulate up the aquatic food web easily are those that are likely to change from inorganic to organic forms, which increases the metals' lipid solubility and allows accumulation in fatty tissue. Mercury (Hg) and arsenic (As) are two trace elements which bioaccumulate. However, even if Pb is not bioaccumulating up to higher trophic levels to any significant degree, it does adversely affect the health of the organisms in which it is accumulating.

1.3.3 The rural-urban contamination gradient

Much of the Pb found in stream sediments can be attributed to contaminants carried in urban runoff; thus it stands to reason that sediments in stream segments in urban areas will be significantly more contaminated than sediments in rural segments. In a USGS study on water quality of the Connecticut-Housatonic-Thames River basins, Breault and Harris (1997) reported that Pb concentrations were lowest in the northern, forested region, 87 mg/kg, while the highest Pb levels were found in the southern, urbanized region, 310 mg/kg. Another USGS study on the South Platte River basin indicated that Al, As, Cr, and Pb concentrations in stream sediments were highest at or just below Denver and then decreased in sediments derived from mixed and agricultural land use areas (Heiny and Tate, 1997).

Here in Hawai`i, Sutherland (2000a) analyzed bed sediments from the rural, headwaters area of Manoa Stream to the junction with Palolo Stream and found that Pb concentrations increased from the low density upper areas to the heavily residential/educational/commercial districts nearer Waikiki. Some of the areas with the highest Pb levels were associated with storm sewers and sediments in the lower, highly urbanized segments.

Increased contamination in urban areas is often correlated to traffic density and population density, and high population density often is highly correlated with high traffic density, which means increased Pb contributions to the environment. Indeed, there are many studies that support this contention. Along the Chattahoochee River in Georgia and
Florida, Callender and Rice (2000) found that population density was strongly correlated with traffic density and that both were strong predictors of anthropogenic Pb and Zn concentrations in the aquatic environment. For two Virginia watersheds, Helsel et al. (1979) reported strong nonlinear correlations between Cu, Pb, and Zn and traffic and percent impervious surface cover, lending support to earlier arguments that RDSs are important sources of metal contamination in streams. In New Jersey streams sampled in the National Water Quality Assessment (NAWQA) program, O’Brien (1997) found that the probability of detecting Pb in concentrations greater than 10 mg/kg in bed sediments was related to population. In summarizing findings of NAWQA sites, Rice (1999) presented a good correlation between the sum of the concentrations of Cu, Hg, Pb, and Zn and population density ($\rho = 0.54, n = 539$) and argues that population density can be used as a substitute for automobile density in urban and suburban areas.

### 1.4 Background and baseline concentrations

To evaluate the level of Pb enrichment in stream sediments, some form of background or baseline concentration for that area must be established. Rice (1999) defined the background concentration of an element to be that concentration occurring as a result of natural processes, such as weathering and erosion of parent material and non-anthropogenic atmospheric deposition. However, because anthropogenic activities have affected almost every place on Earth, the term baseline concentration might be more appropriate. According to Rice (1999), the baseline concentration reflects a low-level anthropogenic influence and is a combination of background levels and other concentrations that are representative of the study area at that particular time.

There are various methods for determining background or baseline concentrations of an element. Rice suggested several methods for identifying a baseline: average crustal
abundance, probability plots of the distribution, median concentrations of representative indicator sites, and median concentrations in local parent material and soils (Rice, 1999).

Sutherland (2000a) used the average metal concentration in parent material to determine an index of geoaccumulation for Manoa Stream sediments. By estimating the concentration of the element in question in the Koʻolau Basalts, any increase in that element in stream sediments could be attributed to anthropogenic contamination. Moon et al. (1994) and Parker et al. (2000) both used a version of this last method as well. By sampling sediments well below the streambed, any recent anthropogenic influence was assumed to be negligible. Moon et al. (1994) used an exposed soil profile in a nearby trench to collect baseline samples, while Parker et al. (2000) looked for a change in horizon color from dark brown to lighter reddish brown and assumed that this latter layer was representative of the background concentration before stormwater sediments were deposited. There has been some speculation as to whether this approach to calculating a baseline is very accurate as some trace metals may be mobile in soil profiles and have the ability to leach down into the lower layers of the subsoil where they would elevate any baseline concentration (Ellis and Mellor, 1995). Other common methods for establishing a baseline include sampling soils from forested sites well removed from roads and sampling sediments from lake or reservoirs below the contaminated layers.

1.5 Effects of the geomorphologic environment

When examining the distribution of trace metals in the aquatic environment, many geomorphologic factors must be taken into account. To explain a certain pattern of metal enrichment, grain size, method of transport, organic content, mineralogy, and pH must all be considered.
1.5.1 Pathways of metal transport

In general, there are two phases in which trace metals exist in the aquatic environment: the dissolved phase and the particulate phase. Hart (1982) further defined each category, the dissolved phase includes free metal ions and colloidal associated metal species, while the particulate phase includes biotic and abiotic particulates. As discussed in previous sections, Pb is mostly associated with the particulate phase in aquatic environments with very little Pb in the dissolved state. Moon et al. (1994) found average Pb concentrations in the dissolved phase to be $<0.001$ mg/L while the particulate phase ranged from 0.003 to 0.012 mg/L in water samples. In analyzing stormwater runoff from an urban catchment, Morrison et al. (1984) found that, of the common trace metals found in urban runoff, Pb was least likely to be associated with the dissolved phase. Generally, much higher levels of Pb can be found in bed sediments except during times of high flow when much of the sediment may be entrained in the water column. Estébe et al. (1997) discovered that levels of Cd, Cu, Pb, and Zn all decreased in River Seine bed sediments during the winter. This decrease they attributed to the higher water velocity in the winter, leading to erosion and entrainment of contaminated sediments and redistribution downstream as well as transport into the area of uncontaminated sediments from upstream. Issues of temporal and seasonal variability in metal concentrations in sediments will be discussed in detail later. However, it is important to note that the majority of sediment studies are conducted on bed sediments in times of low flow when metal concentrations would be at their peak detection level.

1.5.2 Effects of grain size

Most research on trace metals in relation to sediment grain size indicate that silts and clays concentrate metals more than sands, and unless the particulate metals are themselves gravel sized, there is very little association between metals and grains larger than 2 mm.
There are several reasons for this association between trace metals and fine grain sizes. First, silts and clays have higher surface to volume ratios on which metals, organic matter, and Fe/Mn oxides can adsorb. Secondly, some clay minerals have high cation exchange capacities (CEC), which facilitates metal sorption (Horowitz, 1991).

In their research on the Limski Kanal, Martincic et al. (1990) detected several peaks in Pb concentrations, one in grain sizes from 150 to 1000 μm and another in grain sizes < 10 μm. When they explored correlation analyses, they found that the coarser grain size fraction was highly correlated with organic matter whereas the finer grain size fraction was not. Stone and Droppo (1996) for Big Creek and Big Otter Creek in Ontario reported a more consistent pattern between metal concentration and grain size. For Pb, total concentration in bed sediments increased with a decrease in grain size, with a maximum concentration in the finest fraction, < 8 μm. Application of sequential extraction procedures indicated that Pb was primarily associated with iron (Fe) and manganese (Mn) oxides and that organic matter was also most concentrated in the finest grain size fraction. However, since this experiment only tested grain sizes smaller than 63 μm, no comparison could be made to coarser grain sizes.

In contrast, Jain and Ram (1997) examined a river system with < 1% clay and silt and thus looked at the relationship between coarser grain size fractions and trace metal adsorption. They found that the sand-sized fraction did have some affinity for trace metals, although certainly to a lesser extent than clays and silts. Still, in a river system composed primarily of sand-sized particles and larger, the mass contribution of contaminated sands can be significant. This study illustrates the difference between metal concentration and mass loading. Although silts and clays may have the highest concentrations of metals, if they compose only a small percentage of the sediment in that area, their contribution to the metal mass loading will be minimal. However, in terms of bioaccumulation concerns,
benthic feeders primarily process silts and clays; therefore, the concentration of trace metals in the fine size fraction can be more critical than loading.

While studying differences in trace metals among fluvial sedimentological units, Ladd et al. (1998) provided more support for the relationship between the finest grain sizes and high metal concentrations. The authors found that attached bars and eddy drop zones contained the highest concentrations of trace metals and the finest grain sizes of the morphologic units. Other units, such as glides and riffles, contained more coarse grain sediments and had lower metal concentrations.

In their chapter on methods in trace metal contamination research, Shelton and Capel (1994) suggested that the fine grained fraction of bed sediment samples (< 63 μm) should be separated and used for analysis to maximize the probability of detecting trace metals and make inter-comparisons between data sets possible. This approach also reduces spatial variability between sample sites, but that will be discussed in detail later. However, for Manoa Stream, Sutherland (2000b) found that the 63 - 125 μm grain size fraction contained Pb concentrations that correlated very strongly with Pb concentrations in the < 63 μm fraction. Thus, in areas with minimal quantities of clay and silt, analyzing fine sands may also be valuable in assessing contamination patterns.

It is generally accepted in sediment research that smaller grain sizes have higher surface area to volume ratios on which organic and inorganic complexes can adsorb. In their chapter on the structure and properties of clay minerals, Moore and Reynolds (1997) explain this phenomenon as caused by the high number of unsatisfied and broken bonds on the surface of a small object as compared to a large object. These unsatisfied bonds produce a charge, which attracts ions, such as trace metals, organic matter, and Fe/Mn oxides. Combest (1991) found strong positive correlations between sediment clay percentage and Fe, Mn, and organic carbon as well as negative correlations between sand-sized particles and the aforementioned variables.
1.5.3 Trace metal complexation in sediments

There is a well-documented direct relationship between organic matter and trace metals. Generally, organic matter is a common substrate onto which trace metals complex in sediments. Thus, most research on trace metals in sediments will include an analysis for organic matter, such as loss on ignition (LOI). In the Suquia River system in Argentina, Gaiero et al. (1997) found that in the springtime, an increase in total non-residual Pb levels in sediments corresponded to an increase in organic matter and precipitated carbonates. Garban et al. (1996) reported a strong link between metal concentrations and particulate organic carbon in River Seine sediments, and Stone and Droppo (1996) also discovered a high association between organic matter and trace metals, especially in the springtime when runoff from soil surfaces was high in Ontario. However, Mellor (2001) found that organic matter was not significantly correlated with Pb in stream sediments. This lack of correlation suggests that type of organic matter may be more important than the overall organic content of the sediments (Mellor, 2001).

Iron and Mn oxides are also important in trace metal complexation in sediments. According to works cited in Konhauser et al. (1997), Fe/Mn oxides complex metals through two mechanisms, either by binding transition metals to their surface or by co-precipitating them as metal coatings. In some systems, these oxides can be more important than the clay content, although in these cases, clays and silts may be acting as a substrate for oxide coatings, which then bind the metals. In Combest’s study, he reported that Pb was more strongly correlated with the Mn content than the clay percentages of the sediment of White Rock Creek (Combest, 1991). Stone and Droppo (1996) found evidence that Pb and Zn levels in the Fe/Mn oxide phase were a function of grain size. They attributed this result to the presence of water-stable aggregates coated with amorphous Fe/Mn oxide surfaces that were delivered to the fluvial system during runoff events.
Of less importance in metal adsorption are carbonates, which seem to be the main factor only in systems with low amounts of organic matter and Fe/Mn oxides, and which are of minimal importance in the tropics and semi-tropics. An example of this effect can be seen in Stone and Droppo’s study, where 30-40% of total Pb in the three largest grain size fractions (19-31, 31-42, and 42-63 μm) was bound to carbonates in the summer. This association was less apparent in the spring when organic content and Fe/Mn oxides were more prevalent from runoff events (Stone and Droppo, 1996). Gaiero et al. (1997) found that Pb was significantly, positively correlated to precipitated carbonates in the spring but was more highly correlated with organic matter.

In studies where clay mineralogy is quantified, patterns emerge concerning certain clay minerals’ ability to incorporate trace metals into their matrix and onto their outer surfaces. Vermiculite and smectite, two clay mineral species that have the ability to expand their structure, are especially important in trace metal research because they trap metals in the fine-grained sediment fraction. Konhauser et al. (1997) found that fine-grained sediments in the Mahanadi, Brahmani, and Baitarani Rivers had a clay mineral assemblage of kaolinite and illite with small amounts of smectite, which they presumed increased this fraction’s ability to adsorb trace metals. Sediment from the Vesdre River in Belgium had a clay mineral assemblage of mostly illite with virtually no vermiculite or smectite, which explained why the authors found no significant positive correlation between trace metals and clays (Houba et al., 1983).

Although Pb in sediments has been discussed thus far as being in a static relationship with the surrounding environment, the relationship between Pb in the surficial sediment and the overlying water is actually in a constant state of flux. According to Chapman et al. (1998), even a small change in redox potential in these surficial sediments can release metals complexed with organics and Fe/Mn oxides to the porewaters of the bed sediment. This release is important in that it makes the metals more bioavailable. The
authors list several reasons as to why the redox potential might change. The first is particle deposition and microbial activity change based on temporal and spatial scales. The longer a particle is exposed to overlying stream water, the greater the chance that the redox potential will alter enough to release the metals into solution. Also, if new sediments are not periodically deposited onto the bed, the metals adsorbed to the older layer will, over time, have lower concentrations of metals available for transfer to the surrounding water. Secondly, biotic activity in the bed sediments can change the redox potential of the system. In tropical, aerobic environments, there is little seasonality in this activity; in fact, in a reasonably healthy system, bioturbation is bound to be very high in the warm, wet climate of Hawai‘i. In addition, diurnal cycles of photosynthetic activity may change the pH and dissolved oxygen in the system, which can increase the release of trace metals from complexation. Finally, sediment resuspension due to stormflow discharge events and tidal currents can change the redox potential. Again, this potential is due to new sediments being deposited in an area and older sediments being exposed to the overlying water, etc. For Nu‘uanu Stream, all three of these factors have a high probability of occurring in the bed sediments. Seasonal rainfall differences, high flow events, the lower, tidal section of the stream, and burrowing organisms in the sediments will all affect the ratio of trace metals adsorbed to the surficial sediments compared to that in the porewater and dissolved in the overlying water column.

In general, trace metals bound to sediments become more mobile as the pH of the surrounding water decreases. This phenomenon is easily observed in streams draining mining sites. As the highly acidic mine drainage flows into the fluvial system, the pH of the water increases and the metals in the leachate are precipitated. Jain and Ram (1997) reported that metal adsorption increased in bed sediments from the River Kali in India as pH was increased. At a pH of 6.0, the researchers could no longer detect trace metals in the solution, indicating that most of the metals were complexed onto the sediments. Tarvainen
et al. (1997) described how streams and small lakes in Finland were more likely to undergo significant acidification from atmospheric deposition than large lakes and that this acidification increased trace metal solubility. Indeed, the researchers found that trace metal concentrations and pH were negatively correlated, lending support to the idea that metals bound to sediments are more soluble in acidic waters. With this in mind, it is important to consider the pH of a fluvial system when examining metal contamination because should the system become more acidic, those metals will become more soluble and thus more bioavailable, which is a major health concern.

1.5.5 Factors controlling the distribution of trace metals

As this research examines the spatial relationship between storm sewer outlets and trace metal concentrations in sediments, some discussion of how geomorphology affects metal distribution is necessary. As previously discussed in relation to grain size effects, Ladd et al. (1998) found that certain types of fluvial morphologic units are more likely to concentrate metals than others. Eddy drop zones and attached bars had the highest concentrations of metals, lateral scour pools and detached bars had intermediate concentrations, and riffles and glides had the lowest concentrations. This pattern is generally associated with grain size distributions since, as water velocity drops, suspended sediment will begin to settle out. In areas with minimal turbulence and velocity, the finest sediments, to which metals tend to be adsorbed, settle out on the bed surface (Ritter et al., 1995). In a study on the River Seine, Estebe et al. (1997) found that peak metal concentrations in river sediments occurred after major combined sewer overflow (CSO) discharges and that most of the suspended solids in these discharges settled out within a couple of days, concentrating the contamination downstream from Paris. Rhoads and Cahill (1999) also found evidence to support the above relationship in their research on the Kaskaskia River basin. In these river sediments, the highest metal concentrations were
found in low flow velocity areas such as vegetated point bars and stagnation zones at confluences, as well as areas of intermediate velocity where metal particulates settled.

1.6 Sampling

Fluvial systems are constantly changing as water resuspends sediments, erodes the channel, redeposits sediments, and dissolves some molecules and precipitates others. This dynamic environment makes representative sampling very difficult, both on the spatial scale and the temporal scale. To ensure that the results of an experiment can be accurately generalized to other sites, a sampling scheme must be selected that minimizes potential sources of variation. Which scheme is most appropriate depends on the goal of the research.

In Combest’s research, he chose a random sampling scheme to examine metal trends along the length of the stream and the sediment sorption relationships (Combest, 1991). By first identifying five areas and then applying a grid to each area, random grid cells could be selected as representative of that area. His data indicated that it is necessary to take into consideration sediment characteristics when studying trace metal contamination. Otherwise, variability between different sites will be too large for meaningful comparisons.

Another approach to sampling can be seen in Sutherland’s research on Manoa Stream sediments (Sutherland, 2000a). He chose a systematic sampling scheme to highlight any enrichment trends along the length of the stream, from rural headwaters to the urban mouth. By sampling every 50 m, a general pattern emerged of increasing Pb contamination downstream. This type of sampling did not take into account morphological differences in sample sites. However, since he was sampling primarily fine-grained sediments, most of the samples were most likely taken from similar morphological units.

To study the affect that morphological units have on variability in trace metals, Ladd et al. (1998) chose a stratified sampling scheme. First, they identified seven different types
of fluvial bedform morphologies from which to sample: lateral scour pools, eddy drop zones, glides, low-gradient riffles, high-gradient riffles, bank-attached bars, and detached island bars. Within each morphological unit type, 10 samples were collected and a complicated compositing scheme was used to reduce the spatial variability within each unit. This sampling scheme highlighted major differences between certain morphological units, which the authors strongly suggest should be taken into consideration in any fluvial sediment study. In addition, they criticize both the random and systematic approaches to sampling in a highly variable environment, as the first would require too many samples to realistically encapsulate the variability in the area while the second would most likely miss smaller units where high levels of trace metals may be stored. Stratified sampling of only one morphological unit also comes under attack, despite being the classical sampling scheme for this sort of research, because this type of sampling will only characterize one particular unit and miss the full range of metal concentrations in the system. However, feasibility is a consideration which must be factored into any research design. Stratified sampling of all major morphological units of the area in question may exceed the allotted budget or time constraints, and many urban streams, especially those in Honolulu, do not have well-developed geomorphic features. Ultimately, a balance must be struck between feasibility and accuracy and precision in sampling.

1.7 Spatial variability

Ladd et al. (1998) found that lateral and longitudinal variations within morphological units were not significant. However, they did find that variations between morphologic units were very significant with up to 34% variation between morphological units only meters apart. These results indicate that location within a morphologic unit does not matter, but that comparing concentrations between different morphologic units may be inappropriate. Using analysis of variance (ANOVA), Brandvold and McLemore (1998) concluded that
using the $< 63 \mu m$ sediment fraction reduced analytical variance due to spatial variation in their duplicate samples. Surprisingly, they found that, in analyzing the $< 63 \mu m$ fraction, the greatest differences in Cu, Pb, and Zn concentrations were found between adjacent duplicate sample sites. Truckenbrodt and Einax (1995) found that non-representative sampling, i.e. sampling from sites that do not reflect the average surroundings, was the main source of variance, independent of grain size. Thus, analyzing only the silt and clay fraction in a poorly designed sampling scheme will not reduce distribution variance between sites. In addition, they reported that lateral sampling exhibited spatial dependence while longitudinal sampling did not. The implications are that researchers should consider compositing at each sample site to reduce lateral variation, but that variation longitudinally within the sample site need not be considered.

1.8 Temporal variation

Seasonal and temporal variance are also important to consider in any fluvial sediment research design. Generally, Birch et al. (2001) found that temporal changes in trace metal concentrations in sediments where data have been normalized by grain-size to reduce spatial variability were related to the ambient energy of the system. More specifically, Estébe et al. (1997) found that trace metal concentrations in River Seine sediments were much higher in summer than winter. This seasonal variation they attributed to decreased flow in the summer which allowed for sediment deposition on the bed surface, while winter, with increased precipitation inputs, entrained much of the sediments and transported it downstream. Similarly, Gaiero et al. (1997) discovered that the impact of the city of Córdoba on Suquía River sediments was seasonally dependent; there were higher concentrations of metals in the spring than the summer, which the authors attributed to increased urban runoff during the rainy season. In the Kaskaskia River basin, some sites were resampled over the course of several months to establish temporal variability, with the
result being that some concentrations changed by an order of magnitude over this time span (Rhoads and Cahill, 1999). Thus the authors suggest periodic sampling at certain sites to characterize this variation. Shelton and Capel (1994) suggested that research designs should be flexible and avoid sampling after major discharge events to allow suspended sediment to settle back out of the water column. For the USGS, sampling is conducted during low flow conditions to minimize seasonal streamflow variability. However, it is not always possible to sample at low flow levels due to time constraints on research.

1.9 Extraction techniques

There are many different techniques for extracting trace metals from sediments for analysis, including total extraction, sequential extraction, and weak leach or bioavailable extraction. Which extraction technique is most appropriate depends on the goal of the research, as each has advantages and disadvantages.

1.9.1 Total extraction

In the past, total extraction of metals from sediments was the favored approach as it provided a relatively fast assessment of the total amount of metal in the system. The general procedure for total digestion involves placing sediment in a hot mixture of HF (hydrofluoric), HNO₃ (nitric), HClO₄ (perchloric), and HCl (hydrochloric) acids in a block digester or in a microwave. However, HClO₄ has the disadvantage of being explosive. The result of such digestion procedures is the breakdown of clays, organic matter, Fe/Mn oxides, carbonates, and most of the crystal matrix itself except for some resistant minerals, which releases adsorbed and complexed trace metals into solution (Agemian and Chau, 1976). HF acid is particularly strong, as it is the only acid capable of fully dissolving silicate minerals (Agemian and Chau, 1976). The main disadvantage to this technique is that it releases into solution trace metals, that would not normally be available in the environment,
such as those bound into the silicate mineral matrix. Thus, total metal concentrations
represent not only the bioavailable metals in the environment in question but also the
residual metals, which are unlikely to be causing any adverse effects.

1.9.2 Sequential extraction

Sequential extraction procedures have recently come into favor in sediment studies
because they provide an operational assessment of the trace metal partitioning in an
environment. The most commonly applied sequential extraction scheme was developed by
Tessier et al. (1979) and involves separating the trace metals into five phases: exchangeable,
carbonates, Fe/Mn oxides, organics, and residual. This separation is accomplished by
applying harsher and harsher digestions to the sediment in a sequential pattern. According
to Kersten and Förstner (1989), "the concept of chemical leaching is based on the idea that
a particular chemical solvent is either phase or mechanistic specific" (p. 259). However, the
acid extractants are often not as selective as would be desired and comparisons between
individual metal leaches and the corresponding step in a sequential leach often indicates that
there is some "contamination" occurring across sequential leaches. In addition, the Tessier
sequential extraction technique is time consuming as it involves many steps.

Some researchers have been using simplified versions of the aforementioned
sequential extraction technique with mixed results. Sutherland et al. (2000) used a new
standardized procedure called the optimized European Community Bureau of Reference
(BCR) sequential extraction procedure, which separates metals into four phases: acid
extractable, reducible, oxidizable, and residual. In comparing the results from this method to
the Tessier extraction, the authors found that the Tessier method leached far more Pb out in
the exchangeable and carbonate fractions combined than the BCR did in the exchangeable
fraction. Carapeto and Purchase (2000) simplified the extraction scheme even further by
reducing the number of phases to three: exchangeable, bound to organic matter, and
residual, which then contained carbonate and Fe/Mn associated metals. They justified leaving out the carbonate and Fe/Mn associated leaches because the pH of the system in question was stable throughout the study period, and the samples were not subjected to anoxic conditions. Their results compared favorably with the Tessier extraction scheme. These simplified sequential extraction techniques are useful in studies where information about the phase associations of the metals is desired but the budget is tight.

1.9.3 Bioavailable extraction

For researchers only interested in the bioavailable phase of metals, total and sequential extraction techniques are unnecessarily harsh and time-consuming, unless only the initial steps are used in the sequential technique. Instead, weak acids, such as cold, dilute HCl or EDTA (ethylenediaminetetraacetic acid), dilute HNO₃, or dilute acetic acid can be applied to the sediments. Mellor and Bevan (1999) used 0.5M acetic acid to extract what they called the “plant-available” metal fraction, or that fraction of Pb that is environmentally mobile. According to Sutherland and Tolosa (2000), a dilute HCl leach will liberate adsorbed detrital and non-detrital carbonate-bound metals and much of the Fe/Mn oxide and organic-associated metals while minimizing the effect on the residual silicate-bound metals.

1.10 Normalizing the data

In geochemical research it is common to normalize trace metal concentrations to “conservative” elements to minimize variability caused by differences in parent material, sedimentation rates, and grain-size distribution. The theory behind such comparisons is that “conservative” elements are assumed to have uniform variability in the study area as a result of natural processes (Rice, 1999). Aluminum (Al), titanium (Ti), lithium (Li), and scandium (Sc) are common “conservative” elements to which trace elements are compared.
(Rice, 1999). Some researchers normalize metal contents to organic matter in an effort to reduce the influence of varying organic matter inputs between sites. Soares et al. (1999) normalized metal concentrations to volatile matter content in Ave River location sediments. Other researchers attempt to control this variation in organic matter by controlling grain size in their experiments as discussed previously.

1.11 Enrichment ratios

As a means to evaluate the level of trace metal contamination in a system, enrichment ratios are invaluable. An ER is the ratio between the trace element concentration of the sample and that same element’s background or baseline concentration.

\[
ER_n = \frac{\text{Concentration}_n}{\text{Concentration}_{\text{baseline}}} \quad [1.1]
\]

Normalized enrichment ratios are computed as follows:

\[
ER_n = \frac{\frac{C_{n, \text{Sample}}}{C_{A1, \text{Sample}}} \frac{BE_n, \text{Baseline}}{BE_{A1, \text{Baseline}}}} \quad [1.2]
\]

where BE is the best estimate of the element in parent material (Sutherland, 2000a).

Sutherland (2000a) proposed a five-category pollution index based on enrichment factors:

- ER < 2, indicates no or minimal pollution
- ER 2 – 5, indicates moderate pollution
- ER 5 – 20, indicates significant pollution
- ER 20 – 40, indicates a very strong pollution signal
- ER > 40, indicates an extreme pollution signal.

Often cited in the literature is the work conducted by Long et al. (1995). In this research, the authors established two thresholds of contamination as a means to evaluate the health of an aquatic system. The effects range-low (ERL), or the lower 10\(^{th}\) percentile of the biotic effects data, for Pb was defined as \(\sim 47\) mg/kg while the effects range-median (ERM), or the median of the biotic effects data, of Pb was defined as \(\sim 218\) mg/kg. Using these guidelines for trace metal concentrations from total digestion of sediments, samples with <47 mg/kg of Pb produce only rare incidences of biotic effects, samples with Pb between 47 - 218 mg/kg produce occasional incidences, and samples with >218 mg/kg produce frequent incidences of biotic effects. In addition to Pb, Cu and Zn thresholds of contamination are important in urban streams. For Cu and Zn, ERL was defined by Long et al. (1995) as 34 and 150 mg/kg, respectively, while ERM was defined as 270 and 410 mg/kg, respectively. Enrichment factors can be an important measure of the probable affect that metal contamination will have on biotic life in the aquatic environment and thus are very useful in establishing environmental law and policies.

Finally, it is important to mention the U.S. Geological Survey’s (USGS) benchmarks for trace elements in stream sediments. These benchmarks are based on Canadian sediment quality guidelines to protect aquatic health (MacDonald et al., 2000). A probable effects level (PEL), similar to ERM, and a threshold effects level (TEL), similar to ERL, are defined for Cu, Pb, and Zn (Table 1).
Table 1. PEL and TEL guidelines for Cu, Pb, and Zn

<table>
<thead>
<tr>
<th>Metal</th>
<th>PEL (mg/kg)</th>
<th>TEL (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>35.7</td>
<td>197</td>
</tr>
<tr>
<td>Pb</td>
<td>35.0</td>
<td>91.3</td>
</tr>
<tr>
<td>Zn</td>
<td>123</td>
<td>315</td>
</tr>
</tbody>
</table>
OBJECTIVES AND RESEARCH QUESTIONS

This study will examine the geographic distribution of Pb in an urban stream in relation to storm sewer outlets and determine the factors controlling this distribution. To this end, five research questions were formulated.

• Are Nuʻuanu Stream sediments enriched in Cu, Pb, and Zn relative to Koʻolau Basalt baseline levels?

• Do particle size, percent organic matter, and Fe/Mn oxides play a role in trace metal concentrations and patterns?

• Do trace metal concentrations in fluvial sediments occur in a particular spatial pattern surrounding storm sewer outlets? Specifically, are sediments downstream of storm sewer outlets enriched in trace metals relative to sediments upstream of the outlets?

• What is the major source of trace metals in this stream?

• Are road deposited sediments being carried in runoff into the storm sewer outlets and deposited in the stream?

• How does the inorganic contamination in Nuʻuanu Stream compare to other urban watersheds in Honolulu as well as to those of the mainland US?
CHAPTER 2. STUDY AREA AND METHODS

2.1 Nu‘uanu Valley history

Nu‘uanu Valley is one of the oldest developed valleys on O‘ahu (Figure 3). The first development was constructed in what is now the Pu‘unui neighborhood in the decade from 1900 to 1910 (Figure 4). A remote sensing exercise aimed at detecting land-use change in the valley between 1985 and 1996 SPOT imagery, via a vegetation index and change detection function, indicated that there has not been any significant change in land-use in recent history (Andrews, GEOG 470 final project). This can be explained by the fact that Nu‘uanu Valley has very little land for new development.

According to preliminary work done by the USGS, 51% of the land in Nu‘uanu watershed is classified as “other”, while 49% is classified as “developed”. Most of the land categorized as “other” is presumably the forested region of the upper watershed. Of the area considered “developed” in the lower watershed, approximately 9% of it is commercial, 6% is manufacturing/industry, 14% is open space, 16% is public infrastructure, 46% is residential, and 9% is social services (Steve Anthony, personal communication).

Unfortunately, the 1990 and 2000 census tracts do not follow the topographic constraints of the Nu‘uanu drainage basin in the lower sections. Thus, population had to be estimated and most likely is overestimated as neighborhoods were included in the calculation that are also part of the Kalihi drainage basin. Using this method, the 1990 and 2000 populations of Nu‘uanu Valley can be estimated to be ~30,000 residents, with negligible change between the two censuses (The State of Hawaii Data Book, 2000). However, according to Brasher and Anthony (2000), the population density of Nu‘uanu Valley is 1,287 persons per km², which would indicate a population of ~15,000. Nu‘uanu Valley is slightly less densely populated than Manoa Valley, which has a density of 1,565 persons per km². Comparing neighborhoods within the watershed and the city shows that
Figure 3. Map of O'ahu depicting the location of Nu‘uanu watershed.
Figure 4. Map of important streets and neighborhoods in the Nu‘uanu watershed
neighborhoods below Wyllie St. and above N. King St. (Figure 4), as well as Chinatown, are some of the most densely populated tracts in Honolulu, with 1,000-5,000 residents per km$^2$ (The State of Hawaii Data Book, 2000). Population density decreases significantly in the area west of the stream where the main land-use shifts from residential to light industrial and shipping. However, although population density may be lower in these areas, it may still be a significant source of trace metals through the heavily traveled roads or industrial and shipping byproducts.

In terms of traffic density for Nu‘uanu Valley, telemetry information available on the web has traffic volume reports for the Pali Highway at the tunnels that cross through the topographic divide from windward to leeward sides of the Koʻolau Range. Here, in the years from 1998 to 2000, an average of about 46,000 cars passed by in a 24-hour period. This is a higher traffic volume than the Likelike Highway, which also connects leeward Honolulu to windward Kailua and Kaneʻohe, with an average traffic volume of about 31,000 cars in a 24-hour period (The State of Hawaii Data Book, 2000).

According to the State of Hawaiʻi Department of Transportation, Nu‘uanu Stream is used as a ‘screenline’ to determine traffic volumes coming into and out of Honolulu (Gail Okaneku, personal communication). Thus, 24-hour traffic volumes are available for major roads crossing the stream. Roads crossing Nu‘uanu Stream are heavily traveled, especially in the lower drainage basin (Table 2).
Table 2. 24-hour traffic counts for major roads crossing Nu`uanu Stream

<table>
<thead>
<tr>
<th>Street Name/Direction</th>
<th>24-hour Traffic Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pali Highway at tunnels</td>
<td>46000</td>
</tr>
<tr>
<td>Nu`uanu Avenue</td>
<td></td>
</tr>
<tr>
<td>Southbound</td>
<td>9704</td>
</tr>
<tr>
<td>Northbound</td>
<td>7656</td>
</tr>
<tr>
<td>Vineyard Boulevard</td>
<td></td>
</tr>
<tr>
<td>Westbound</td>
<td>10845</td>
</tr>
<tr>
<td>Eastbound</td>
<td>15870</td>
</tr>
<tr>
<td>Beretania Street</td>
<td></td>
</tr>
<tr>
<td>Westbound</td>
<td>19496</td>
</tr>
<tr>
<td>Eastbound</td>
<td>3443</td>
</tr>
<tr>
<td>Nimitz Highway</td>
<td></td>
</tr>
<tr>
<td>Westbound</td>
<td>43697</td>
</tr>
<tr>
<td>Eastbound</td>
<td>37795</td>
</tr>
</tbody>
</table>

2.2 Geology of Nu`uanu Valley

Situated on the southern side of the Ko`olau volcanic range on the island of O`ahu, Nu`uanu Valley is a long, deep valley, formed through the fluvial action of Nu`uanu Stream, Waolani Stream, and many other smaller systems. Forming the east rim of Nu`uanu Valley is the tallest peak of the Ko`olau Range, Pu`u Konahuanui, at 960 m, while the west rim is formed by a lesser peak, Pu`u Lanihuli. The northern side of the Ko`olau Range is characterized by steep pali cliffs formed by a giant landslide that occurred about two million years ago, but the southern side, into which Nu`uanu Valley is carved, is of a much gentler slope (Herrero-Bervera et al., 2002). Although much of the valley is now covered with layers of alluvial deposits and soils, the underlying geology consists of basaltic lavas from two main eruption phases: the Ko`olau Basalts and the Honolulu Volcanic Series. The
Ko`olau Basalts formed during the main shield building stage of the Ko`olau Range and are composed of tholeiitic and olivine basalts, while the Honolulu Volcanic Series is part of the post-erosional rejuvenation stage of the Ko`olau Volcano and consists of magnesium and iron-rich nephelinites, melilite nephelinites, basanites, and alkalic olivine basalts (Macdonald et al., 1983). In the lower part of the valley, an area termed the Honolulu plain, lavas are interbedded with reef deposits, overlain by layered alluvium (Macdonald et al., 1983).

From these parent materials, a variety of soils have formed in Nu`uanu Valley (Foote et al., 1972). In the upper reaches of the watershed, a fine textured (silty clay loam) ultisol (Loleka`a) occurs. In the low density residential area around Wyllie and Kuakini Streets, the soils are classified as silty, kaolinitic clay mollisols (Ewa). The stream channel in this section cuts through clay loam soils classified as Kawaihapai mollisol, alluvial soils. By the high density residential areas near the H-1 Freeway and Vineyard Blvd., the soil is classified as a stony montmorillonitic clay vertisol (Kaena). The soils of the lower watershed near Honolulu Harbor and the commercial district where the stream is fully channelized are classified as Ewa mollisols.

2.3 Physical Geography of Nu`uanu Valley

Although Hawaii’s drainage basins are smaller than many on the mainland, they are extremely important morphological constraints on the hydrologic cycle. In general, Hawaii’s streams have steep gradients, high precipitation inputs in the mountainous areas, rapid response to these precipitation inputs, and very little sediment build-up in the upper reaches due to frequent flushing stormflows. In the urban areas especially, Hawaii’s streams are often channelized, partially in the upper sections and usually fully in the lower sections. In downstream, channelized sections, sediment build-up is more common and can pose problems for contaminant concentration. Honolulu’s drainage basins have both natural and anthropogenically modified sections, but it is unlikely that even the natural
sections of the basin in the headwaters area can be considered to be unaffected by automobile emissions, especially the Nu’uanu drainage basin through which runs the Pali Highway (Figure 4).

As is common on the leeward sides of the Hawaiian Islands, precipitation in the Nu’uanu drainage basin is extremely variable spatially. From 1989 to 1999, mean annual rainfall at Nu’uanu Reservoir No. 4 (Figure 5), at an elevation of 320 m above sea level, varied from a low of about 189 cm to a high of 322 cm, with an average of 256 cm (The State of Hawaii Data Book, 2000). According to the National Oceanic and Atmospheric Administration (NOAA, 2002), the monthly precipitation normals for the years 1971 - 2000 at Nu’uanu Reservoir No. 4 were highest in November, March, and April, with average monthly inputs of around 26 cm (Figure 6). Precipitation was lowest in the summer months, June, August, and September, at about 19 cm. For the station at Nu’uanu Reservoir No. 5 (Figure 5) at an elevation of 125 m above sea level, the monthly precipitation inputs for these same time periods were 19 cm and 13 cm, respectively (Figure 6). Contrasting these data with precipitation information from the Honolulu International Airport at just over 2 m above sea level, clearly indicates the rainfall gradient of the Honolulu area. At the airport, the monthly normal for precipitation for the three wettest months, November, December, and January, was 6 cm, while the monthly normal for the three driest months, June, July, and August, was 1 cm. Although Honolulu International Airport is not part of the Nu’uanu drainage basin, it has a similar climate regime to the Honolulu Harbor area.
Figure 5. Map of study area and sample sites in the Nu’uanu watershed
Figure 6. Mean monthly precipitation inputs at selected Honolulu stations 1971 – 2000

The Nu‘uanu drainage basin is approximately 11.7 km$^2$ in area, from the topographic divide of the Ko‘olau Range to the confluence with Waolani Stream, and is formed by two main streams draining the area, Nu‘uanu Stream and Waolani Stream (Figure 5). Pauoa Stream, which drains Pauoa Valley, also contributes to the lower Nu‘uanu watershed. The Nu‘uanu and Waolani Stream confluence is just upstream of the School St. bridge (Photos 1 and 2, Appendix, p. 93), while the confluence of Nu‘uanu and Pauoa Stream is at an artificial channel located between Kukui and Beretania Streets.
The average depth of Honolulu Harbor, where Nu‘uanu Stream empties, was estimated to be about 12 m in 2000 (The State of Hawaii Data Book, 2000). For this study, Nu‘uanu Stream was the focus, although some measurements on Waolani Stream were also included.

Nu‘uanu Stream has a length of ~9-10 km. Of this length, ~1 km is completely channelized from School St. to the mouth of the stream in Honolulu Harbor (Photos 3, 4, and 5). Portions of the stream are partially channelized at higher elevations, usually with bank stabilization characterized by a cemented rock wall rather than a concrete-lined bed. At the Kuakini St. bridge, the stream is channelized under the bridge but returns to a more natural bed state downstream of this site. The headwaters of Nu‘uanu Stream include many smaller streams draining the steep gradients of the Koʻolau Range. However, some of this flow is captured and held in three reservoirs located in the upper drainage basin. The largest of these reservoirs, the Nu‘uanu Reservoir Spillway, was completed in 1910 and has a maximum surface area of 14.4 km². Nu‘uanu Dam No. 4, which forms this reservoir, is 20 m in height and 527.5 m in length (The State of Hawaii Data Book, 2000). Thus, it is apparent that Nu‘uanu Stream is highly modified from its headwaters to the downstream urbanized sections.

Human influence on the stream system is visually evident from the frequent storm drains and pipes that empty into the streams, the trash that accumulates along the banks and in sediment traps, and the unnatural black coloration of the sediments in the heavily urbanized area of Chinatown. For the Nu‘uanu Aquifer System as a subset of the Honolulu Aquifer System, there are as many as 58 leaking underground storage tanks (LUST) as well as one Superfund (CERCLIS) site in the lower drainage basin. These tanks are likely discharging various contaminants into the aquifer, which even if they do not leak into the stream, are most certainly contaminating the groundwater and most likely the estuarine environment.
In a previous reconnaissance study on this stream, the NAWQA program found that, at a site above the Waolani Stream confluence, Nu’uanu Stream bed sediments had the highest levels of Pb of any stream surveyed in Hawai’i (n = 24) at 220 mg/kg (USGS, 2001). Manoa Stream, reported as having the highest surveyed levels of Pb in fish tissue samples of any stream tested by the US Fish and Wildlife Service, had a bed sediment Pb level of 120 mg/kg. Other trace metals were also elevated at the Nu’uanu site, including Zn and chromium (Cr) (USGS, 2001). Trace metals in fish tissues from Nu’uanu Stream were consistently lower than those found in Manoa Stream (USGS, 2001). In terms of organochlorine pesticides, Nu’uanu Stream bed sediments had the highest levels of cis-Chlordane, trans-Chlordane, Dieldrin, Endrin, Heptachlor epoxide, and trans-Nonachlor of the five systems sampled, including Kaneohe and Manoa Streams in the urbanized area and Poamoho and Waihee Streams in more rural areas of O’ahu. In addition, Nu’uanu Stream had concentrations of PCBs that were at least one order of magnitude higher than the others, at 9511 μg/kg. Organic carbon levels were also highest in Nu’uanu Stream, at 80 μg/kg, which is significant in that organic matter is an excellent binder of trace metals (Horowitz, 1991).

2.4 Sampling

In general, a systematic sampling scheme was utilized for the baseline stream sediment samples and a stratified sampling scheme around storm sewer outlets. The majority of the road sediment sample sites were selected based on the storm sewer outlet samples. For this research, time constraints prohibited periodic sampling. Therefore, results reflect a ‘snap-shot’ of the Nu’uanu Stream system and cannot be generalized to trace metal concentration and behavior from season to season.

All samples were collected over the course of a month, from January 26 to February 27, 2002, during an unusually rainy winter, which slowed down the sampling work.
considerably. January was an especially rainy month, with 53.4 cm of precipitation at Nu‘uanu Reservoir No. 4, representing a 181% increase in rainfall from normal. According to NOAA, January was the wettest month at the Nu‘uanu raingauge since March 1994, and the highest 24-hour total, 24.8 cm, for the month of January on O‘ahu occurred there during the January 26 Kona low precipitation event. Consistent with Kona low conditions, even coastal, leeward Honolulu was unusually wet in January; the raingauge at Aloha Tower recorded 12.3 cm of rain, which is 135% of what usually falls in that area in January. February was drier than usual on O‘ahu, with a precipitation input of 15.9 cm at the Nu‘uanu Reservoir, only 68% of the normal input (Kodama, 2002).

In addition to the amount of rain falling on the island in these two months, the frequency of rainfall events was also important. Because the events were of high frequency, especially in January, local soils became saturated and did not have a chance to dry out until mid-February. Thus, near-saturated soil conditions led to high levels of overland runoff and very rapid discharge responses in the stream. Usually within hours of the rainfall event, the stream discharge would respond by peaking sharply. Even in February, with lower than usual precipitation inputs, the soil moisture conditions continued to influence stream discharge, so that even small precipitation events led to high peak discharges in Nu‘uanu Stream.

Due to precipitation events, Nu‘uanu Stream could not be considered to be at baseflow during the sampling period, but rather near-baseflow, except for those samples collected on February 27 (Photos 6 and 7). There was some variation in stream discharge between sampling days. A hydrograph of nearby Manoa Stream shows the dynamic nature of the Honolulu streams during this rainy period (Figure 7). Stream bed sediment samples were not collected when the stream appeared turbid.
Provisional Data Subject to Revision

Figure 7. Daily mean discharge (cfs) for Manoa Stream, Honolulu, HI for study period, January – February 2002
2.4.1 Baseline samples

Similar to the methodology described by Sutherland (2000a), the baseline samples were collected from stream bed sediments in the headwaters of the Nu’uanu drainage basin, above all residential, commercial, and industrial areas. Initially, it was proposed that sampling begin above the Nu’uanu Reservoir to minimize anthropogenic input to the stream, but stream access above the reservoir was determined to be very difficult. In addition, since the Pali Highway runs through the Nu’uanu drainage basin, anthropogenic effects on even the upper reaches of the stream were expected. Thus, sampling began on a tributary to Nu’uanu Stream where baseline concentrations were still likely and access to the stream reasonable (Figure 5).

A small man-made dam on a tributary to Nu’uanu Stream was deemed the starting sampling point as it would be easy to relocate (Photos 8 and 9). A random starting point above the dam was found by identifying a depositional zone from which to sample. From this starting point, nine additional samples were collected from depositional zones at approximately 50 m intervals. The final baseline sample had to be collected about 4 m above the intended point as a small pipe outlet was found debouching into the stream, the first sign of human modification to the stream aside from the dam at the starting point.

Baseline samples were collected by measuring the approximate distance with a fiberglass tape and then finding a depositional zone in close proximity. As the baseline sampling was in the upper reaches of the stream, where water velocities were high and the slope of the bed steep, locating a depositional zone with enough fine material in 50 m intervals was often challenging. Most samples were collected in the drop zones behind large rocks or vegetation or from small point bars along the stream banks. Spatial variability was accounted for by compositing six 5 cm cores from a depositional zone at each 50 m interval. At each new sample site, the clear, 5 cm internal diameter Plexiglass tube
sampler corer was cleaned before sampling. Samples were temporarily stored in doubled, locking plastic bags for transport back to the laboratory.

2.4.2 Road sediment samples

Fifteen road sediments samples were collected from the Nu‘uanu drainage basin (Figure 5). Ten samples were collected from storm sewer inlets in the lower, heavy traffic areas while five samples came from inlets in upper, light traffic areas. For the heavy traffic samples, inlets were chosen based on proximity to storm sewer outlets that were likely to be the focus of sampling in the stream. In this manner, there would be a linkage between the road and stream sediments for each site (Photos 10 and 11). As bridges tend to have relatively obvious and short direct links to the stream via storm inlets and outlets, most heavy traffic samples were taken from inlets near bridges in dense residential to dense commercial areas (Photos 12 - 15).

To determine the effects of lower traffic areas, five road sediment samples were collected from inlets in the residential areas. These samples were collected more randomly than the heavy traffic samples. Less dense residential areas were identified as potential sampling areas on a map and then samples were collected from inlets in those areas that were accessible and that had significant sediment accumulation.

Using an acid-soaked plastic scoop, a mean grab sample of ~390 g of surface road sediments was collected from each inlet (median sample size was ~440 g with a minimum of ~180 g and a maximum of ~610 g), with the large organic matter removed prior to transport (Photo 16). Between sample sites, the scoop was decontaminated. To avoid contamination from site to site, areas with a low likelihood of trace metal build-up were sampled first followed by areas with a high probability of significant metal contamination. Again, samples were stored in doubled, locking plastic bags until taken to the laboratory.
2.4.3 Stream sediment samples

Prior to sample collection, all visible storm sewer outlets were identified during field reconnaissance trips. The necessary criteria for an outlet to be a viable sampling area included low water velocity, wadeability, sediment deposition zones, a direct and obvious connection from the road inlet to the storm sewer outlet, and at least 40 m between upstream and downstream outlets. The outlet by King and Hotel Streets was to be the lowest sampling site but had to be excluded because the stream was not wadeable that close to the harbor. Thus, six outlets were selected as viable locations, and one more outlet was added that debouched into Waolani Stream just above the confluence with Nu‘uanu Stream (Figure 5). The Judd St. outlet was the furthest upstream followed by the Nu‘uanu St. outlet ~500m downstream. The Kuakini and Waolani St. outlets were each ~250 m downstream from the previous outlet. The Vineyard Blvd. outlet (Photos 17 and 18) was ~450 m below the Waolani St outlet, and Kukui and Beretania St. outlets (Photo 19) were each ~100 m below the previous outlet.

For the stream outlet sediment samples, a different sampling scheme was devised in an effort to illuminate the effect these outlets have on trace metal distribution. Samples were collected at 20 m, 10 m, and 5 m above the outlet, at the outlet mouth, and 5 m, 10 m, and 20 m below the outlet. This sampling methodology was devised for two reasons: (1) to determine if a distance decay function was apparent for trace metal sediment concentrations from urban runoff and (2) to allow for paired statistical comparison of sample units above and below the outlets.

Most samples were collected in the lee of rocks or vegetation or near the point bar bank where flow velocities dropped sufficiently for sediment deposition (Photo 6). From these depositional zones, six 5 cm cores were collected and double-bagged in locking plastic bags for transport back to the laboratory (Photo 20). The corer was thoroughly cleaned between sites.
2.4.4 Water parameters

For the length of the stream, pH and electrical conductivity (EC) were determined at random points in the baseline area at sample site 1, the dense residential area in both Waolani and Nu`uanu Streams before their confluence, and the dense Beretania commercial area at the lowest sampling point. These measurements were taken at the end of the month of fieldwork when the stream had returned to baseflow conditions.

At each of the three points, a small, acid-washed bottle was rinsed three or four times in the ambient water before being filled with stream water. Three drops of concentrated, trace metal grade HNO₃ were added to the 60 mL bottles before they were capped to stabilize the solution and kill any organisms. Unfiltered water samples were analyzed using inductively coupled plasma-mass spectroscopy (ICP-MS). A certified standard water reference material, NIST 1643d, was also analyzed along with the Nu`uanu water samples to assess the accuracy of the laboratory techniques.

In addition to each water sample, a Teflon beaker was used to collect stream water at each point for field measurement of pH, temperature, and electrical conductivity (EC). For EC, the water was gently stirred with the probe to determine a proxy measure of total dissolved solids. pH and temperature (°C) were measured by placing the probes in the water and allowing them to equilibriate. After each use, the probes were washed with distilled water and wiped clean with Kimwipes.

The results of the analysis for trace elements in the water samples were examined for trends in anthropogenic pollutant concentrations and compared to the sediment trace element data. This comparison was for descriptive purposes rather than to establish a statistical relationship.
2.5 Grain size distribution

Upon arrival at the laboratory, each sediment sample was placed in a weighed, labeled, and acid-washed beaker. Samples were oven-dried for 48 h at 105°C and transferred to a dessicator before re-weighing. Each sample was then gently disaggregated by manual crumbling, unless a mud-crack crust had formed on the surface of the sample, in which case gentle grinding with a diamonite mortar and pestle was necessary to release the fines. Initially, the samples were passed through the 2 mm stainless steel sieve, and after the > 2 mm portion was weighed, it was discarded. The remaining sediment was passed through a series of new stainless steel sieves, grading from 1 mm, to 500 μm, to 250 μm, to 125 μm, then finally to 63 μm, using the Ro-Tap automatic sieving machine set at 10 minutes per sample. Samples larger than 500 g were split in half and each half was run through the sieving machine separately to prevent sieve clogging. Between samples, the sieves were thoroughly cleaned with brush and paper towel, and the sieves were washed periodically with distilled water and oven dried at 40°C for 24 hours. Once each sample was partitioned according to grain size, fractions were individually weighed, labeled, and bagged.

2.6 Index of organic matter concentration

To analyze for organic matter in the partitioned samples, loss-on-ignition (LOI) was used. The particular LOI procedure used was adapted from Rhodes et al. (1981) and Ben-Dor and Banin (1989). Approximately 500 mg of the < 63 μm split for each sample (if there was not enough of the < 63 μm split, some of the 63 - 125 μm split was added to the sample to bring the mass up to 500 mg) was placed in a dried and weighed ceramic dish and then in the muffle furnace, set at 450°C, for a minimum of 16 hours. Loss-on-ignition burns off the organic carbon while leaving inorganic carbon behind; temperatures above 500°C liberate carbon from CaCO₃, which is not desired in this experiment. After the
samples were cooled for at least 0.5 h in the dessicator, they were re-weighed, the difference between the two masses being the amount of organic matter in each sample. Using the equation:

$$\text{LOI}_{\text{OM}}\% = \frac{\text{Mass}_{105^\circ C} - \text{Mass}_{450^\circ C}}{\text{Mass}_{105^\circ C}}$$  \hspace{1cm} [2.1]$$

percent organic matter (OM) of the samples was determined.

2.7 Pb analysis

Using a Teflon spatula, between 600 and 700 mg of the < 63 \mu m grain size split from each sample was weighed using an analytical balance and then placed in a clean, plastic 2 mL vial. A total of 100 samples were analyzed: 10 baseline stream sediments, 15 road sediments, 49 outlet stream sediments, 14 duplicate samples, and 12 certified reference material (CRM) samples. The duplicate samples were included to determine measurement precision. The CRM chosen has element concentrations certified for a total digestion procedure and thus cannot be used to assess accuracy. However, they were used as an additional measure of the laboratory’s precision. The CRM that was used was NCS DC73317 (GBW07307), a stream sediment from China with a Pb concentration of 350 mg/kg (total digestion).

To check for instrument drift while at the same time minimizing contamination, the samples were arranged in a specific order. The 10 baseline samples were analyzed first in random order because they were expected to have the lowest levels of levels of pollutants. Three duplicates and a standard followed these baseline samples. Outlets were subsequently analyzed, beginning with the uppermost outlet and ending with the lowermost.
Within each outlet, the samples were randomized, and standards were analyzed between each outlet. For the outlet samples, seven duplicates were included. Finally, the road sediments were analyzed in random order with three standards and four duplicates included.

At the Acme Analytical Laboratory in Vancouver, British Columbia, each 0.5 g sample was mixed with 10 mL of 0.5 M HCl and shaken for 1 hour at room temperature. Finally, each sample solution was filtered and analyzed for Pb and 34 other elements with inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.8 Data analysis

2.8.1 Enrichment ratios

As discussed in the previous chapter, enrichment ratios are an accepted way to evaluate the degree of anthropogenic pollution in sedimentological studies. As the analyses performed in this study include analysis for normalizing elements, such as aluminum (Al), equation 1.2 was employed to determine ER for Cu, Pb, and Zn. Guidelines for enrichment and the thresholds of contamination established by Long et al. (1995) were used to evaluate the degree of enrichment for stream and road sediments and the potential adverse effects of this enrichment on the aquatic system.

Finally, Cu, Pb, and Zn levels on a site by site basis were compared to USGS benchmarks for these metals in sediments to determine if any of the sites exceeded aquatic safety and health levels in the Nuʻuanu drainage basin.

The Al-normalized ER values for sediments in Nuʻuanu Stream and road sediments were compared to data gathered by identical protocols and sediment acquisitions by Sutherland and associates for Palolo Stream (unpublished data). This comparison provided a larger picture of trace metal contamination in Honolulu, as these streams are two of the major streams draining the highly urbanized area. In addition, trace metal values found in these two Honolulu streams were compared to concentrations in major US mainland river
basins as summarized in Rice (1999). This final analysis allowed Honolulu to be compared
to larger drainage basins across the US.

2.8.2 Quantitative analyses

Spearman's non-parametric rank order correlation coefficient ($r_g$) was used to make
global assessments of the relationship between LOI$_{om}$ (%) and % silt/clay and Cu, Pb, and
Zn for stream and road sediment samples. In addition, correlation analysis was used to
determine the relationships between % LOI$_{om}$, % silt/clay, Fe, Cu, Pb, and Zn.

The non-parametric (paired) Wilcoxon signed rank test was used to quantitatively
assess whether statistical differences exist ($\alpha = 0.05$) between samples 5, 10, and 20 m up
and downstream of the outlets.

In StatView 5.0, one way analysis of variance (ANOVA) of log$_{10}$ transformed data
followed by post-hoc testing was used to characterize differences or similarities between Cu,
Pb, and Zn concentrations in baseline sediments, road sediments, and stream outlet samples.
In addition, ANOVA and post-hoc testing was performed on the stream outlet data to
determine whether statistical differences existed between trace metal concentrations in
samples from the upper, residential sites and the lower, commercial sites. Finally, ANOVA
and post-hoc tests were run on the outlet samples to determine if differences existed
between specific sites.

Using the one sample sign test, the Cu, Pb, and Zn concentrations in bed sediment at
the Waolani site were compared to the Pb value the USGS found at a nearby site in 1998.
CHAPTER 3. RESULTS

3.1 Reference precision

Although the stream sediment reference material used in this analysis was designed for total digestion procedures, the precision of ACME Laboratory's procedures can still be examined. GBW07307, under total digestion, has a certified Pb concentration of 350 mg/kg. Using the 0.5 M HCl leach for this experiment, approximately 61% of the Pb was removed from the sediments, or on average, 214 mg/kg. The variation in Pb concentration between the 11 replicate samples of GBW07307 was very low, with a coefficient of variation (CV) of 5.8%. Other important elements examined in this thesis also had low variability between replicate samples of the standard. Aluminum and Fe had CV values of 9.1% and 14.0%, respectively, while Cu and Zn had values of 10.6 and 10.2%, respectively.

The CV for 15 replicate analyses of LOI_{om} was ~20%. With this degree of variation, the LOI_{om} analysis can be considered accurate and thus the variation of organic matter within each sample to be small.

3.2 Descriptive statistics

A detailed statistical summary of the trace metal data is given in Table 3. Trace metal concentrations in road sediment samples were highly variable, with one or two samples exhibiting extremely high concentrations, e.g., Pb concentration of 3140 mg/kg in the sample from Henry Rd. (Figure 5). The occurrence of one or two outlying concentration values has a strong effect on the arithmetic mean and standard deviation for road samples, while the median and median absolute deviation from the median (MAD) values are more robust. For the baseline and stream outlet samples, the mean and median values are closer together, indicating that these sample subsets are less skewed.
Table 3. Descriptive Statistics for trace metals in Nu `uanu drainage basin samples (mg/kg)

<table>
<thead>
<tr>
<th>Metal/Code</th>
<th>Mean ± SD</th>
<th>Median ± MAD</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline (n=10)</td>
<td>22.2 ± 6.1</td>
<td>21.3 ± 3.2</td>
<td>16.5</td>
<td>37.2</td>
</tr>
<tr>
<td>Road (n=15)</td>
<td>235.0 ± 207.1</td>
<td>184.6 ± 135.2</td>
<td>11.8</td>
<td>684.7</td>
</tr>
<tr>
<td>Outlet (n=49)</td>
<td>68.6 ± 25.3</td>
<td>61.4 ± 18.6</td>
<td>33.6</td>
<td>136.1</td>
</tr>
<tr>
<td>Residential (n=28)</td>
<td>48.1 ± 8.9</td>
<td>46.5 ± 7.8</td>
<td>33.6</td>
<td>65.3</td>
</tr>
<tr>
<td>Commercial (n=21)</td>
<td>84.0 ± 22.5</td>
<td>85.6 ± 13.8</td>
<td>44.7</td>
<td>136.1</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>2.9 ± 1.5</td>
<td>2.4 ± 0.5</td>
<td>1.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Road</td>
<td>445.1 ± 787.0</td>
<td>186.3 ± 155.4</td>
<td>11.2</td>
<td>3140</td>
</tr>
<tr>
<td>Outlet</td>
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<td>98.2 ± 29.0</td>
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<tr>
<td>Commercial</td>
<td>158.7 ± 54.5</td>
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<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>20.1 ± 3.6</td>
<td>19.0 ± 2.8</td>
<td>15.5</td>
<td>25.0</td>
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<tr>
<td>Road</td>
<td>902.3 ± 1058</td>
<td>675.0 ± 370.0</td>
<td>36.0</td>
<td>4537</td>
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<tr>
<td>Outlet</td>
<td>174.5 ± 90.5</td>
<td>175.0 ± 77.0</td>
<td>61.0</td>
<td>380.0</td>
</tr>
<tr>
<td>Residential</td>
<td>85.6 ± 16.7</td>
<td>89.0 ± 15.0</td>
<td>61.0</td>
<td>113.0</td>
</tr>
<tr>
<td>Commercial</td>
<td>241.1 ± 59.9</td>
<td>232.5 ± 32.0</td>
<td>130.0</td>
<td>380.0</td>
</tr>
<tr>
<td>Al</td>
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<tr>
<td>Baseline</td>
<td>2750 ± 513</td>
<td>2825 ± 400</td>
<td>1900</td>
<td>3400</td>
</tr>
<tr>
<td>Road</td>
<td>3567 ± 2242</td>
<td>3100 ± 1250</td>
<td>1100</td>
<td>9200</td>
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<tr>
<td>Outlet</td>
<td>4327 ± 1514</td>
<td>3900 ± 1050</td>
<td>1700</td>
<td>8500</td>
</tr>
<tr>
<td>Residential</td>
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<td>3100 ± 500</td>
<td>1700</td>
<td>4200</td>
</tr>
<tr>
<td>Commercial</td>
<td>5268 ± 1273</td>
<td>5450 ± 1075</td>
<td>3250</td>
<td>8500</td>
</tr>
<tr>
<td>Fe</td>
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<tr>
<td>Baseline</td>
<td>1285 ± 492</td>
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<td>800</td>
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<td>3503 ± 2351</td>
<td>2900 ± 900</td>
<td>600</td>
<td>8800</td>
</tr>
<tr>
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<td>4100 ± 1600</td>
<td>1500</td>
<td>9700</td>
</tr>
<tr>
<td>Residential</td>
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<td>2400 ± 400</td>
<td>1500</td>
<td>3500</td>
</tr>
<tr>
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<td>5943 ± 1855</td>
<td>5600 ± 1200</td>
<td>3350</td>
<td>9700</td>
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</table>
Overall, concentrations of trace metals (Cu, Pb, and Zn) in baseline samples appear to be at least an order of magnitude lower than those found in stream outlet samples (n = 49) and road samples (n = 15). When the bed sediment data are divided into two groups, (1) the primarily residential area (n = 28) and (2) the primarily commercial and large highway area (n = 21), it is apparent from the table that trace metal concentrations are higher in the commercial area.

Organic matter and grain size data are summarized in Table 4. For LOI, the road samples had the highest concentrations with a mean value of 22.4% and the highest CV of 29%. The baseline samples had a mean value of 19.8% and a very small CV of 9%. In terms of grain size, the outlet samples had the most silt/clay and sand content, while the road and outlet samples were comprised primarily of gravel with lesser amounts of silt/clay and sands. Sample sites in the upper, residential areas were comprised mostly of sand, while the lower, commercial sites had higher concentrations of gravel and silt/clay sized particles.
Table 4. Descriptive statistics for LOI\textsubscript{OM} and grain size analysis in road and stream sediments in Nu'uanu drainage basin

<table>
<thead>
<tr>
<th>Variable/Code</th>
<th>Mean ± SD</th>
<th>Minimum</th>
<th>Maximum</th>
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</thead>
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<tr>
<td>% LOI\textsubscript{OM}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline (n = 10)</td>
<td>19.8 ± 1.9</td>
<td>16.6</td>
<td>22.6</td>
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<tr>
<td>Road (n = 15)</td>
<td>22.4 ± 6.6</td>
<td>14.0</td>
<td>35.3</td>
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<td>Outlet (n = 49)</td>
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<tr>
<td>Residential (n = 28)</td>
<td>12.9 ± 2.1</td>
<td>7.4</td>
<td>16.2</td>
</tr>
<tr>
<td>Commercial (n = 21)</td>
<td>17.5 ± 4.7</td>
<td>11.5</td>
<td>27.6</td>
</tr>
<tr>
<td>% silt/clay\textsuperscript{*}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>0.6 ± 0.5</td>
<td>0.3</td>
<td>22.6</td>
</tr>
<tr>
<td>Road</td>
<td>1.8 ± 1.8</td>
<td>0.2</td>
<td>35.3</td>
</tr>
<tr>
<td>Outlet</td>
<td>2.3 ± 4.7</td>
<td>0.1</td>
<td>27.6</td>
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<tr>
<td>Residential</td>
<td>0.4 ± 0.3</td>
<td>0.1</td>
<td>16.2</td>
</tr>
<tr>
<td>Commercial</td>
<td>3.7 ± 5.9</td>
<td>0.2</td>
<td>27.6</td>
</tr>
<tr>
<td>% sand\textsuperscript{*}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>34.1 ± 11.4</td>
<td>14.2</td>
<td>51.2</td>
</tr>
<tr>
<td>Road</td>
<td>45.3 ± 20.2</td>
<td>18.8</td>
<td>87.8</td>
</tr>
<tr>
<td>Outlet</td>
<td>56.0 ± 19.1</td>
<td>23.7</td>
<td>94.1</td>
</tr>
<tr>
<td>Residential</td>
<td>61.1 ± 19.4</td>
<td>23.7</td>
<td>94.1</td>
</tr>
<tr>
<td>Commercial</td>
<td>52.2 ± 18.2</td>
<td>28.4</td>
<td>81.2</td>
</tr>
<tr>
<td>% gravel\textsuperscript{*}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>65.3 ± 11.8</td>
<td>16.6</td>
<td>22.6</td>
</tr>
<tr>
<td>Road</td>
<td>52.9 ± 21.6</td>
<td>14.0</td>
<td>35.3</td>
</tr>
<tr>
<td>Outlet</td>
<td>41.7 ± 21.6</td>
<td>7.4</td>
<td>27.6</td>
</tr>
<tr>
<td>Residential</td>
<td>38.5 ± 19.5</td>
<td>7.4</td>
<td>16.2</td>
</tr>
<tr>
<td>Commercial</td>
<td>44.1 ± 23.1</td>
<td>11.5</td>
<td>27.6</td>
</tr>
</tbody>
</table>

\textsuperscript{*}silt/clay = < 63 μm; sand = 63 – 2000 μm; gravel = > 2000 μm
3.3 Water chemistry

When Nu‘uanu water samples were analyzed for trace elements, anthropogenic influence on the aquatic systems was less evident than in the sediment samples. Using NAWQA water benchmarks for Pb (15 µg/L) and Zn (2000 µg/L), Nu‘uanu Stream did not exceed these water quality standards for the samples drawn in late February (Table 5). However, selenium (Se) concentrations in the lowest two sites, where the water is brackish due to tidal influences, were above the USGS freshwater benchmark of 50 µg/L. Unfortunately, the USGS benchmarks do not include values for Cu. Nonetheless, Cu and Pb increased in concentration downstream, indicating greater influence of anthropogenic activity. The trace metal concentrations analyzed from the reference material were consistently above the certified values for NIST 1643d, but considering that neither Pb nor Zn appeared at high enough levels for concern, this level of accuracy is tolerable. Sulfur (S) concentrations also increased by at least one order of magnitude below the School St. confluence of Nu‘uanu and Waolani Streams.

In general, the temperature and EC of the water increased downstream, especially for the sample sites below School St., which is generally considered to be the extent of saltwater intrusion into the stream. In contrast, pH remained relatively constant along the length of the stream, at about 8.
### Table 5. Water parameters and trace metal concentrations for five water samples in the Nu’uanu drainage basin

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu (µg/L)</th>
<th>Pb (µg/L)</th>
<th>Zn (µg/L)</th>
<th>S (µg/L)</th>
<th>Se (µg/L)</th>
<th>Temp (°C)</th>
<th>EC (µS/cm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>0.8</td>
<td>&lt; 0.1</td>
<td>1.4</td>
<td>3000</td>
<td>&lt; 0.5</td>
<td>16.8</td>
<td>105</td>
<td>8.1</td>
</tr>
<tr>
<td>Waolani</td>
<td>1.1</td>
<td>0.7</td>
<td>3.1</td>
<td>11000</td>
<td>&lt; 0.5</td>
<td>20.4</td>
<td>456</td>
<td>8.0</td>
</tr>
<tr>
<td>confluence</td>
<td>3.6</td>
<td>0.3</td>
<td>1.5</td>
<td>5000</td>
<td>&lt; 0.5</td>
<td>20.2</td>
<td>206</td>
<td>8.0</td>
</tr>
<tr>
<td>Nu’uanu</td>
<td>24.8</td>
<td>0.9</td>
<td>10.3</td>
<td>154000</td>
<td>54.3</td>
<td>22.5</td>
<td>9430</td>
<td>8.1</td>
</tr>
<tr>
<td>confluence</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kukui St.</td>
<td>24.8</td>
<td>0.9</td>
<td>10.3</td>
<td>154000</td>
<td>54.3</td>
<td>22.5</td>
<td>9430</td>
<td>8.1</td>
</tr>
<tr>
<td>Beretania St.</td>
<td>60</td>
<td>1.1</td>
<td>6.3</td>
<td>246000</td>
<td>101.3</td>
<td>24.1</td>
<td>223000</td>
<td>8.0</td>
</tr>
</tbody>
</table>

*Distance from mouth: Baseline = 7.5 km, Waolani confluence = 1.1 km, Nu’uanu confluence = 1.1 km, Kukui St. = 0.6 km, Beretania St. = 0.2 km

#### 3.4 Spearman’s correlation analysis

The majority of the sample subsets were positively skewed for Cu, Pb, and Zn concentrations; therefore, \( r_s \) was used to determine whether statistically significant relationships existed between trace metal concentration and % LOI\(_{OM} \), % silt/clay, and % sand, as well as between % LOI\(_{OM} \) and % silt/clay (Tables 6 and 7). For the road sediment samples, there was no significant (\( \alpha = 0.05 \)) correlation between the three trace metals examined and % LOI\(_{OM} \), % silt/clay, and % sand, nor was there a significant correlation between % LOI\(_{OM} \) and % silt/clay. The results for the stream sediments were more varied. Zinc did show significant correlation at an \( \alpha \)-level of 0.05 with % silt/clay in the stream sediments. In addition, % silt/clay and % LOI\(_{OM} \) were significantly correlated in stream sediments. According to the \( r_s^2 \) value, just over 25% of the variation in % LOI\(_{OM} \) can be explained by the % silt/clay of the samples, while 9% of the variation in Zn concentrations can be explained by the % silt/clay of the samples. Thus, even though there is a significant
relationship between these trace metals and the fines of the stream samples, there appears to be one or more additional factors affecting the trace metal concentrations.

Table 6. Spearman correlation matrix for stream outlet sediments

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>%LOI&lt;sub&gt;OM&lt;/sub&gt;</th>
<th>%silt/clay</th>
<th>%sand</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.855&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(&lt;0.0001)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%LOI&lt;sub&gt;OM&lt;/sub&gt;</td>
<td>0.929</td>
<td>0.789</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(&lt;0.0001)</td>
<td>(&lt;0.0001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%silt/clay</td>
<td>0.058</td>
<td>-0.137</td>
<td>0.058</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.66)</td>
<td>(0.30)</td>
<td>(0.66)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%sand</td>
<td>0.245</td>
<td>0.035</td>
<td>0.301</td>
<td>0.506</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.062)</td>
<td>(0.79)</td>
<td>(0.02)</td>
<td>(0.0001)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.141</td>
<td>0.110</td>
<td>0.095</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.28)</td>
<td>(0.40)</td>
<td>(0.47)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.303</td>
<td>0.465</td>
<td>0.140</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.036)</td>
<td>(0.0013)</td>
<td>(0.33)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>r, and <sup>b</sup>P-value

Boldface values are statistically significant at an α level of 0.05.

NA indicates that the correlation analysis was not run between these two variables.
To determine if trace metals were associated with Fe and Mn oxides in Nu‘uanu Stream, Spearman’s test was run on the three trace metals and Fe and Mn. Surprisingly, Fe and Mn were only significantly correlated in road sediment samples. Copper, Pb, and Zn were all significantly correlated to Fe and Mn in road sediment samples. In the outlet samples, Fe was significantly correlated with all three metals, but only Pb was significantly correlated to Mn. Not one of the trace metals was correlated to Fe in the baseline samples, while Mn was significantly correlated to Cu in baseline samples. With $r_s^2$ values ranging...
from 0.09 to 0.77, anywhere from 1/10 to 3/4 of the variance in trace metal concentration can be attributed to the Fe/Mn oxide concentration in the sediments.

Finally, Spearman’s test was used to determine whether any covariation exists between Cu, Pb, and Zn. Indeed, Cu and Zn as well as Pb and Cu concentrations were significantly correlated in road and sewer outlet samples, while Pb and Zn concentrations were significantly correlated in baseline samples as well. These strong correlations indicate that the metals covary within the sediments and are more than likely from similar sources.

3.5 Wilcoxon signed rank analysis (paired)

To determine whether significant differences existed between trace metal concentrations above and below the storm sewer outlets, the non-parametric (paired) Wilcoxon signed rank test was applied to the stream sediment data (n = 21). At α = 0.05, none of the trace elements, Cu, Pb, and Zn, could be said to have significantly different median concentration values above as compared to below the outlets (Table 8).

Table 8. Summary of P-values for the Wilcoxon signed rank analysis: above vs. below the outlets

<table>
<thead>
<tr>
<th>Metal</th>
<th>P-value (α=0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.52</td>
</tr>
<tr>
<td>Pb</td>
<td>0.073</td>
</tr>
<tr>
<td>Zn</td>
<td>0.83</td>
</tr>
</tbody>
</table>

3.6 Analysis of variance

By log_{10} transforming the trace metal data, Zn could be considered normally distributed at α = 0.05. However, log values of Pb and Cu were still more positively
skewed than a normal distribution ($\alpha = 0.05$). Further transformation of these two metals would render the results difficult to interpret, so ANOVA was run on the skewed log$_{10}$ transformed data, followed by a more robust post-hoc comparison test (Games-Howell).

From ANOVA and Games-Howell post-hoc testing, it was apparent that, with P-values ranging from 0.10 – 0.30, there were no significant statistical differences between concentrations of metals above, below, and at the outlets (Table 9). Therefore, these three subgroups were combined into one subgroup, ‘stream outlet’, for the remaining analyses.

### Table 9. Summary of mean metal concentrations for ANOVA analysis on sample position relative to outlet

<table>
<thead>
<tr>
<th>Metal</th>
<th>Mean concentration ± SD (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Above outlet ($n = 21$)</td>
</tr>
<tr>
<td>Cu</td>
<td>67.9 ± 24.6</td>
</tr>
<tr>
<td>Pb</td>
<td>124.9 ± 49.1</td>
</tr>
<tr>
<td>Zn</td>
<td>170.4 ± 88.4</td>
</tr>
</tbody>
</table>

For a summary of ANOVA statistics on the resulting three sample groups, see Table 10. Beginning with the Cu data, ANOVA indicated that there were significant differences between at least two of the groups: baseline, road, and outlet. Since the Cu data are skewed even after transformation, running the more robust Games-Howell post-hoc test was more appropriate than Fisher’s PLSD. This test indicated that only the baseline samples (median concentration = 21.3 mg/kg) were significantly lower than the others. Since ANOVA may be affected by skewed data, the robust Kruskal-Wallis test was also applied to the Cu data and also confirmed that there were in fact significant differences between the groups.
Boxplots of the groups show that the baseline samples were indeed much lower than the other groups but also that the Cu concentration in road sediment samples was higher than the stream outlet sediments, but because the 95% confidence bands overlap, the two are not statistically different (Figure 8). However, the small sample size for some of the groups leads to inaccuracies in the intergroup comparisons as the large confidence bands (representing the 95% confidence band around the median) fold over themselves.

Table 10. Summary of ANOVA and Games-Howell post-hoc testing on Cu, Pb, and Zn median concentrations in Nu‘uanu watershed: baseline, road, and outlet

<table>
<thead>
<tr>
<th>Subgroup</th>
<th>Median concentration + MAD (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Baseline</td>
<td>21.3 ± 3.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>(n = 10)</td>
<td>(n = 15)</td>
</tr>
<tr>
<td>Road</td>
<td>184.6 ± 135.2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>(n = 15)</td>
<td></td>
</tr>
<tr>
<td>Outlet</td>
<td>61.4 ± 18.6&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>(n = 49)</td>
<td></td>
</tr>
</tbody>
</table>

*Letters in the same column that are similar indicate no statistical difference at α = 0.05

Results from ANOVA on the Pb may be biased because of skewness; however, these results agreed with the Kruskal-Wallis test. Both indicated that there were in fact significant differences between the groups. The Games-Howell post-hoc test indicated that the Pb data for the baseline samples were significantly lower than the other groups, and a boxplot of the data supports this claim (Figure 8). However, there was no significant difference between road and outlet samples.

Finally, for Zn, which was normally distributed after transformation, ANOVA indicated that there was at least one significant difference between groups. Once again, Fisher’s PLSD post-hoc test showed that the baseline samples were significantly lower than the other groups. In addition, for Zn, concentrations in stream samples around the outlets
Figure 8. Boxplots of Cu, Pb, and Zn concentrations in sample groups: notches indicate 95% confidence bands while the center line indicates the median value.
were significantly lower than the road sediment samples, as seen in the boxplot (Figure 8).

By splitting the sewer outlet samples into two subgroups, the difference between primarily residential and commercial land-use in the Nu’uanu lower basin could be examined (Table 11). The outlets at Judd, Nu’uanu, Kuakini, and Waolani Streets were dominated by dense residential run-off, while the outlets at Vineyard, Kukui, and Beretania Streets were dominated by runoff from major highways and commercial activity. Applying ANOVA and Fisher’s PLSD to these subgroups indicated that outlets in the commercialized lower basin had mean trace metal concentrations significantly higher (mean concentration of Cu = 80.3, Pb = 147.0, Zn = 222.3 mg/kg) than outlets in the residential mid-basin area (mean concentration of Cu = 59.8, Pb = 122.0, Zn = 138.2 mg/kg). The more robust Games-Howell test confirmed these results. For the parametric tests, a P-value of < 0.0001 and a power value of 1 demonstrated that the ANOVA test was very powerful and that the null hypothesis could be rejected with a high level of confidence.

Table 11. Summary of ANOVA and Games-Howell post-hoc testing on Cu, Pb, and Zn median concentrations in Nu’uanu bed sediments: residential vs. commercial sites

<table>
<thead>
<tr>
<th>Subgroup</th>
<th>Median concentration ± MAD (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Residential</td>
<td>46.5 ± 7.8&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Commercial</td>
<td>85.6 ± 13.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

*Letters in the same column that are similar indicate no statistical difference at α = 0.05
Finally, by coding the outlet samples by site name, ANOVA and post-hoc tests could be used to analyze whether differences in trace metal contamination existed between each outlet (Table 12). Indeed, with a P-value of < 0.0001 and a power of 1, the ANOVA tests showed significant differences between at least two of the outlets.

Table 12. Summary of ANOVA and Games-Howell post-hoc testing on Cu, Pb, and Zn median concentrations in Nu‘uanu watershed: outlets

<table>
<thead>
<tr>
<th>Subgroup</th>
<th>Median concentration ± MAD (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Judd</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.2 ± 4.3a</td>
</tr>
<tr>
<td>Nu‘uanu</td>
<td>46.5 ± 4.1a</td>
</tr>
<tr>
<td>Kuakini</td>
<td>54.7 ± 1.3a</td>
</tr>
<tr>
<td>Waolani</td>
<td>100.2 ± 12.6c</td>
</tr>
<tr>
<td>Vineyard</td>
<td>52.6 ± 7.9c</td>
</tr>
<tr>
<td>Kukui</td>
<td>98.5 ± 13.2ab</td>
</tr>
<tr>
<td>Beretania</td>
<td>85.5 ± 1.4bc</td>
</tr>
</tbody>
</table>

Letters in the same column that are similar indicate no statistical difference at $\alpha = 0.05$

By applying the Games-Howell test to the metal data, it was apparent that the Judd St. outlet in particular was significantly lower in trace metal concentration (median concentration of Cu = 45.7, Pb = 70.2, Zn = 75.0 mg/kg) than the downstream, more urbanized outlets and that the Kukui St. outlet (median concentration of Cu = 113.7, Pb = 227.1, Zn = 288.5 mg/kg) was significantly enriched in metals compared to the other outlets.
3.7 Effects range low/effects range moderate

In general, it can be seen that Cu, Pb, and Zn concentrations in sediments were highest in road samples and lowest in baseline samples (Table 3). For the baseline samples, only Cu levels were higher than the ERL (low effects) threshold of 34 mg/kg, and that only occurred in 1 of the 10 samples of the samples. The other two metals were below the ERL guideline values in the baseline samples.

It was a much different story for the stream outlet and road sediment samples, which had concentrations of metals at levels that were more likely to cause adverse effects on aquatic life. For the stream samples associated with storm sewer outlets, Pb concentrations were especially alarming, with 6.1% of the samples having Pb levels greater than the ERM (median effects) threshold and ~92% of the samples having levels between ERL and ERM (Figure 9). Copper concentrations were also elevated in the stream outlet samples, with 98% of the samples having Cu concentrations between the ERL and ERM thresholds (Figure 10a). Zinc concentrations were not quite as elevated in the outlet samples; just fewer than 45% of the Zn concentrations were below the ERL thresholds for these elements (Figure 10b). Lead was the only metal examined that had levels exceeding the ERM threshold in stream outlet samples (Figure 9).
Dashed lines represent ERL and ERM values for Pb in aquatic sediments, 47 and 218 mg/kg, respectively.

Figure 9. Pb concentrations in Nu`uanu Stream bed sediments and RDS compared to ERL and ERM thresholds
Dashed line represents ERL and ERM values for Cu in aquatic sediments, 34 and 270 mg/kg, respectively.

Figure 10. (a) Cu and (b) Zn concentrations in Nu `uanu Stream bed sediments and RDS compared to ERL and ERM thresholds
Concentrations of trace metals in road sediments were much higher than in the baseline and stream outlet samples. Interestingly, Zn contamination was most prevalent in road samples, with just under 75% of the samples having Zn concentrations higher than the ERM threshold. Lead and Cu had concentrations that fell between these two extremes; approximately 47% of the road samples had Pb levels that exceeded the ERM threshold while 27% exceeded the Cu ERM threshold. Applying the Long et al. (1995) guidelines to road sediments is extending this analysis beyond its capabilities because it was originally designed for marine and estuarine sediments with total digestion. However, the majority of these road sediments end up being flushed into the storm sewer system and ultimately into the streams and ocean, so the high trace metal concentrations are very relevant.

It is important to emphasize that RDS were analyzed following a weak acid leach procedure rather than using a total digestion, and thus it is even more alarming that so many of the samples exceed Long’s thresholds. In Palolo RDS, Sutherland and Bussen (unpublished data) found that Cu, Pb, and Zn recoveries (metal from an HCl leach/metal from a total digestion) were as follows: Cu = 58%, Pb = 84%, and Zn = 73%. Assuming similar recovery relationships would occur in Nu‘uanu RDS, Cu levels would be even more elevated were this research to use total digestions.

3.8 USGS thresholds

When the USGS benchmarks for the protection of aquatic health are compared to the Nu‘uanu stream and road sediment data, Pb contamination is very apparent. Of the 74 total samples, 50 exceed the 91.3 mg/kg PEL (probable effects) benchmark. Of these 50 samples, 11 are road samples (73% of the road sediment samples) and the remaining 39 (80%) are bed sediment samples from around the outlets (Figure 11). These results are alarming considering that over half of the samples taken from the stream have Pb contamination levels higher than what the USGS would recommend for a healthy aquatic
ecosystem. Copper and Zn contamination is less obvious as only 7 road samples (47%) exceeded the Cu benchmark (197 mg/kg) and 11 road (73%) and 4 (8%) outlet samples exceeded the Zn benchmark (315 mg/kg) (Figure 12). Still, the presence of Zn in the stream system is just another indication of the translation of road runoff to Nu‘uanu Stream.

![Graph showing Pb concentrations in Nu‘uanu Stream bed sediments and RDS compared to USGS benchmarks](image)

Dashed line represents the USGS benchmarks for the protection of aquatic life for Pb, TEL = 35.0 and PEL = 91.3 mg/kg, respectively.

**Figure 11.** Pb concentrations in Nu‘uanu Stream bed sediments and RDS compared to USGS benchmarks
Dashed line represents the USGS benchmarks for the protection of aquatic life for Cu, TEL = 35.7 and PEL = 197 mg/kg, respectively.

Dashed line represents the USGS benchmarks for the protection of aquatic life for Zn, TEL = 123 and PEL = 315 mg/kg, respectively.

Figure 12. Cu and Zn concentrations in Nu `uanu Stream bed sediments and RDS compared to USGS benchmarks
3.9 Enrichment ratios

When ERs are calculated for Cu, Pb, and Zn, it is apparent that the road and stream outlet samples are enriched compared to baseline concentrations (Table 13). Lead is the most enriched, with over 3/4 of the samples having ER values of 20 or more, indicating very strong to severe pollution signals. In fact, in both road and outlet samples, ER was > 5 for all samples, meaning that Pb is a significant contaminant in the urban Nu'uanu system.

Zinc also shows a strong to extreme pollution signal in the road sediments, with 3/4 of the road samples having an ER value of 20 or more. For stream outlet samples, Zn enrichment compared to baseline levels is more moderate with 100% of the samples having ER values between 2 and 20.

Finally, Cu exhibits the lowest levels of enrichment in the urban Nu'uanu system. Even in road samples, 20% of the samples have ER values of < 2 which indicates no to minimal pollution. The majority of road samples have ER values of 5 – 20, indicating that road samples are significantly enriched in Cu compared to baseline samples. For stream outlet samples, nearly 100% of the samples are only minimally to moderately polluted with Cu.

3.10 One sample sign test

Using the one sample sign test, the Pb levels at the Waolani Stream sample site (n = 7) were compared with USGS Pb levels, 220 mg/kg, found near the confluence of Nu'uanu and Waolani Streams in 1998 (Figure 5). With a P-value of 0.125, the Waolani HCl leached samples cannot be considered to be statistically different than the USGS total digestion samples. Using the Pb recovery value for Palolo RDS (84%), total Pb at the Waolani sites can be estimated as 245 mg/kg, and the new P-value as > 0.999. Thus, both as analyzed in the weak leach and as estimated in a total digestion, Waolani Pb
concentrations were at levels that were statistically the same as those found by the USGS 4 years ago.

On the other hand, for Cu and Zn, the weak leach Waolani sites (Cu median = 100 mg/kg and Zn median = 300 mg/kg) were significantly lower in concentration than the total digestion USGS levels (Cu = 180 mg/kg and Zn = 480 mg/kg) found in 1998. However, using the recovery values from Palolo RDS for these two metals, the median value for Cu in Nu’uanu Stream under total digestion can be estimated as 172 mg/kg and the median value for Zn as 410 mg/kg. Both of these estimated medians are statistically the same as the USGS concentrations from 1998 (Cu, P-value = 0.45: Zn, P-value = 0.13).

Table 13. Summary of enrichment ratios for Cu, Pb, and Zn

<table>
<thead>
<tr>
<th>Element Code</th>
<th>ER &lt; 2</th>
<th>ER 2-5</th>
<th>ER 5-20</th>
<th>ER 20-40</th>
<th>ER &gt; 40</th>
<th>Median</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Road</td>
<td>20 (3)*</td>
<td>7 (1)</td>
<td>67 (10)</td>
<td>7 (1)</td>
<td>0 (0)</td>
<td>7.53</td>
<td>1.20</td>
<td>23.6</td>
</tr>
<tr>
<td>Outlet</td>
<td>55 (27)</td>
<td>43 (21)</td>
<td>2 (1)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>1.95</td>
<td>0.89</td>
<td>5.19</td>
</tr>
<tr>
<td>Pb Road</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>27 (4)</td>
<td>7 (1)</td>
<td>67 (10)</td>
<td>52.45</td>
<td>13.76</td>
<td>444</td>
</tr>
<tr>
<td>Outlet</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>18 (9)</td>
<td>59 (29)</td>
<td>22 (11)</td>
<td>28.33</td>
<td>13.76</td>
<td>74.4</td>
</tr>
<tr>
<td>Zn Road</td>
<td>0 (0)</td>
<td>7 (1)</td>
<td>27 (4)</td>
<td>40 (6)</td>
<td>27 (4)</td>
<td>25.77</td>
<td>4.48</td>
<td>117</td>
</tr>
<tr>
<td>Outlet</td>
<td>0 (0)</td>
<td>55 (27)</td>
<td>45 (22)</td>
<td>0 (0)</td>
<td>0 (0)</td>
<td>4.59</td>
<td>2.93</td>
<td>14.7</td>
</tr>
</tbody>
</table>

*Values outside parentheses are ER percentages while values in parentheses are ER counts in each pollution category for Cu, Pb, and Zn in Nu’uanu drainage basin bed and road sediments (< 63 μm). Median, minimum, and maximum ER values were calculated from actual ER values rather than percentages.
CHAPTER 4: DISCUSSION

4.1 Baseline sediments

Compared to best estimate baseline values cited in Sutherland (2000a) for the Koolau Basalts and Honolulu Volcanic series, the baseline trace metal values for Nu’uanu Stream are quite low. For example, for Pb, the Nu’uanu baseline concentration value was on average, 2.9 mg/kg (weak leach digestion), while the value cited in Sutherland (2000a) was between 6 and 7 mg/kg (total digestion). However, the values cited by Sutherland (2000a) were total digestion values, which would necessarily make them higher than values garnered from Nu’uanu. Despite the fact that the Pali Highway runs through Nu’uanu Valley, the headwater streams feeding into Nu’uanu stream proper appear to be minimally influenced by anthropogenic activity; limited aerosol transport from traffic on the Pali would produce a significant trace metal concentration decay with distance from the road. In other words, trace metal contamination is expected to decrease exponentially as distance from the Pali Highway increases.

4.2 Road sediments

For the most part, the concentrations of trace metals found in road sediments were not surprising. Generally, samples taken from inlets on the less traveled, upper valley roads had lower levels of Cu, Pb, and Zn, while concentrations increased down valley and near heavily traveled roads. However, there were some interesting exceptions. The Henry Rd. inlet sample had an incredibly high concentration of Pb, at 3139 mg/kg, and moderately high concentrations of Cu (548 mg/kg) and Zn (1172 mg/kg). Considering that this road is in a moderately dense residential neighborhood in the upper valley (Figure 5), one would not expect such high contaminant values. Quite possibly, there may be Pb weights from vehicles collected in the inlet that are releasing high levels of Pb into the road sediments upon breakdown. According to Root (2000), Pb weights commonly fall off automobile
wheels, are rapidly abraded, and accumulate as fine particles along the curb. This accumulation would make very high concentrations of Pb available for transport in urban runoff where it would accumulate in the storm sewer inlets.

The samples taken from inlets on Kukui St. and Liliha St. have very high concentrations of trace metals (Zn = 4357 and 675 mg/kg, respectively), but this is expected at these sites considering the highly urbanized and commercialized environment and the daily traffic volume. Interestingly, both King and Beretania Streets have relatively low concentrations of trace metals in the road sediments (Pb = 105 and 164 mg/kg, respectively). These two roads are very heavily traveled, and one would expect Cu, Pb, and Zn contamination to be higher in the storm inlet sediments. As these streets are in such a high traffic area, it is possible that they are swept more often, thereby removing much of the contaminated RDS before it can collect in the inlets. Another possibility is that there is very little soil in this area to erode into the streets, as Chinatown is highly urbanized with the only green space being A’ala Park. As it is postulated that the majority of the Pb in the stream system is from relic soils where Pb from leaded gasoline emissions is stored, a soil source must be in the area before Pb contamination can build up in the road sediments.

4.3 Anthropogenic influence on the stream system

From the ANOVA and ER analyses of the storm outlets versus the baseline samples, it is obvious that there are major anthropogenic influences on Nu’uanu Stream. Copper, Pb, and Zn concentrations are all extremely elevated in the bed sediments taken from around storm outlets relative to bed sediments sampled from the relatively undisturbed headwaters. Even in the urban-influenced area, Pb levels generally increase from outlet to outlet downstream except for the Beretania St. outlet (Figure 13). This outlet, despite being the closest to the mouth of the stream, and thus probably the most heavily influenced outlet,
had Pb concentration values closer to the Kuakini St. outlet. Kukui St. was the site with the highest contamination levels.

![Graph showing trace metal concentrations and relative distance from the headwaters for Nu 'uanu Stream](image)

**Figure 13. Relationship between trace metal concentrations and relative distance from the headwaters for Nu 'uanu Stream**

Some possible reasons for this deviation from expected results include the fact that the Beretania St. site is extremely brackish, with an EC of 22300 μS/cm. With such a high EC, trace metals may be released into solution easier at this outlet than at the Kukui St. outlet, which is less brackish, or the freshwater sites above School St.. Therefore, less Pb
would be sorbed onto the bed sediments at this site. However, if this scenario were the case, one would expect contaminant levels in the water column greater than those measured. There was some increase in contaminant load in the water samples from Beretania, and especially Kukui St., for Cu and Zn, but not for Pb. Finally, as with the RDS from the Chinatown area, contaminant levels may be lower at the Beretania St. outlet because of the lack of soil in the area or because of dilution from less contaminated RDSs. Without a soil source, Pb contamination may not be as prevalent.

In addition to these possibilities, sediments from the lower outlet sites, at Vineyard Blvd., Kukui St., and especially Beretania St., were visually and in an olfactory sense very different from the upper outlet sites. The sediments from the lower sites were characterized by more fines, a black coloration, and a pungent odor. Bed sediments at Beretania St. were the finest measured (\%silt/clay ranged from 8.6 to 19.6), with the upper sites exhibiting \%silt/clay from 0.1 to 1.6. Also, these lower elevation sites had far more sediment accumulation than the upper sites. Therefore, it is also possible that the metal contamination in the lower reaches of the stream may have been diluted by other contaminants, as well as large sediment influxes. With the number of LUST sites in the Chinatown area of Nu‘uanu, it is likely that organic contaminants play a significant role in the lower watershed.

4.4 Contaminant distribution

One of the major hypotheses in this thesis, that the bed sediments sampled from below the storm outlets would have higher concentrations of contaminants than those from above, had to be rejected. Statistically, the two subgroups were indistinguishable at an \(\alpha\)-level of 0.05. This rather unexpected result may have been influenced by the frequent and higher than normal precipitation inputs in the month of January, just prior to and during sampling. During the sampling period, the stream could not be considered to be at
baseflow. This excess water in the stream system produced a flushing effect, which probably served to evenly distribute contaminants downstream from storm outlets. In addition, contaminants were probably carried further downstream than they would have been under baseflow conditions, thereby affecting the “above” samples in lower storm outlet samples.

Higher discharge in the stream meant that turbulence and shear stress on the bed increased as well, which served to entrain bed sediments into the water column to a greater extent than usual (Knighton, 1998). As more bed sediments were entrained as part of the suspended load in the stream, contaminants that may have been adsorbed and stored in the stream bed were also entrained and carried downstream, thus reducing the distance decay effect at each point source, i.e. storm outlet.

By carrying the contaminants further downstream, storm outlets higher in the stream probably had a greater effect on the contaminant distribution at storm outlets lower in the stream than usual as well. Rather than most contaminated sediments settling out of suspension shortly after exiting from the outlets, the higher discharge may have prevented settling and actively promoted erosion of bed sediments, thus carrying the contaminants into the 40 m area surrounding the next outlet downstream and even further. In addition, sediments from the headwaters with low trace metal concentrations may have diluted the metal concentrations at lower outlet sites.

Despite the heavy rains and high discharges during portions of the sampling period, trace metal contamination in the stream sediments does not appear to have been reduced from previously measured values at the Waolani site. The one sample sign test indicated that the Waolani site metal concentrations were statistically the same as the USGS values from 1998, once the data were corrected to estimates of total digestion concentrations. Such results are not surprising because, although the system was flushed by the high precipitation inputs during winter 2002, heavy rains also can mean lower infiltration rates and thus more
overland flow as well as rilling, higher erosion rates, and transport of road sediments over
greater distances. Indeed, soil moisture contents for much of January were high to the point
where limited precipitation inputs would result in rapid overland flow (runoff) and a flashy
storm hydrograph. Overland flow and rill processes are much more efficient at eroding and
transporting surface sediments, soil or road, downgradient than subsurface transport
processes (Knighton, 1998). Therefore, more surface-associated sediment contaminants
may have been introduced into the system in January and February than usual, as Pb stored
in soils and road sediments was efficiently flushed into storm outlets and ultimately the
stream system.

4.5 Inter-metal linkages

Copper, Pb, and Zn concentrations are significantly correlated in road and stream
sediments. Originally it was postulated that these three metals have anthropogenic sources
that are traceable to automobile use, and the correlation analysis supports this argument.
Without Pb isotope analysis, the correlation between Cu, Pb, and Zn is the only sourcing
tool presently available for this research. By comparing the pattern of trace metal
concentration versus outlet site, the source linkage between the metals is obvious (Figure
13). All three metals follow the same general enrichment pattern from the upper sites to the
mouth. Were one or more of the metals to have a different source than the automobile, the
enrichment pattern in the stream sediments would most likely be different, but instead,
where one is high, all three are high.

4.6 Linkages between RDS and outlet sites

Each outlet bed sediment sample in the stream had a corresponding inlet in the area
that was sampled for RDS. Thus, it is useful to graphically examine the relationship
between each outlet and inlet (Figure 14). An interesting pattern emerges for the three trace
Figure 14. The relationship between Nu'uanu inlets and outlets for Cu, Pb, and Zn.
Figure 15. The ratio relationship between inlet and outlet for Cu, Pb, and Zn at each site (Note: log_{10} Y-axis)

metals, in which most pairs of inlet/outlet were inversely related: as one decreased in metal concentration, the other increased. In addition, traveling downstream, each inlet/outlet pair was the opposite of the one preceding it (Figure 15). This pattern was not expected as it seemed more likely that should metal concentration in an inlet be high, the same metal concentration in the outlet would also be high, and vice versa. Also, a more consistent pattern of metal enrichment downstream was expected.

One possible explanation of the inverse relationship between linked inlet and outlet may have been that metal concentrations at each outlet site was more linked to the inlet at the
sample site upstream. As stream discharge was high during the sampling period, it is likely that sediments flushed into the stream from storm inlets were not deposited until further downstream and thus did not affect the sediments at the linked outlet, but rather the next sampling point down.

As for the pattern of inverse variation between each inlet/outlet pair and adjacent inlet/outlet pairs, other factors, such as dilution effects may have affected the concentrations. However, I could not come up with a plausible explanation for this phenomenon.

4.7 Aquatic health thresholds

According to the comparison with both Long’s thresholds and USGS TEL/PEL guidelines, Nu‘uanu Stream bed sediments have levels of trace metals that are most likely adversely affecting aquatic health. Lead especially was above these two thresholds, particularly in the lower portion of the drainage basin. Considering that Hawai‘i has problems with alien species flourishing in stream ecosystems while native flora and fauna gradually disappear, high trace metal concentrations in the streams are of concern. Alien species generally have higher tolerances for polluted stream ecosystems, so when urban streams degrade, as Nu‘uanu Stream has, alien species are given the advantage over native species (State of Hawaii Department of Land and Natural Resources, 2002).

4.8 Trace metal complexation

From correlation analysis it appears that the trace metals Cu, Pb, and Zn are significantly related to Fe/Mn oxides in the sediments, but not significantly related to the % LOI\textsubscript{om} or % silt/clay, as originally assumed. Although this result was somewhat surprising, it is not inexplicable. Lead especially is often more highly correlated to Fe and Mn oxides than with organic content in a system, and the correlation between Pb and the fines in bed sediment is dependent on the coating on the particles. According to Horowitz (1991), many
trace metals, including Cu, Pb, and Zn, bind most readily to amorphous Fe oxides, followed by organic matter, total extractable iron, and particles smaller than 63 μm. In the Nu‘uanu system, it seems likely that the silt and clay particles may be coated with Fe oxides more than organic matter, resulting in the lack of correlation between LOI_{om} and Cu, Pb, and Zn.

It is also important to consider grain size distribution in Nu‘uanu Stream as a factor in this correlation analysis. Limited availability of clay and silt sized particles in a stream system would influence metal sorption processes. However, in Nu‘uanu Stream, the primary grain size, sand, was also not significantly correlated to metal loadings, which may suggest that grain size is not as important a factor in this system as was assumed initially.

4.9 Sulfur

As a brief aside in this discussion, the S concentrations in the lower watershed are worth mentioning. Sulfur levels were negligible in the water samples from Nu‘uanu Stream until the two brackish water samples at Kukui and Beretania Streets, where they suddenly increased by a factor of 31 – 49. Judging from the discoloration and texture of the sediments in this area, it seems possible that the sedimentary environment at these two sites was anaerobic. If the sediments were anoxic, then anaerobic bacteria, which usually produce S as a byproduct of respiration, would flourish in the sediments, thereby increasing S concentrations in the area.

4.10 Comparisons to other data sets

For many bed sediment studies across the US, total digestion procedures were used for analysis rather than the more appropriate bioavailable extraction used in this thesis. This difference in digestion procedure makes comparing data sets challenging. As previously mentioned, total digestion releases more trace metals into solution than weak leaches.
However, it is still interesting to compare the various data sets, as some of the sites in Nu’uanu Stream exceed sites from other data sets despite the weaker leach.

4.10.1. Pb intercomparison: US mainland rivers and Honolulu streams

Contaminant data from 20 drainage basins across the US were compiled by Rice (1999). The median Pb concentration values from these basins are graphically compared to median Pb values from another urban Honolulu system, Palolo Stream (Sutherland and Bussen, unpublished), as well as Nu’uanu Stream (Figure 16). Lead values for the continental US basins were the result of total digestion procedures, and yet Nu’uanu Stream has the highest median Pb concentration of all the drainage basins aside from Palolo Stream. If these two Hawai‘i streams had been studied using total digestion, Pb levels would have been even more elevated. What is alarming is that many of the US drainage basins examined in Rice’s (1999) paper are located in areas that have been major metropolitan and industrial centers for hundreds of years. And yet, it is apparent from this graph that Pb contamination is a more significant problem in Honolulu despite the fact that there are no major industrial sources of Pb in the Hawaiian Islands and that Honolulu is a fairly young city.

Figure 16. Comparison of median Pb bed sediment concentrations (mg/kg) across the conterminous US and Hawai`i
4.10.2 Cu, Pb, and Zn: Comparison to major US rivers and Palolo Stream

It is also valuable to compare Cu, Pb, and Zn concentrations in Nu’uanu and Palolo Streams to three of the major river systems in the mainland US (Figure 17). Both the Hudson River and the Connecticut-Housatonic-Thames River system drain sections of the northeast US, and the Upper Susquehanna River drains the upper Mid-Atlantic Region. These three systems all traverse major metropolitan and/or industrialized centers where anthropogenic influences are known to be significant. Compared to the streams in Honolulu, these rivers support much more extensive but less dense populations, greater traffic volumes, although not always in close proximity to the rivers, and industrial and mining discharges. Despite these differences, Honolulu stream bed sediments appear to be similarly polluted in terms of Cu, more polluted in terms of Pb, and only slightly less polluted in terms of Zn. In addition, once again it should be mentioned that the three mainland river systems were analyzed using total digestion procedures, which elevates the trace metal concentrations above the bioavailable fraction that was found in Honolulu’s stream bed sediments.
Concentrations included in this figure were extracted from Rice (1999) and Sutherland and Bussen unpublished data.

**Figure 17. Comparison of trace metals between three major US mainland river systems and Honolulu streams**

4.11 ER Comparisons to Palolo Stream data

4.11.1 Bed sediments

Within urban Honolulu, it is also helpful to compare ER values of Nu`uanu and Palolo Streams (Table 14 and Figure 18). Sampling in Palolo Stream was in 50 m intervals rather than focused around major storm outlets. In terms of Cu contamination, Palolo Stream is slightly more contaminated than Nu`uanu Stream, but both have relatively low ER values, with most sites < 5. Nu`uanu Stream had a higher percentage of extremely polluted
sites, > 50%, while Palolo Stream had a high percentage of strongly polluted sites, > 60%. Zinc contamination is slightly higher in Nu‘uanu Stream; however, Palolo Stream has a wider distribution of ER values, ranging from minimally to extremely polluted; all the sites in Nu‘uanu Stream have ER values that indicate moderate to significant pollution.

Table 14. Summary of Median ± MAD ER values for Palolo and Nu‘uanu Stream sediments

<table>
<thead>
<tr>
<th>Watershed/Metal</th>
<th>Median ER ± MAD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Palolo</strong></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.1 ± 0.6</td>
</tr>
<tr>
<td>Pb</td>
<td>25 ± 7</td>
</tr>
<tr>
<td>Zn</td>
<td>4.9 ± 1.3</td>
</tr>
<tr>
<td><strong>Nu‘uanu</strong></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>Pb</td>
<td>29 ± 7</td>
</tr>
<tr>
<td>Zn</td>
<td>6.3 ± 1.2</td>
</tr>
</tbody>
</table>
Figure 18. Comparison of Al-normalized enrichment ratios for Cu, Pb, and Zn between Nu`uanu and Palolo Stream bed sediments.
4.11.2 Road sediments

Comparing RDS between the two Honolulu drainage basins reveals that Nu’uanu and Palolo (n = 20) have similar contamination problems (Table 15 and Figure 19). For Cu, pollution levels in both basins were relatively low, with most of the sites falling in the moderately to significantly polluted ER categories. Nu’uanu basin had more sites in the significantly polluted category than Palolo. Looking at Pb, it is apparent that both basins have significant Pb contamination in road sediments; greater than 66% of Palolo sites and greater than 60% of Nu’uanu sites fall into the extremely polluted category. Finally, for Zn, Nu’uanu had significantly more sites in the very strong to extreme pollution categories than Palolo.

Table 15. Summary of Median ± MAD ER values for Palolo and Nu ‘uanu RDS

<table>
<thead>
<tr>
<th>Watershed/Metal</th>
<th>Median ER ± MAD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Palolo</strong></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>6.4 ± 3.2</td>
</tr>
<tr>
<td>Pb</td>
<td>47 ± 20</td>
</tr>
<tr>
<td>Zn</td>
<td>8.3 ± 3.5</td>
</tr>
<tr>
<td><strong>Nu’uanu</strong></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>7.4 ± 2.8</td>
</tr>
<tr>
<td>Pb</td>
<td>53 ± 37</td>
</tr>
<tr>
<td>Zn</td>
<td>26 ± 15</td>
</tr>
</tbody>
</table>
Figure 19. Comparison of Al-normalized enrichment ratios for Cu, Pb, and Zn between Nu'uanu and Palolo RDS.
Future Research

This research indicates that trace metal contamination in the Nu‘uanu watershed is a very significant problem, and further research is needed to fully analyze the extent of this problem. Future research on the linkages between RDS, storm sewer outlets, and distribution of these trace metals would do well to avoid periods of stormflow and resample at a later date to determine temporal variability. Lead isotope analysis on the sediments collected for this research would help to answer questions about the main source of Pb in the stream, which is important to consider, as Honolulu streams have anomalously high levels of Pb. Toxicity studies on aquatic organisms would be useful to corroborate the importance of the empirical thresholds used in this study. Finally, organic contaminants most likely play an important role in the state of the ecosystem in the lower reaches of Nu‘uanu Stream, and research focusing on this problem would help to draw a more complete picture of the extreme effects that the urban environment has on stream systems.
Conclusions

It is apparent that trace metal pollution is a problem in Nu‘uanu Stream. Results from this research support the idea that the likely source of Cu, Pb, and Zn in the urban environment is automobiles. Copper and Zn likely have contemporary sources while the source of Pb is more likely relic, presently undergoing remobilization through soil erosion. In Hawai‘i, high population densities on such small watersheds probably contribute to the elevated levels of pollution compared to larger, continental watersheds. Road-deposited sediments have very high concentrations of contaminants, and ultimately, these sediments are flushed into the stream systems, where they have the potential to adversely affect aquatic health. Ultimately, pollution in Honolulu streams is not going to improve as long as RDSs are allowed to flush into the streams untreated. Filtering the stormwater runoff before allowing it to debouch into the streams might help to curb trace metal pollution. Significant findings from this thesis include the following:

- Concentrations of Cu, Pb, and Zn in bed sediments in the urban Honolulu area, Nu‘uanu Stream, were significantly higher than baseline concentrations.
- Concentrations of Cu, Pb, and Zn generally increased with distance downstream in both water samples and bed sediment samples.
- Trace metals were associated mainly with Fe/Mn oxides in Nu‘uanu Stream with no significant correlation to the fines or organic matter.
- Copper, Pb, and Zn concentrations were significantly inter-correlated, indicating that these three metals are likely from a similar anthropogenic source (probably automobiles).
- There was no significant difference between metal concentrations in bed sediments above and below the outlets, most likely due to the heavy precipitation and frequent storm events during the sampling period, January and February 2002.
• Road-deposited sediment samples (median concentrations of 185, 186, and 675 mg/kg for Cu, Pb, and Zn, respectively) were significantly enriched in trace metals compared to baseline (median concentrations of 21, 2, and 19 mg/kg for Cu, Pb, and Zn, respectively) and outlet concentrations (median concentrations of 61, 122, and 175 mg/kg for Cu, Pb, and Zn, respectively).

• Road-deposited sediments associated with storm sewer inlets were inversely related to bed sediments around storm sewer outlets, suggesting that material from the storm sewer system was carried further downstream before settling out.

• ERL/ERM, TEL/PEL (USGS), and ER analyses all suggest that trace metals are likely to be adversely affecting the aquatic environment in Nu‘uanu Stream, especially in the case of Pb, where ~ 98% of the outlet samples had concentrations higher than ERL, ~ 80% exceeded the USGS PEL standard, and > 75% had an Al-normalized ER value of > 20.

• Compared to data from other US watersheds, Nu‘uanu Stream has higher Pb concentrations than all other NAWQA-sampled streams, despite the fact that USGS used total digestion while this research used a weak acid leach. Copper and Zn levels are more comparable to concentrations found across the US, but again two different extraction techniques were used, so levels in Nu‘uanu Stream are more alarming than might appear at first glance.

• Compared to Palolo Stream and road sediments, Nu‘uanu Stream showed a similar pollution pattern, with very high ER values for Pb and ER values for Cu and Zn high enough to cause concern. These two watershed analyses point to a serious inorganic pollution problem in Honolulu streams.
Appendix: Photographs

Photo 1: Waolani Stream just before the confluence with Nu‘uanu Stream: view upstream

Photo 2: Nu‘uanu Stream just before the confluence with Waolani Stream: view upstream
Photo 3: School Street park where the channelization of Nu’uanu Stream begins

Photo 4: Birdseye view of the beginning of the channelization of Nu’uanu Stream
Photo 5: Fully channelized section of Nu'uanu Stream passing under School St. and the H-1 Freeway: view downstream

Photo 6: Exposed sediment bar downstream of Vineyard Blvd. and view of Chinatown: low-tide, near-baseflow conditions
Photo 7: Exposed sediment bar and turbid water downstream of Vineyard Blvd.: low tide, decreasing discharge after a rainfall event

Photo 8: Baseline starting point: man-made dam
Photo 9: Baseline starting point: pool behind dam

Photo 10: Nu’uanu inlet: RDS sample site
Photo 11: Nu'uanu outlet with evidence of high discharge: flattened vegetation

Photo 12: Residential area opposite the Nu'uanu outlet
Photo 13: Residential area just above the Waolani outlet

Photo 14: Beretania St. bridge crossing Nu‘uanu Stream: view upstream
Photo 15: Beretania St. bridge crossing Nu`uanu Stream: view downstream toward Honolulu Harbor and the industrial sector

Photo 16: Road-deposited sediment sampling (inlet): Ross Sutherland and Stephanie Andrews
Photo 17: Vineyard Blvd. storm sewer outlet

Photo 18: Nu‘uanu Stream passing under Vineyard Blvd.: view downstream towards Downtown and Chinatown
Photo 19: Beretania St. storm sewer outlet

Photo 20: Stream bed sediment sampling at the Kukui St. outlet: Toby Vana and Ross Sutherland
References


http://www.hawaii.gov/dbedt/db00/index.html

http://www.hawaii.gov/dlnr/dar/stream_aliens.htm


