Analysis of Marine Sediments Collected in Cook's Bay, Mo'orea, French Polynesia

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Abstract Sediments can act as a major pollutant reservoir for heavy metals that will often bioaccumulate through the food chain. To determine background concentrations of heavy metals in marine sediments, as well as sediment size distribution and percent organic content, samples were collected from Cook's Bay, Mo'orea, French Polynesia. Sediment traps were placed in the east side of Cook's Bay and collected weekly. Samples were then decanted, filtered, and dried. They were analyzed for heavy metal content using Inductively Coupled Plasma Emission Spectrometry (ICP). Sediment size distribution was determined using Stoke's Law, and percent carbon was measured using a muffle furnace. Enrichment factors were determined for elements with high average concentrations to determine excess input of these elements into Cook's Bay. Aluminum, iron, magnesium, nickel, and silicon negatively correlated with distance from the freshwater inlet as originally hypothesized. Sediment size and percent carbon did not correlate with distance from the freshwater inlet as hypothesized. According to enrichment factors, aluminum, iron, manganese, and silicon are lithogenous in origin while it is unclear whether nickel and sulfur are anthropogenic in origin. Overall heavy metal and elemental contamination is low in Cook's Bay, but it should be monitored in the future with the advent of increasing agriculture and housing development.

Introduction

A distinguishing characteristic of volcanic islands is their extreme susceptibility to disturbance (Fosberg 1963). These include natural disturbances such as cyclones and erosion, but also anthropogenic stresses. Evidence from Hawaii, New Zealand, Easter Island, Mangaia, Tikopia, Aneityum, and Fiji reveal pre-historic human impacts including deforestation, erosion and alluvial extension of coastal plains, and faunal depletion (especially endemic species) (Hughes, et al. 1979). In addition, human cultivation of land for agriculture can also cause disturbances to natural vegetation and composition of soils.

Agriculture may be disruptive by releasing toxic chemical byproducts and causing land degradation and loss of vegetative matter. The loss of vegetation that binds soils increases sediment loading into streams, estuarine, and marine environments (London and Tucker 1992). Sedimentation is an increase in the thickness of a sediment body caused by the addition of material from a plume or run-off from the land at a body of water's upper surface (Larcome and Woolfe 1999). Sedimentation can cause severe damage to marine ecosystems by reducing light availability for photosynthesis of algal and coral species.

In addition, sediments can act as a major pollutant reservoir because metals and other contaminants can bind to the sediments and become bioavailable to the rest of the food chain (London and Tucker 1992). Several organisms such as filter feeders take in low levels of heavy metals which then bioaccumulate through the food chain. Bioaccumulation is the accumulation of food contaminant by oral uptake and digestion (Streit 1998).

Heavy metals, in particular, have a high affinity for fine sediment particles. Most fine sediment particles are discharged by rivers and transported into the sea by means of small particulate matter (Palanques et al. 1995). These are highly concentrated in surface and near bottom turbid layers of the ocean. High concentrations of heavy metals have also been correlated with a higher content of organic matter (Palanques et al. 1995).

The sources of heavy metal contamination vary from natural abundance in volcanic basalts to contamination from non-point sources of pollution. Lead and cadmium are mainly distributed to the environment from airborne chemicals that are natural and man-made (such as fossil fuel burning), industrial airborne chemicals, auto exhausts, intensive agriculture, and forestry. Cadmium, zinc, copper, and nickel are used in several fertilizers, fungicides, and pesticides used mainly for the sugarcane and pineapple industries (McMurtry et al. 1995). Lead is found in areas near roadways where unleaded fuel is used. A significant amount of total lead present in surface waters exists as suspended matter.

Previous studies have found extremely large quantities of fine sediment (clay particles) in Cook's Bay, Mo'orea, French Polynesia. Clay particles are more likely to be found in areas downstream of exposed topsoil such as is the case in the Pao Pao Watershed (Cox 1964). The area encompassing the Cook's Bay watershed contains Pao Pao Valley and Pao Pao River that runs fresh water directly into the marine environment of the bay. Agriculture, housing, and roads are the main form of development, and the pineapple plantations in Pao Pao Valley are the main constituents of agriculture within the watershed. These pineapple plantations make use of frequent ditches for drainage and lack significant ground cover. London and Tucker (1992) proposed that these ditches increase the rate that water flows through the valley and into the marine environment. If these ditches were absent, water would flow overland or as subsurface flow to the stream. In addition, the lack of ground cover in the fields contributes to a significant sediment plume created in Cook's Bay during heavy rainfall.

The current concentrations of heavy metals, the types of heavy metals, and the presence of various elements that may be present in the existing sediment entering Cook's Bay are unknown. The purpose of this study is to determine background concentrations of heavy metals and elements found in sediments of Cook's Bay, as well as to determine whether they are antropogenically introduced. In addition, this study will analyze sediment size and percent organic (carbon) content. Hypotheses are 1) higher concentrations of heavy metals will be found in sediments closer to the inlet of freshwater, 2) elements present in high concentrations will be anthropogenic in origin, 3) larger sediment sizes will be found closer to the inlet of freshwater, and 4) a higher percent of carbon (organic matter) will be found closer to the inlet of freshwater.

Materials and Methods

Study Site Spot sampling was completed within coral reefs of Cook's Bay, and at the east back reef near the barrier reef in Mo'orea, French Polynesia. Mo'orea is a volcanic island, the second youngest island in the Society Archipelago, and it is located in the Eastern Pacific at 17° S and 149° W (see Figure 1). Steep volcanic mountains surround Cook's Bay on all sides, and there is a valley at the south end of the bay. Several agricultural fields consisting of pineapple plantations are scattered within the valley and Pao Pao River runs through the valley into the bay. During heavy rains (starting in November and ending approximately around April), a sediment plume develops that causes a huge influx of sediment particles into the bay (London and Tucker 1992). At the time this study was conducted (October and November of 2002), there was an extensive dry spell that lasted until the last week of the experiment (November 11-17).

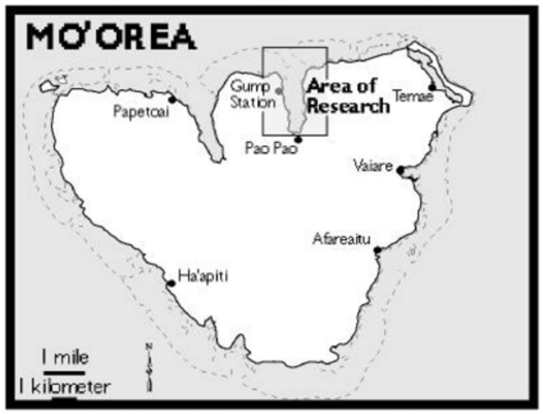

Figure 1. A map of Mo'orea, French Polynesia showing where the research for this study was completed.

Because Mo'orea is a volcanic island, there are several different types of glassy basalts, and porphyritic oceanites and ankaramites. Many of the porphyritic types can be found along the shores of Cook's Bay. Several metals and elements exist within the lavas and oceanites found naturally on Mo'orea. These include silica, aluminum, iron, magnesium, calcium, sodium, potassium, tin, phosphorus, and manganese (Williams 1933).

Collection Methods Sediment samples were collected in Cook's Bay starting near the entrance of the freshwater source out to the back reef (see Figure 2). Ten sediment traps were made and placed at five sites along the east side of Cook's Bay. The spot testing took place on the east side of Cook's Bay due to the presence of the coral reef structure that extends along that side of the bay as opposed to the west side which has no coral in addition to a steep drop-off. Two sediment traps were located at each spot within the bay and south of a colony of *Porites*. The sediment traps were left out for a week and then the sediment was collected.

The traps were made using PVC piping with a height:diameter ratio of 5. According to Hargrave and Burns (1979), this is the best method to collect sediment in a turbulent area without resuspension of sediments within the traps (see Figure 3). The pipes were placed in plastic flowerpots and wet mixed cement was placed around them. The traps were placed in an air-conditioned room to be dried overnight. The traps were placed randomly at each of the five sites.

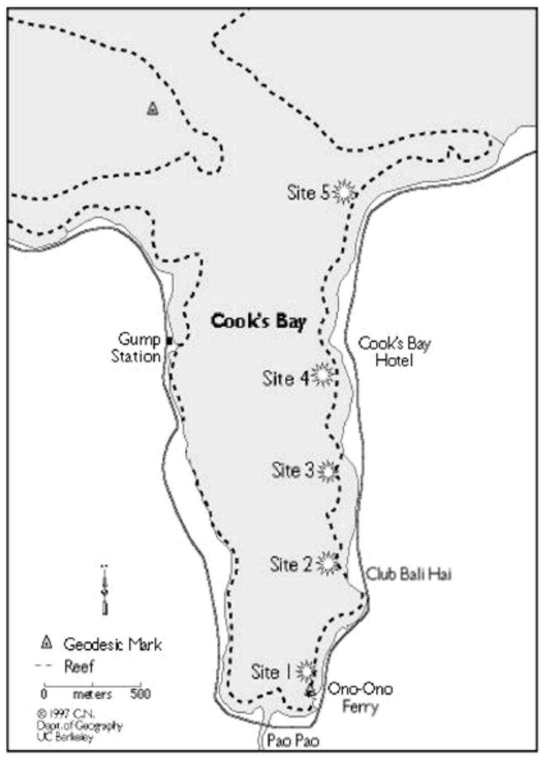

Figure 2. A map of the location of the five sites within Cook's Bay at the East side where this study was completed. Department of Geography, University of California, Berkeley.

The traps were collected every Wednesday for 5 weeks. For sediment collection, each trap was emptied into a plastic or glass bottle and then the lid was shut. At the dry lab, samples were allowed to settle and then the liquid was decanted. Samples were then filtered using 125-millimeter filter paper and allowed to dry in an air-conditioned room (approximately 1.5 days).

The dried samples were then taken back to the University of California, Berkeley to be analyzed for heavy metals, sediment size, and percent carbon.

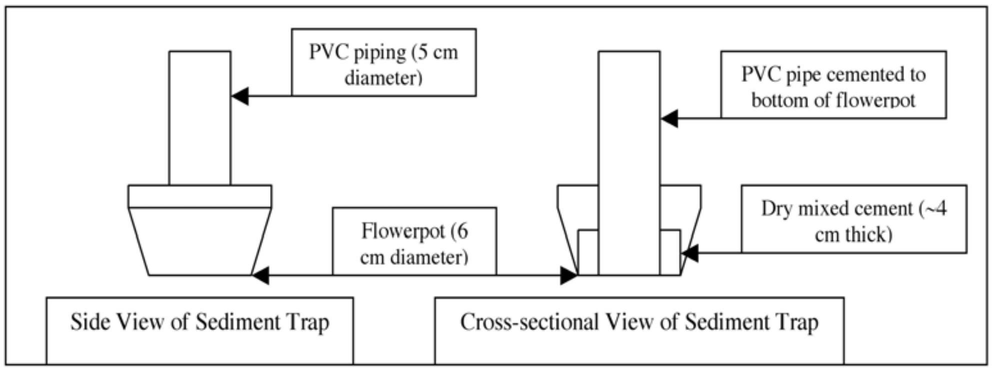

Figure 3. Side and cross-sectional view of sediment traps (with measurements) used for this study.

Analysis of Sediments The marine sediments were wet acid digested using 70% nitric acid to extract weakly bound metals that originated from anthropogenically contaminated waters (Palanques et. al 1995). The samples were then analyzed for heavy metals using Inductively Coupled argon-Plasma emission spectrometry (ICP). Sediment size and composition of the sediments were analyzed using a settling tank and percent carbon was determined using a muffle furnace.

Enrichment Factors To determine whether certain heavy metals and elements were present in high concentrations relative to the their concentrations in the earth's crust, an enrichment factor was calculated using the equation from Szefer et. al (1996). This includes normalization of element concentrations relative to a conservative element that is dominantly lithogenous in origin (in this case aluminum). This calculation is as follows:

$$EF = \frac{C^{MX} - C^{NaX}(C^{M}/C^{Na})s \; : \; C^{MC} - C^{NaC}(C^{M}/C^{Na})s}{C^{AlX} - C^{NaX}(C^{Al}/C^{Na})s \; : \; C^{AlC} - C^{NaC}(C^{Al}/C^{Na})s}$$

where superscripts X, S, C, M refer to sediments, seawater, the earth's crust, and the element respectively. The average earth's crust values and seawater concentrations were taken from Harte (1988). Enrichment factors close to one are comparable to concentrations found in the earth's crust. In contrast, elements with enrichment factors larger than one may be due to sources other than natural weathering of the earth's crust. In addition, strong correlations with aluminum and enrichment factors close to one, represent elements present in marine sediments due to natural weathering processes.

Statistics A linear regression was completed to determine whether heavy metals correlated with distance from the freshwater inlet. Linear regressions were also completed to determine if sediment size and percent carbon content correlated with distance from the freshwater inlet. The program JMP™ was used for all statistics.

Results

ICP Results The results from ICP show that only certain metals out of those tested were present in high concentrations and only some metals had correlation with distance from the freshwater inlet. Of those metals present in high concentrations the following negatively correlated with distance from the shore: aluminum (r^2 = 0.924, p<.0001), iron (r^2 = 0.947, p<.0001), manganese (r^2 = 0.911, p<.0001), nickel (r^2 = 0.919, p<.0001), and silicon (r^2 = 0.503, p=.0001) (see Figure 4).

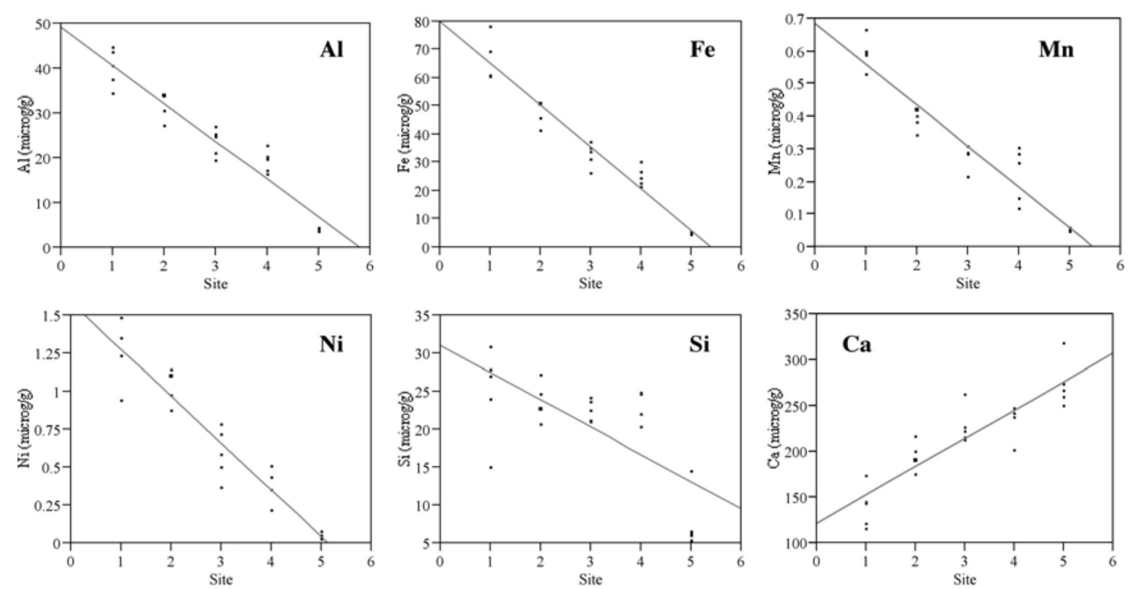

Figure 4. Concentrations (μg/g) of aluminum, iron, manganese, nickel, silicon, and calcium and the correlation of each metal with sites 1-5 in Cook's Bay, Moorea, French Polynesia.

Calcium was the only mineral to positively correlate with distance from the freshwater inlet ($r^2 = 0.799$, $p<.0001$).

Other minerals were present in the marine sediments in high concentrations, but these did not follow any regular pattern regarding distance from the freshwater inlet. There was no correlation with distance from the inlet for potassium ($r^2 = 0.243$, $p=0.014$), magnesium ($r^2 = 0.006$, $p=0.714$), and sulfur ($r^2 = 0.000$, $p=0.993$).

Enrichment Factors The enrichment factors for all of the elements, as well as each element's correlation coefficient with aluminum, are shown in Table 1. A minor correction was added to the equation to take into consideration not only the amount of the element present in the sediment, but also the amount of sodium (assuming it is purely of seawater origin).

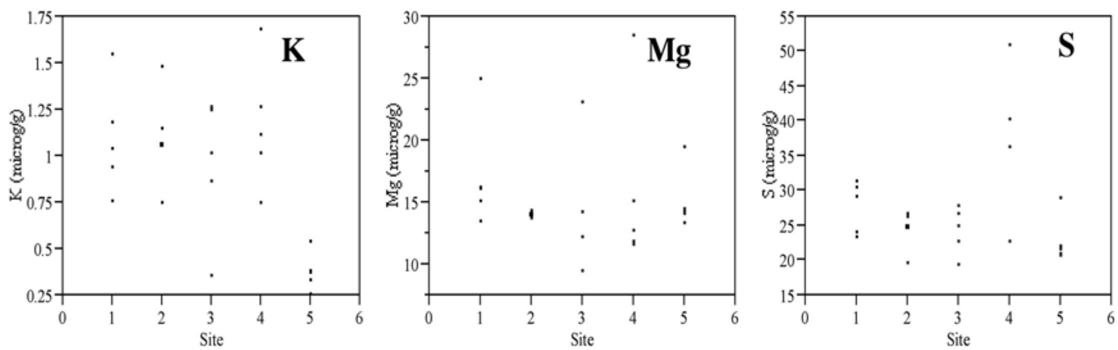

Figure 5. Concentrations (μg/g) of potassium, magnesium, sulfur and the correlation of each metal with sites 1-5 in Cook's Bay, Moorea, French Polynesia.

Sediment Size The analysis of sediment size between sites 1-5 show that there was no correlation between percent of sediment particles of 62.5 μm or greater and distance from the freshwater inlet ($r^2 = 0.026$, $p > .4881$). There is no significant difference in sediment size between sites 1-5 (see Figure 6).

Percent Carbon The analysis of percent organic content between sites 1-5 showed that there was no correlation between percent organic content of each sample and distance from the freshwater inlet ($r^2 = .003$, $p > .8285$). There was no significant difference in percent organic content between sites 1-5 (see Figure 6).

Element	Enrichment Factor	r^2	p-value
Aluminum	1.00	1.00	< .0001
Calcium	36.70	0.84	< .0001
Iron	1.90	0.96	< .0001
Potassium	0.13	0.39	.0012
Magnesium	3.89	0.03	.4477
Manganese	1.00	0.94	< .0001
Nickel	20.03	0.87	< .0001
Silicon	0.34	0.60	< .0001

Table 1. Enrichment factors for elements aluminum, calcium, iron, potassium, magnesium, manganese, nickel, sulfur, and silicon and r-squared values for correlations with aluminum.

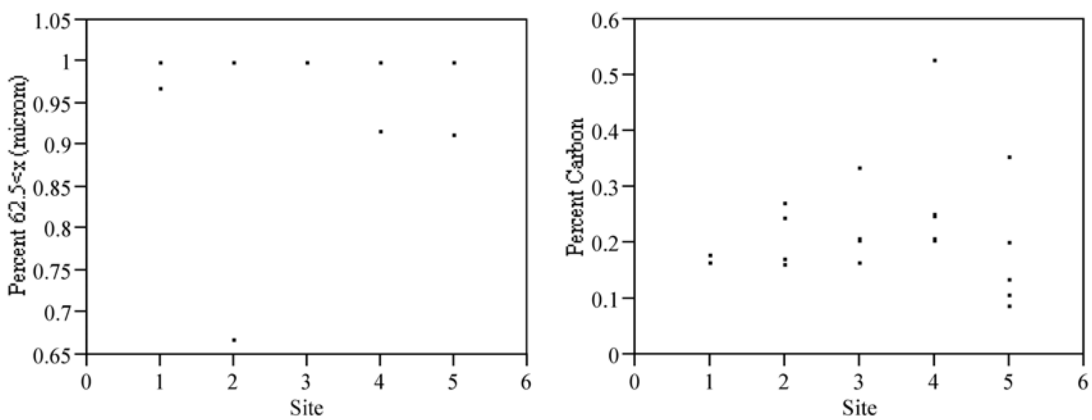

Figure 6. Correlations between 1) percent of sediment particles 62.5 μm and larger and distance from the inlet of freshwater and 2) percent carbon and distance from the inlet of freshwater in Cook's Bay, Mo'orea.

Discussion

The results collected from ICP support the alternative hypothesis that certain metals will negatively correlate with distance from the freshwater inlet. In regard to the high concentrations of aluminum, iron, magnesium, nickel, and silicon found in sediments near the freshwater inlet, this result was to be expected because when a freshwater river enters a marine environment flocs form. Flocculation occurs in areas where freshwater mixes with saltwater. This causes fine sized particles to cluster together forming flocs that have larger settling velocities than individual particles (Larcome and Woolfe 1999). It has been suggested that metal anomalies (high concentrations relative to other elements) are caused by rapid settling of highly contaminated flocs (Palanques et. al 1995). According to Gibbs (1986), this process is due to the scavenging of metals that takes place when flocculation occurs at transition zones. This often is the reason that marine sediments have higher concentrations of mobile heavy metals and elements than the surrounding water column (James and Evison, 1979).

Potassium, magnesium, and sulfur did not correlate with distance from the freshwater inlet, and there are several reasons for these results. The sample size for each site was only 5, which is normally not large enough to yield statistically significant data. There is a possibility that the samples do not accurately reflect concentrations of these elements due to the dry season encountered during this study. Lastly, these elements may be associated with absorption to the water column rather than binding to the fine sediment collected for this study.

The concentrations of aluminum, iron, magnesium, potassium, and silicon were high relative to the concentrations of some of the other elements tested in ICP, but this is not necessarily a sign of contamination. These elements are normally lithogenous in origin (found naturally in the earth's crust) (Szefer et. al 1996). Therefore, the high concentrations present near the inlet of freshwater was not surprising because of the formation of flocs and the natural abundance of these elements in the earth's crust.

The enrichment factors were useful in determining whether the metal concentrations or elemental concentrations were mostly lithogenic in origin or were anthropogenically introduced. For iron and manganese, the enrichment factors were close to one and both metals correlated with aluminum. This implies that these metals are mostly lithogenic in origin and are not anthropogenically introduced. This poses a lower risk for contamination of these metals in Cook's Bay. In addition, potassium and silicon had enrichment factors less than one and these elements showed either no correlation or weaker correlation with aluminum. This suggests that these elements are associated with the water column or bind to sediments of larger size and of a different composition.

As for magnesium and nickel, these elements showed results opposite of that found in previous studies. In this study, magnesium was not correlated with aluminum and had a high enrichment factor (see Table 1), whereas in previous studies magnesium correlated with aluminum and had an enrichment factor of one. This suggests that the sample size used for testing magnesium concentration of sediments may not have been large enough to detect a correlation with aluminum. The enrichment factor may be site specific to Cook's Bay, or it could be that concentrations of magnesium are high and controlled by sources other than continental weathering. This is not likely, however, because most of the sources of magnesium are natural in origin (Global Environment Managing System 2002).

Nickel positively correlated with aluminum, but it had a high enrichment factor. Previous studies have found much higher ranges of nickel concentrations in marine sediments but with enrichment factors less than one (Szefer et al. 1996). The previous study was conducted in the Gulf of Gdansk, Poland, which is highly urbanized unlike Mo'orea (Szefer et al. 1996). This could explain the large enrichment factor and the overall low concentrations of nickel from sediments collected in Mo'orea. According to previous studies done in Oahu (McMurtry et. al 1995), high levels of nickel were found in highly cultivated soils. Possible sources for these high levels are agricultural fertilizers, fungicides, and pesticides primarily used in the sugarcane and pineapple industries. Because Pao Pao Valley is highly cultivated for pineapple plantations, it is likely that the source of this nickel is organo-mercuric fungicides. These fungicides normally contain copper enrichments, which the data from this study does not support. Unfortunately, mercury could not be tested using ICP, therefore it is unclear whether the concentration of mercury is also relatively high in the marine sediments found in Cook's Bay. Analysis of mercury would reveal more conclusive results.

Sulfur did not correlate with aluminum but no enrichment factor was determined for this element. Because sulfur is present in higher concentrations in seawater versus in the earth's crust, it causes the enrichment factor to be negative. The relatively high concentration of sulfur can be attributed to natural abundance in the marine environment, but it may also be due to decomposition of organic matter and due to fertilizers. More extensive research is needed to determine the exact source of sulfur and its abundance relative to its natural background concentration.

The enrichment factor for calcium was high, and it did not correlate with aluminum. This result was expected because the reef infrastructure is minimal near the inlet of freshwater and increases in size closer to site 5. The fringing reef present near sites 1-4 is narrower and enlarges as one moves to site 5 where the barrier reef begins to form. The presence of calcareous sediments increases with the presence of the reef.

The analysis of sediment size within Cook's Bay showed no correlation with distance from the freshwater inlet. Normally, in a bay, larger particles with larger settling velocities settle out more quickly and closer to where they were released. In this case, the distribution of particles at all five sites, contained sediment with particles that are 62.5 μm or larger. Only three samples contained sediment particles that were smaller than 62.5 μm. This implies that the method for analyzing sediment size was not precise.

The method employed for sediment size analysis involved resuspending dried sediment, emptying them into a tube, and determining the settling velocities of various particle sizes using Stoke's Law. Because there was such a small amount of sediment (maximum of 1 g), it was difficult to detect differences in the height of settling sediment. If a more precise method such as a computerized settling tank had been employed, it is likely that more accurate results would have been found.

As for percent carbon content (organic content), the data collected showed no correlation with distance from the freshwater inlet, which was surprising. One would expect to find higher organic matter near the inlet of freshwater because this is the area where sediment plumes develop as a result of runoff from the land. Because there are several pineapple plantations in Pao Pao Valley, the content of the soil is rich in organic material. A larger sample size collected during the rainy season would likely reveal this trend.

The soils of the pineapple plantations found in Pao Pao Valley are mainly red (basaltic) while coral sands are normally grey. Consistent with previous studies (Rich 1998), this study documented deep red sediments in the shallow waters closest to the freshwater input while moving further out of the bay, the sediments were characterized by reef derived sediments of a grey color. Sediment found closer to the inlet of freshwater should contain mainly reddish sediments similar to those located in the pineapple plantations, and the overall trend for organic material should be higher in these locations based upon previous studies. According to London and Tucker (1992), the pineapple plantations made frequent uses of drainage ditches with few ground covers. During rain events, these ditches, combined with the lack of vegetative ground cover to stabilize soil, would allow a high degree of sediment to run off into Cook's Bay. In addition, it is likely that this sediment is running off from the pineapple plantations because if it had originated from the roadways, higher concentrations of lead (from gasoline) and copper (from brake pads) would be present in the marine sediment.

While the aim of this study was to look at the concentrations of heavy metals, sediment size, and percent of organic material of marine sediments collected in Cook's Bay, Mo'orea, there is definitely a need for further investigation. Because the sample size for all analyses in this study were 5 (or less in some cases) for each site, a larger sample size would reveal more conclusive results. In addition, this study would yield different results if it had been completed during the rainy season as opposed to an extremely dry season. Rainy weather would bring extensive sediment plumes, a greater amount of sediment per trap, and a more realistic level of heavy metal exposure in Cook's Bay peak output of potential contaminants.

According to this study, heavy metal and elemental contamination is not a threat to the ecosystems found in Cook's Bay. Most of the elements that were found to have high concentrations in marine sediments are lithogenous in origin, and the elements with high enrichment factors, excluding calcium, need to be researched further to determine their full impact to the Pao Pao watershed.

In the long run, it is important to continue to monitor Cook's Bay watershed due to the continual agricultural and housing development (Rich 1996). It has been estimated that if the soil loss in the Pao Pao watershed comes primarily from the current eighteen hectares of land tilled for pineapple production, the rate of soil loss within the tilled area will be 1.2 cm/year. At such a high rate, pineapple production will be drastically reduced, and farmers will be forced to relocate to other areas within the valley. This has been determined as a non-sustainable farming practice and may require future monitoring of Cook's Bay (Harte unpublished), because this may lead to higher concentrations of elements from fertilizers, fungicides, and pesticides running off into Cook's Bay.

There are no metal standards for sediments in Mo'orea, French Polynesia even though marine sediments have been cited to take in much larger concentrations of heavy metals. Moreover, they are fairly accurate indicators of heavy metals in a watershed as opposed to water grab samples (James and Evison 1979, Burton 1992). To assess bioaccumulation standards, however, organisms present in the bay should be analyzed for the accumulation of a variety of heavy metals. These metals are often incorporated into the food chain by phytoplankton, which consume food and metals through the water column. Therefore, standards for water quality and marine sediments are essential for assessing the extent of heavy metal contamination in Cook's Bay as well as other locations around the world.

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