HE’EIA COASTAL WETLAND AS A SINK FOR NITROGEN, PHOSPHORUS, AND POLYCHLORINATED BYPHENYLS IN WATERS ENTERING KANE’OHE BAY

A THESIS SUBMITTED TO
THE GLOBAL ENVIRONMENTAL SCIENCE
UNDERGRADUATE DIVISION IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

GLOBAL ENVIRONMENTAL SCIENCE

DECEMBER 2001

By

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I certify that I have read this thesis and that, in my opinion, it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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ACKNOWLEDGEMENTS

I would like to thank NOAA Hawai'i Seagrant for the fellowship that gave me the opportunity to do this project for my senior thesis. The fellowship allowed me to have PCB and nutrient analysis done on my samples.

I would also like to thank Fred Mackenzie, Jane Tribble, and Dan Hoover for giving me guidance throughout this project. Fred helped with the project from beginning to end. He assisted me in putting everything together so that the project went along smoothly without financial restraints. His advice and knowledge helped me in making this project complete. Jane Tribble was also an invaluable source of advice and knowledge that enabled me to generate new ideas when I was stumped. She was invaluable in looking into new angles and information. Dan Hoover helped me greatly in getting started. He showed me the techniques and procedures to collect samples and maintain the autosamplers around the windward side. Dan also provided me with knowledge and information from his own work in the He'eia areas.

I also thank the GES program for making this project possible. It is a great idea to give students the opportunity to choose an original project that interests them and provides them with hands-on experience before graduation.

ABSTRACT

He’eia Coastal Wetland was monitored over several months to document its potential to remove nitrogen, phosphorus, and polychlorinated biphenyls (PCBs) from He’eia Stream water. He’eia Wetland is classified as a free-water natural wetland, with *Honohono grass (Commelina diffusa)* as the dominant vegetation. Its total area is about 80 ha., and the mean depth of the ponds is less than 1 meter. The wetland receives the majority of its water from He’eia Stream. Water samples for nutrient analysis were collected in two-week intervals from various locations upstream and downstream of the wetland over a period of four months in 2000. The samples were analyzed for nitrate and phosphate concentrations. A United States Geological Survey (USGS) station at the highest elevation sample site provided flow data for that site that were correlated to nitrate and phosphate concentrations. There was a decrease in both nitrate and phosphate after stream water passed through the wetland.

Two soil samples were collected in He’eia Wetland and one core sample was collected in He’eia Fishpond during the study period. These samples were analyzed for PCBs. The results suggest that the He’eia freshwater wetland is a sink for nitrogen, phosphorus and PCBs.

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INTRODUCTION

Excess nutrients in atmospheric deposition and riverine loads derived from human activities can raise natural nitrogen and phosphorus levels in stream waters, therefore changing the retention and release of these nutrients (Sanden and Rahm, 1993). Increased nitrogen and phosphorus fluxes released to downstream ecosystems, such as the coastal ocean, can have devastating effects on marine life. However wetlands have the ability to filter nutrients and retain suspended sediment and other materials when surface runoff and groundwater pass through them (Lowrance et al., 1984). Freshwater wetlands are a net sink for nitrogen and phosphorus from enriched runoff, groundwater, or atmospheric deposition. The value of both natural and constructed wetlands has been recognized worldwide. They have been used for purification of polluted waters from agricultural fields and various non-point and point pollution sources (Kadlec and Knight, 1996). For example, during the past 20 years the concentration of nitrogen in the Baltic Sea has steadily increased due to human activities in the watersheds of rivers entering the sea (Arhiemer and Wittgren 1994). However concentrations of nitrogen entering the Baltic Sea decreased after a wetland was constructed between the coastal zone and a water discharge basin. According to model calculations for the Soderkopingsan drainage basin, conversion of 1% (8.8 km^2) of this basin into wetlands would reduce nitrogen transport by 10-16%. More than 5 % (45 km^2) of basin area would have to be converted to wetlands to reduce the nitrogen transport by 50% (Arhiemer and Wittgren, 1993).

The effectiveness of wetlands to reduce nitrogen and phosphorus from agricultural drainage was also shown in a study of the Embarrass River in central Illinois by Kovacic et al. (2000). Agricultural fields contributed an estimated 75 to 91% of total nitrogen load to the Embarrass River in 1995. Constructed wetlands reduced NO_3 concentrations by more than 80% with runoff residence times of approximately one week. In addition, constructed wetlands were used to treat domestic wastewater in Virginia (Huang et al. 1999). Nitrogen levels decreased exponentially with wastewater residence time in the wetland zone.

Polluted waters have been a problem in Hawai'i since the early 1900's when land clearing and agricultural practices rose dramatically. The State of Hawai'i has only recently begun to recognize the habitat destruction caused by changing the land from its natural state. In the 1950's, raw sewage was discharged into Kane'ohe Bay, adding excess nutrients to the coastal zone. Smith et al. (1981) documented the dramatic alteration of Kane'ohe Bay by this nutritional perturbation. In the mid-1970's the state diverted the sewage to the open ocean. Although state and federal laws now prohibit all point source pollution, nutritional perturbation of the marine ecosystem still exists. Possible sources of non-point source pollution include urban and agricultural runoff from perturbed lands.

The Kane'ohe Bay watershed has also been contaminated by organic pollutants such as PCBs (Figure 1). The U.S. Coast Guard Omega Station (a low-frequency radio-transmission facility) in Haiku Valley, O'ahu, was the site of possible polychlorinated biphenyl (PCB) release between 1973 and 1983 (Figure 2). The PCBs were a contaminant in jet fuel and gasoline from an underground storage tank that were sprayed on vegetation and ignited to clear surrounding areas. Jet fuel contaminated with PCBs was used to clear areas not readily accessible to mechanical clearing devices (Stahl, 1993). Up to 210 gallons of fuel from an on-site underground storage tank were reportedly applied to surrounding areas of the Omega Station every six to twelve months. At other locations at the Omega Station, debris was burned as a means of disposal; however, no records of fuel spraying and burning were kept.

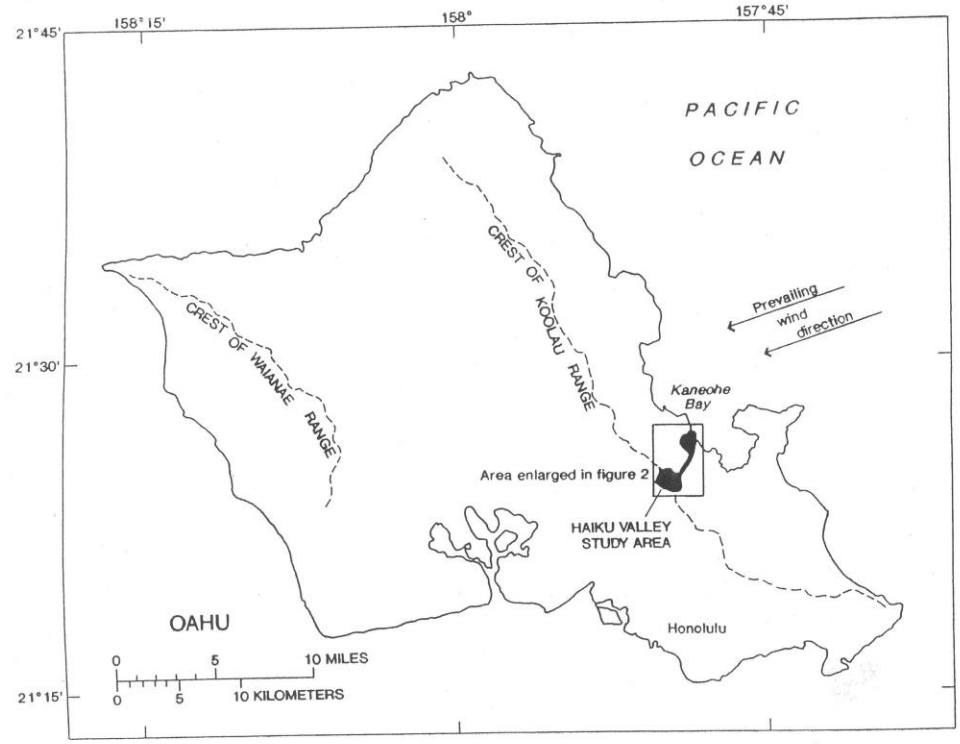
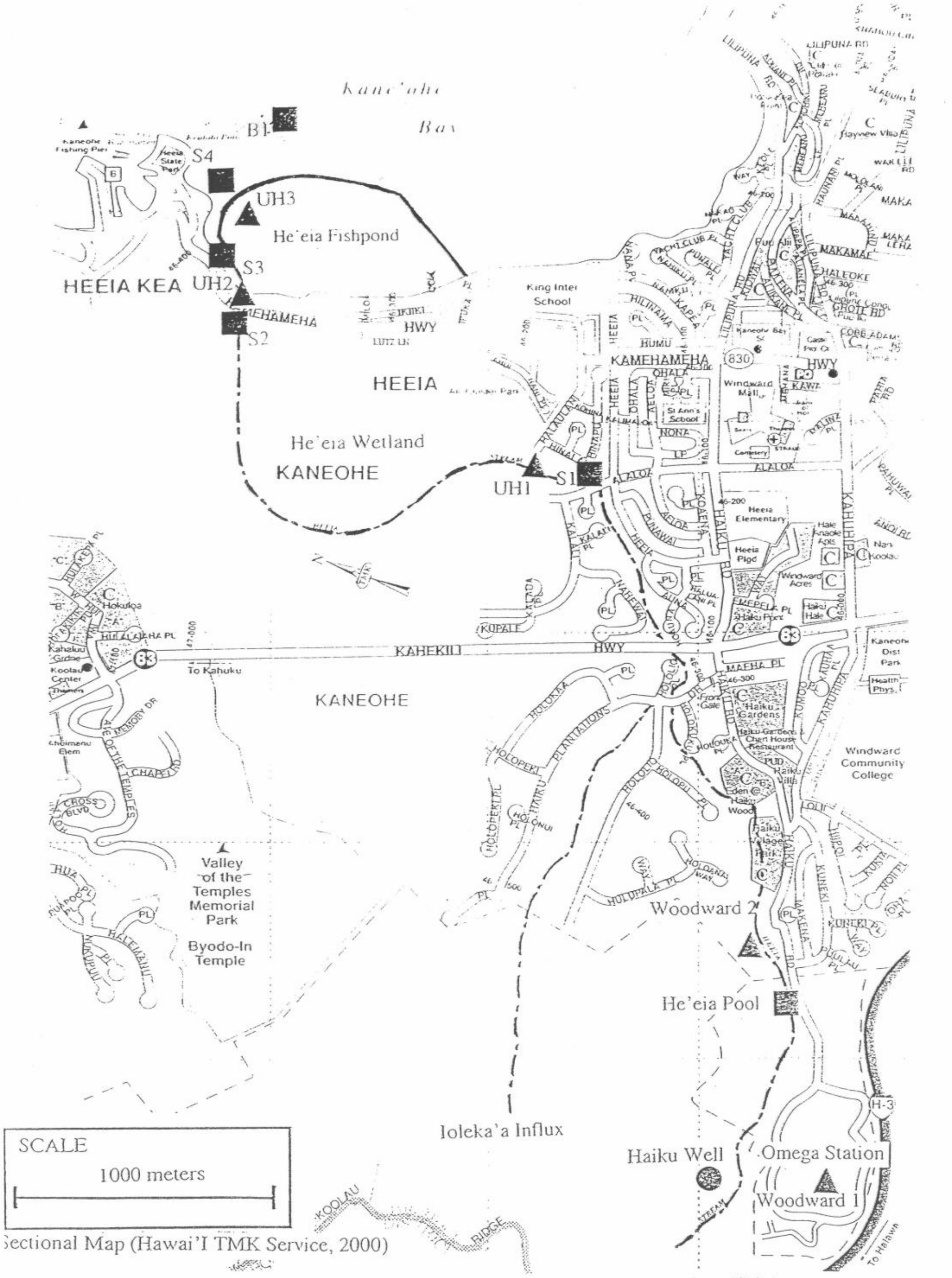


Figure 1. Location of study site in Haiku Valley, O'ahu, Hawai'i. Note the trade winds, which are the prevailing wind direction on O'ahu. Constant trades coupled with the sheer cliffs of the Ko'olau range create high precipitation in very regional areas.



Sectional Map (Hawai'I TMK Service, 2000)

Figure 2. Detailed map of Haiku Valley, showing stream water sampling sites; He'eia Pool, S1, S2, S3, S4, B1 and PCB soil sampling sites; UH1, UH2, UH3, Woodward 1, Woodward 2 and the location of the Omega Station and Haiku Well.

The chemical and physical properties of PCBs are responsible for their contamination potential in the environment. PCBs have a low solubility in water and a strong affinity to absorb on carbon-rich soils (Oloffs et al., 1973). PCBs do not readily degrade in the environment; they tend to bioaccumulate. Fish can take up PCBs through their gills, fins, and skin. The fish then store the PCBs in their fatty tissue. PCBs are also taken in by lower forms of aquatic life such as algae, which then pass them on to consumer organisms. In addition, because PCBs tend to sorb strongly to particulate matter, surface water with low particulate loads may have barely detectable levels of PCBs in the water mass, but high concentrations in the bottom sediments.

This work focuses on He'eia Wetland, a natural wetland in Kane'ohe, O'ahu, Hawai'i (Figure 1). Constructed wetlands are easier to monitor accurately because more variables are known and can be controlled. Massive urbanization within the last 100 years has led to the destruction of the majority of Hawai'i's natural wetlands. The construction of wetlands where previous natural wetlands occurred (i.e. Waikiki) would be economically impractical. Currently, there is no effective solution for the addition of pollutants to Hawai'i's waters, partly due to cost and opposition to the construction of more sewage facilities. Therefore, natural wetlands may be a natural remedy to a growing problem in Hawai'i.

The preliminary results of the study of He'eia Wetland as a nitrogen, phosphorus, and PCB trap are discussed below. The study, conducted over four months in 2000, showed that as waters passed through the wetland, nitrate, phosphate, and PCB concentrations decreased, and the wetland acted as a filter of these nutrients.

HE’EIA SITE DESCRIPTION

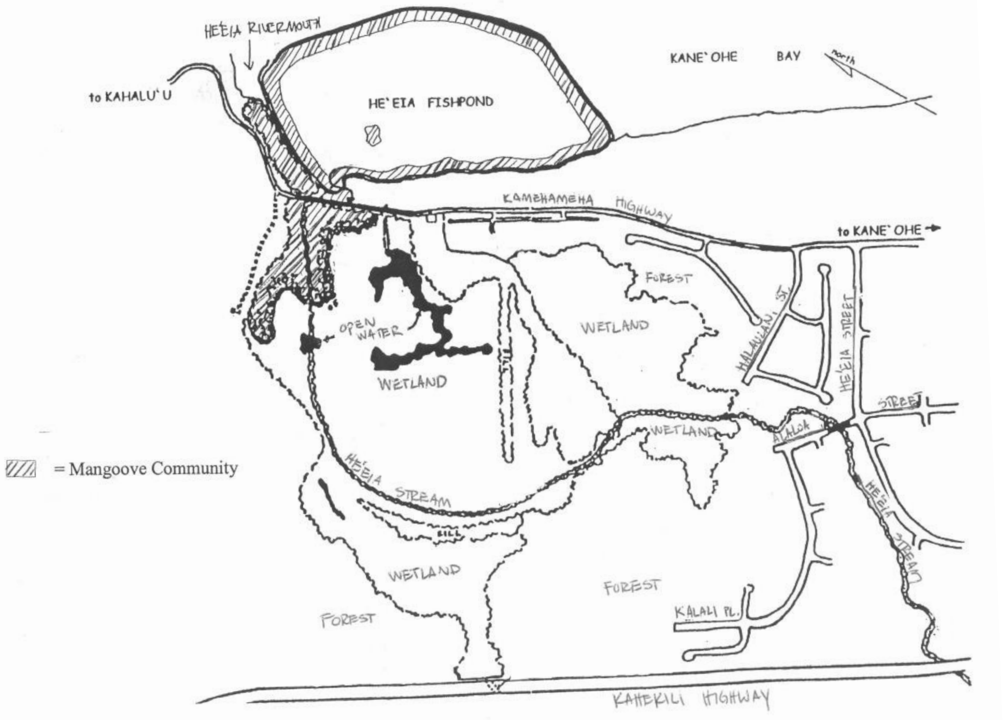
A. General

The study site is located on the eastern side of the Ko’olau Range in Haiku Valley on the island of O’ahu, Hawai’i (Figure 1). The Ko’olau Range was formed at the Hawaiian hotspot and comprises one of the two volcanoes forming the island of O’ahu. Ko’olau Ridge consists almost entirely of tholeiitic basalts and olivine basalts (Macdonald et al., 1983). Erosion has progressed to the stage where the windward flank of the Ko’olau Ridge consists of scalloped cliffs formed by the coalescence of adjacent valleys. The axis of Haiku Valley is oriented east to west and extends approximately 1.61 km from the crest of the Ko’olau Range to the ends of the ridges that bound the valley laterally (Izuka et al, 1993). Haiku Valley receives an average of about 254 cm of rain per year (Giambelluca et al., 1986). He’eia Stream is the main means of outflow for Haiku Valley, and follows a 5.6 km course from the Ko’olau Summit at approximately 850 m elevation through eroded hills, in a series of pool and riffle sequences (Stahl, 1993). Ground water discharge to the stream maintains a continuous flow of approximately 0.03 m^3/sec– 0.06 m^3/sec (Izuka et al., 1993). Between the Coast Guard Omega Station and the confluence with Ioleka’a Stream (Figure 2), He’eia Stream has a steep gradient with small pool outcrops. Ioleka’a Stream provides a small influx of water to He’eia Stream (Figure 2). Its base flow is believed to be about 20% of that of He’eia Stream (Devaney, 1983). The Ioleka’a Stream valley floor is dominated by agricultural land. Downstream of the confluence with Ioleka’a Stream, He’eia Stream flows through a relatively straight reach with a boulder and cobble bed before passing through culverts below Kahekili Highway (Figure 2). About 30 m downstream of the highway, the stream flows over a waterfall approximately 5 m in height and into a pool about 25 m in diameter. He’eia Stream then flows through a flood-control cement channel starting approximately 60 m upstream of the Alaloa Street Bridge and continuing about 30 m downstream of the Alaloa Street Bridge (Figure 2). The stream then turns to the northwest and enters He’eia Wetland.

He’eia Wetland is located between two heavily used highways in Kane’ohe, Kahekili Highway and Kamehameha Highway. The wetland area is about 80 ha.; the dominant vegetation is *Honohono grass*, an introduced species. The current nature of He’eia Wetland has resulted from many years of habitat alteration associated with past land-use practices such as animal grazing and agriculture (Henry, 1993). There is a saturated soil substrate throughout the wetland zone. Stream water enters on the western side of the wetland and flows around the perimeter of the wetland (Figure 3). The difference in depth between the stream and the adjacent wetland is less than 1 m; therefore much of the flow passes through the wetland during low flow periods.

Freshwater from He’eia Stream and He’eia Wetland feed into a mangrove forest, which borders He’eia Wetland on its ocean side (Figure 3). These waters then enter Kane’ohe Bay and He’eia Fishpond (Figure 3).

Figure 3. Detailed map of He'eia Wetland Stream, He'eia Fishpond, and the surrounding Mangroove Communities.



B. PCB Sampling

A total of three (3) sites were chosen in He'eia watershed to determine if PCBs were present and if so, to what extent. Shallow soil samples were taken directly above and below He'eia Wetland and one hand core sample was taken in the adjacent He'eia Fishpond. Wetland soil samples were taken to measure the concentrations of PCBs above and below the wetland (Figure 2). The core sample was taken to measure concentrations of PCBs in the sediment with depth (Figure 2).

UH site 1 (UH1, Figure 2): This site is accessible by a trail at the end of Halaulani Street. Approximately 30 m down the trail from the street, He’eia Stream enters He’eia Wetland. An accumulation of fine organic sediment exists throughout this area of the wetland.

UH site 2 (UH2, Figure 2): UH site 2 is accessible from He’eia State Park in Kane’ohe, O’ahu. The site is located approximately 30 m upstream from the river mouth. The sediment consists of mostly fine organic mud mixed with some sand, which is washed in by tidal mixing. This site experiences variations in salinity due to tidal mixing.

UH site 3 (UH3, Figure 2): UH site 3 is located in He’eia Fishpond, an operational fishpond used to raise fish and seaweed for human consumption. The sediment core sample was taken in an area of the fishpond that was known by its caretaker to have an accumulation of sediment. This site is located in the northeastern section of the fishpond, near He’eia Stream. This core was used to measure concentrations of PCBs with depth.

C. Nutrient sampling

Six (6) sampling sites for nutrients were chosen for accessibility and analytical reasons along the path of He’eia Stream (Figure 2). Most of these sites are accessible to the general public and can be reached by state roads. Sites were also chosen at specific locations to obtain an overall picture of processes throughout the He’eia Watershed from the headwaters to the coastal zone. Nutrient sampling sites are located on Figure 2.

He’eia Pool: He’eia Pool is located approximately 100 m below the Coast Guard Omega Station. A trail located on the right side of Haiku Road leads to the pool. He’eia Pool is a small basin (10 m wide by 1.5 m deep) consisting mostly of loose rock and soil derived from sedimentation and autochthonous matter. The stream width directly upstream and downstream of He’eia Pool is approximately 7 m, and the stream has a steep gradient. The pool was chosen as the most upstream site because it is relatively pristine and because a University of Hawai’i ISCO auto sampler equipped with a flow meter is located there.

S1: Site S1 is located under the Alaloa Street Bridge. He’eia Stream passes through a small-channelized gutter directly under the bridge. Samples were collected before stream water enters the cement gutter beneath the bridge. The streambed consists of fine-grained silt and larger rock particles. Flow is slow due to the low gradient of the stream at this site. The stream has a width of approximately 7m. This site was chosen to represent water quality directly before stream water enters He’eia Wetland.

S2: Site S2 is located beside Kamehameha Highway on the downstream edge of He’eia Wetland. It is accessible via a small trail. At this site, He’eia Stream passes through a marsh-like environment different from that of He’eia Wetland. The marsh consists of various large trees and small shrubs, but lacks *Honohono grass*. The stream floor is covered with detritus and soil. The stream at Site S2 is approximately 20 m wide and is less than 0.5 m deep. This site was chosen because it provides water quality data immediately downstream of He’eia Wetland.

S3: Site S3 is accessible from He’eia State Park in Kane’ohe, O’ahu. Samples were taken at the most upstream site accessible when walking on the footpath along He’eia Stream. The site is located approximately 20 m upstream from the river mouth. The surrounding vegetation is dominated by mangroves and is known as one of the oldest mangrove forests in Hawai’i, approximately 80 years old. The streambed consists of fine-grained silt and sand, which is washed in by tidal mixing. This site experiences variations in salinity with tidal variations. The width of the stream is approximately 3 m and has a depth of approximately 1-2 m. This site was chosen to represent water quality near the Kane'ohe Bay strandline.

S4: Site S4 is located at the river mouth of He'eia Stream, where there is a dominant sand bottom with traces of silt from upstream flow. This site experiences variations in salinity due to tidal mixing. He'eia river mouth is approximately 3 m wide and 0.5 - 1.5 m deep, depending on the tide. This site provides water quality data in the mixing zone of He'eia Stream water.

B1: Site B1 is located approximately 20 m seaward from He'eia river mouth in Kane'ohe Bay. The average depth at this site varies from 1 - 2 m, depending on the tide. Large amounts of algae and seaweed can sometimes be seen floating in the water column. The sea floor consists of sand and coral fragments. Large variations in salinity are observed at this site due to tidal mixing. This site was chosen as the bay end member to get a broad overview of He'eia watershed and the associated environments water quality.

FIELD AND LABORATORY ANALYSIS

A. PCBs

PCBs have a tendency to absorb to organic sediment and particulate matter, so the movement of suspended sediment is a possible transport route of PCBs. Sedimentary deposits in Haiku valley include clastic alluvial and colluvial gravel and conglomerate (Izuka et al., 1993). He'eia Stream has a very low suspended sediment load during normal flow periods, averaging approximately 0.3 mg suspended sediment/L during base flow of approximately 0.04 cubic meters per second (Figure 4). For an in depth study of He'eia Stream sediment transport see Izuka et al. (1993).

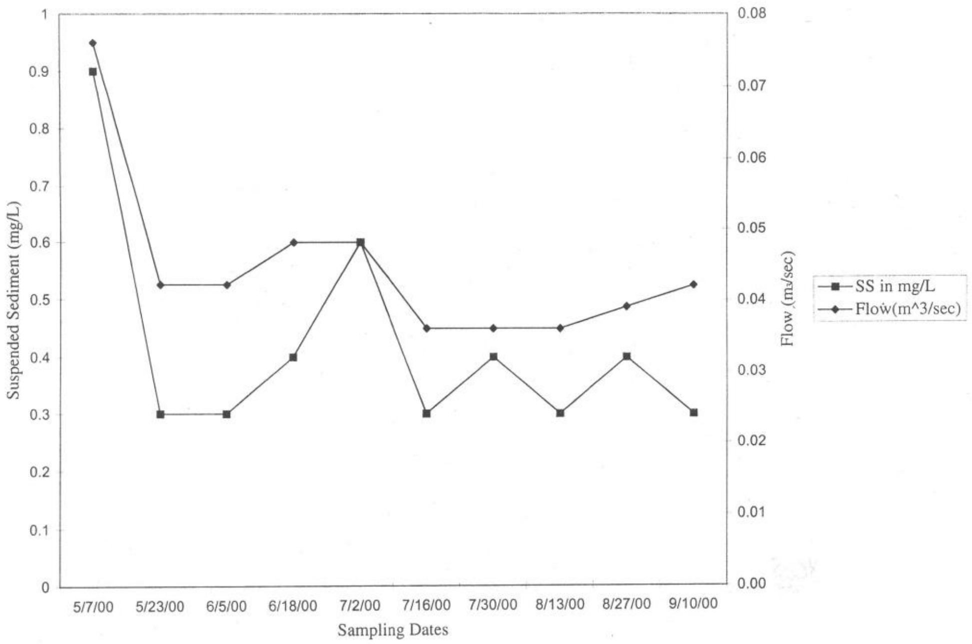


Figure 4. Suspended Sediment vs. Flow. During average precipitation suspended sediment in the stream remains at low concentrations (Board of Water Supply, 2000).

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PCB concentrations in unfiltered stream water collected at the He'eia Pool site (He'eia Pool, Figure 2) were below the detection limit of 0.1 micrograms per liter (μg/L) (Izuka et al., 1993). This observation is consistent with the knowledge that PCBs have a low solubility in water. PCB concentrations in suspended sediment extracted from He'eia Stream water ranged from 64 to 230 micrograms per kilogram (μg/kg), indicating that PCBs in He'eia Stream are carried primarily by suspended sediment due to the absorption reactions. Woodward-Clyde Consultants (1991a) suggest that since most of the fine sediment in He'eia Stream is deposited in the He'eia Wetland, it is likely that PCB concentrations in the wetland would be greater than those measured in upstream sites. PCBs are believed to have been leached downstream and into the coastal environment of the He'eia watershed (Izuka, et al. 1993).

Three (3) different sites where chosen for analysis of PCBs in He'eia watershed. To measure the sediment concentration of PCBs above He'eia Wetland, a sample was taken from an accumulation of fine sediment and gravel near Halaulani street approximately 2.7 km downstream of the Omega Station (UH1, Figure 2). A second sample was taken approximately 30 m upstream of He'eia river mouth (UH2, Figure 2) to measure PCB concentrations in the sediment below He'eia Wetland. The sediment type at this site was a dark sticky clay mixed with sand. Comparison of the two samples should show the uptake properties of the wetland relative to PCBs. The final site chosen was in He'eia Fishpond where PCBs might tend to accumulate due to bioaccumulation in organic material and sedimentation of fine-grained materials. The specific coring site within He'eia Fishpond was chosen with the help of Mary Brookes, the fishpond's former caretaker, because the site is a known sediment trap within the fishpond (UH site 3, Figure 2). The core was approximately 40 cm long and showed sediment types that varied from a dark clay to sand. Core sections with sand were not used for analysis because PCBs sorb to organic material and fine-grained sediment more readily than to sand particles.

Soil samples were collected in sterile sample bags by opening the bag seal and immediately scooping the sediment into the bags. After the sediment was collected, the sample bag was sealed and put on ice. The core sample from He'eia Fishpond was taken by hand-driving a plastic core liner to a depth of approximately 40 cm. The top of the core was sealed with a plug and brought to the surface where the bottom of the core was sealed. The entire core sample was then put on ice. The core was brought to the University of Hawai'i SOEST laboratory to be sub-sampled and stored in a refrigerator at 10 degrees Celsius. The following day samples were shipped on ice to Texas A & M Geochemical and Environmental Research Group for analysis.

The sediment samples were prepared and extracted in accordance with GERG standard operating procedures (www.gerg.tamu.edu/menu_aboutus/about.htm). These procedures are also those used for the U.S. Fish and Wildlife Service Contaminant Analytical Program (ifw2es.fws.gov/Documents/R2ES/AplomadoFalconPreyAZ.pdf).

B. Nutrients

Water samples from sites He'eia Pool, S1, S2, S3, S4, and B1 were taken in order from the most upstream site to the coast. This was done every two weeks during the period 4/2/00 to 9/10/00. Flow data were obtained from the USGS station #839.3 and an ISCO auto sampler located at He'eia Pool. Flow was calculated using level data from both the USGS and the ISCO autosampler and transcribed to a USGS flow chart for the specific site.

Water samples were taken with 500 ml sample bottles soaked in 10% HCl solution for two days. These samples were washed three times with stream water at each site before the final sample was collected. Water samples were then stored in a walk-in refrigerator in the Department of Oceanography at the University of Hawai'i at a temperature of 10 degrees Celsius. Each sample was then filtered for nutrient analysis using 150-ml Monoject© syringe filters and GF/C glass microfibre filters. Filtered water samples were sent to the University of Washington and analyzed according to *“Standard Methods for the Examination of Water”* of the American Public Health Association in the laboratories of the University of Washington for the concentrations of NO_2-N, NO_3-N, total N, and PO_4-P.

RESULTS AND DISCUSSION

A. PCBs

PCB concentrations were found at detectable levels at all three sediment sites. Concentrations of PCBs varied greatly from 1.36 μg/kg– 245.29 μg/kg. The highest concentration of PCBs, 245.29 μg/kg, was measured upstream of the wetland at UH Site 1 (Table 1). Directly downstream of the wetland at Site 2, concentrations decreased to 7.72 μg/kg. This is likely due to the absorption of PCBs into organic particles, which accumulate in the wetland. The wetland zone allows for the settling out of fine-grained particles during high and low flow periods. This is due to the dense vegetation of *Honohono grass* that grows and acts as a sediment trap throughout the wetland.

In the AECOS study (1998), an adjacent wetland was sampled for total PCB concentrations. The wetland in Ioleka’a valley had total PCB concentrations an order of magnitude below levels found in He’eia Wetland. Ioleka’a wetland had total PCB concentrations of 4.057 μg/kg, while He’eia Wetland had a concentration of 23.99 μg/kg.

The fishpond core sample contained the lowest concentrations of PCBs. The concentrations ranged from 1.36μg/kg – 3.24 μg/kg. These concentrations are comparable to background levels measured by AECOS in 1991 in their control wetland.

The pattern of increased concentrations of PCBs with depth within the core (Table 1) most likely indicates that PCBs are being diluted with incoming sediment over time.

Table 1. PCB Concentrations for Three Sites in He'eia Watershed. Concentrations are shown in μg/kg.

Date	**Location**	**PCB Concentration (mg/Kg)**
2/3/01	Site 1 - Halaulani Street	245.29
2/3/01	Site 2 - He'eia Rivermouth	7.72
12/3/00	Site 3a - He'eia Fishpond (0-3 cm)	1.36
12/3/00	Site 3b - He'eia Fishpond (12-15 cm)	1.63
12/3/00	Site 3c - He'eia Fishpond (33-36 cm)	3.24

B. Nutrients

During the sampling dates of 5/7/00 to 9/10/00, He'eia watershed experienced above average precipitation on one occasion. On 7/2/00 approximately 0.79 cm of rain fell, but there was no significant rise in flow. On 5/7/00 approximately 0.23 cm of rain fell, raising the flow of He'eia Stream to approximately 0.08 cubic meters per second. This lack of correlation between precipitation and flow could be attributed to the fact that the He'eia watershed sometimes experiences very local rainfall conditions. The precipitation gauge is not located in the same location as the flow meter. Overall, relatively average base flow was seen throughout the extent of the sampling period (Figure 5).

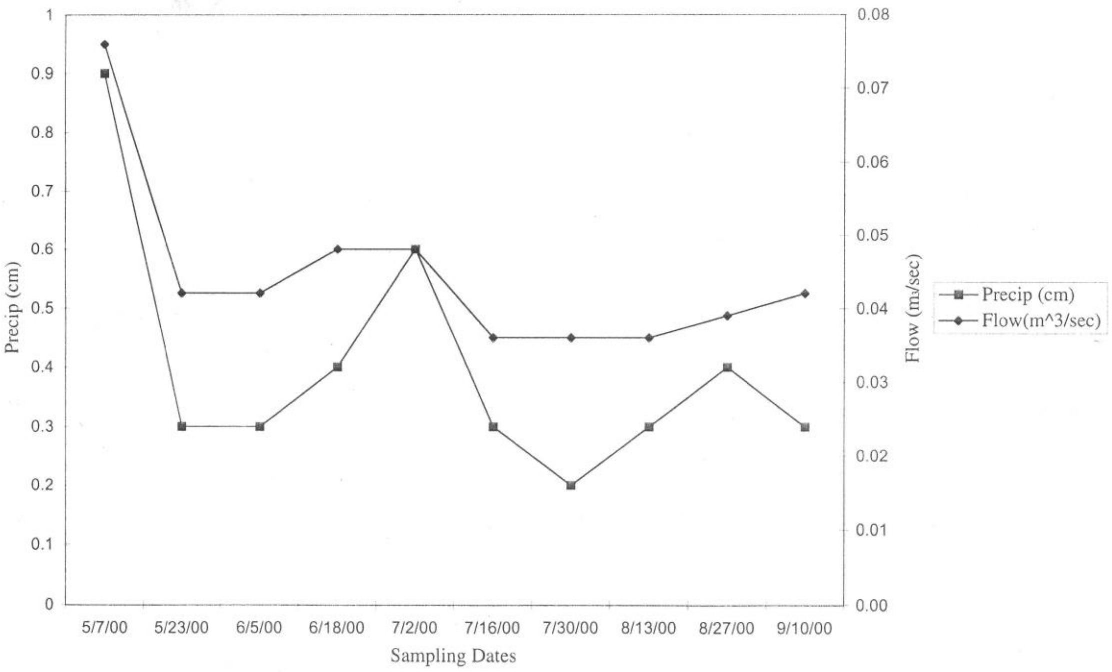

Figure 5. Flow vs. Precipitation. Although precipitation fluxes are high flow remains fairly constant. This is due to very regional rainfall observed in Haiku Valley (Board of Water Supply, 2000).

Nitrate concentrations varied greatly from He’eia Pool to Kane’ohe Bay. Phosphate concentrations exhibited a more uniform concentration gradient, declining throughout the He’eia watershed (Figure 6). Sufficient data were not available to calculate specific mass fluxes of nitrogen and phosphorus. Missing data included flow measurements at each site, flux measurements from Ioleka’a stream, and wetland fluxes. Using the available concentration data and their area distribution, possible nitrogen and phosphorus biogeochemical pathways were deduced.

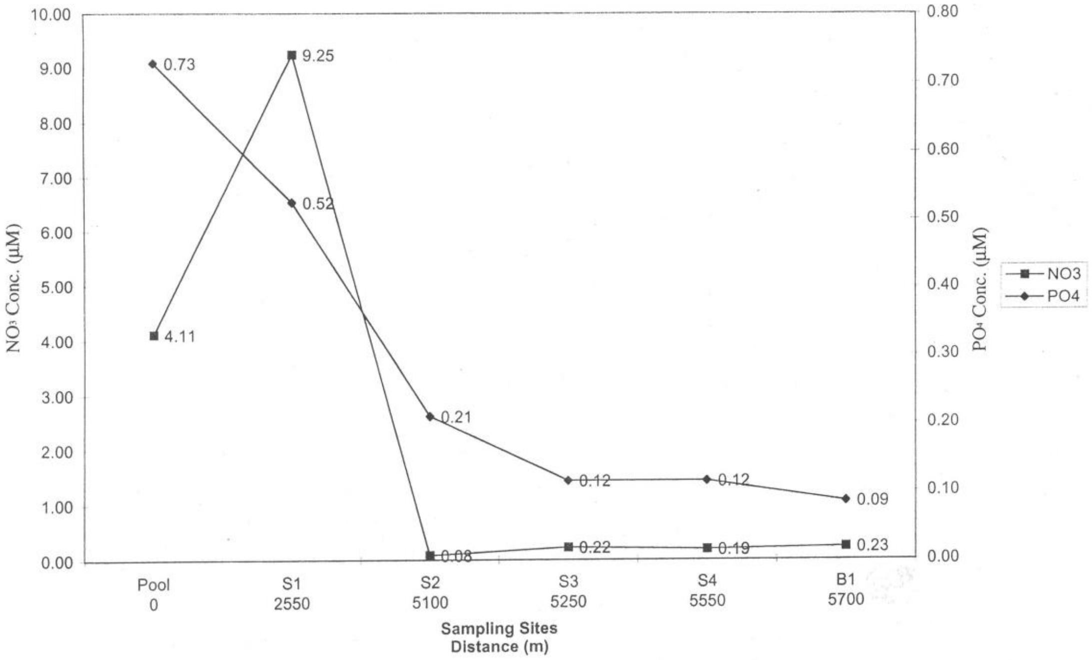

Figure 6. Average NO_3 and PO_4 concentrations (µM) vs. distance (m) from He'eia Pool. Nutrient concentrations vary greatly throughout the sampling sites.

<u>C. REACH 1: He'eia Pool-S1</u> (Figure 2). During the study period, He'eia Pool had an average nitrate concentration of 4.11 µM while S1 averaged 9.25 µM of nitrate (Table 5). Phosphate concentrations at He'eia Pool averaged 0.73 µM, while S1 averaged 0.53 µM.

There are many possible reasons for the observed changes in concentrations of nitrate and phosphate within REACH 1. Urban runoff persists throughout the residential and highway zones. There is a high probability that the runoff affects stream composition. Human additions of fixed nitrogen to the terrestrial biosphere have resulted in marked increased in the nitrogen content of stream waters (Spalding and Exner, 1993). Although concentrations of nitrogen increased along REACH 1 (Figure 2), phosphorus, which is usually characteristic of urban runoff, decreased in concentration. During river transport, phosphorus maybe absorbed on sediments and suspended minerals (Meyer, 1979). Nitrate, in contrast, is very soluble. It is possible that because phosphorus has a tendency to be absorbed to soil and clay particles, high concentrations of phosphorus in dissolved form were not observed in reach waters. Phosphorus levels steadily decline downstream throughout He'eia steam.

Meybeck's (1982) study of carbon, nitrogen, and phosphorus transport by world rivers suggest that urban wastes are higher in ammonium; while agricultural wastes are higher in nitrate. Agricultural lands are persistent throughout Ioleka'a valley. This is a probable non-point source of nitrogen to He'eia steam, resulting from leaching and runoff from agricultural land. Table 2 shows the ammonium and nitrate concentrations at all sampling locations for the sampling date 5/7/00. High nitrate concentration compared to ammonium concentrations at Site S1 could be attributed to the influx of Ioleka'a stream water directly above this sample site.

Table 2. Ammonium and Nitrate Concentrations for 5/7/00 (Hoover, 2000).

Site	**NO3 (uM)**	**PO4 (uM)**
Pool	4.9	0.34
S1	11.28	0.61
S2	0.51	0.21
S3	0.74	1.83
S4	0.67	2.63
B1	0.98	0.64

Another possible reason for increased nitrate in He'eia Stream is groundwater additions throughout the stream. Groundwater usually contains higher concentrations of nitrogen then phosphorus. This is due to the relative insolubility of phases containing phosphorus. Once released by weathering, phosphorus is quickly tied up in the soil as iron, aluminum, and calcium phosphates or by absorption into clay minerals. Izuka et al. (1993) documented the discharge during base flow of He'eia Stream at various locations.

Table 3. Izuka et al. Measured Discharge (m^3/sec) of He'eia Stream During Base Flow in 1991.

Site	11/6/91	11/21/91	11/22/91	12/20/91
1	0.00	0.00	0.00	0.01
2	0.01	0.01	0.01	0.01
3	0.04	0.04	0.04	0.04
4	0.04	0.04	0.04	0.05
5	0.05	0.05	0.04	0.06
6	0.06	0.05	0.05	0.06
7	no data	0.05	0.05	0.07
8	0.13	0.12	0.12	0.12

This table shows that between their sites 7 and 8 there is an almost 2.5 fold increase in flow. The Izuka site 7 is located approximately 500 m downstream of He'eia Pool, and Izuka site 8 is located approximately 200 m upstream of the Ioleka'a influx. From He'eia Pool to the Ioleka'a influx, there are major visible surface flow additions to the stream, therefore the increase in flow is attributed to groundwater addition to the stream.

Groundwater chemistry was measured by the Board of Water Supply at Haiku Well (2450-02) (http://www.hbws.org) located approximately 30 m from the Coast Guard Omega Station (Figure 2). Groundwater in Hawai'i is usually high in dissolved silica due to the weathering of basalts, which contain approximately 50% silica. Silica was used as a baseline indicator for groundwater flux calculations because it does not have any major uptake or release reactions in stream waters. Table 4 shows the silica concentrations for Haiku well as well as silica concentrations for all sampling locations on 5/7/00.

Table 4. Haiku Well Groundwater and 5/7/00 He’eia Sampling Chemical Analysis.

Location	**NO3**	**PO4**	**Si**
Haiku Well	13	2	470
He'eia Pool	4.9	0.7	430
S1	11.28	0.53	445
S2	0.51	0.1	294
S3	0.74	0.16	182
S4	0.67	0.14	215
B1	0.98	0.08	127

He’eia Pool measured 430 μM Si and Haiku well measured 470 μM Si. The fact that the measured Si values are relatively close could mean that Haiku well and He’eia Stream are fed from the same groundwater aquifer. Haiku well’s nitrate concentration, 13 μM, and phosphate concentration, 2 μM, are significantly higher than the values measured at He’eia Pool. This would suggest that there are major biological and /or physical sinks of nitrate and phosphate before the water reaches He’eia Pool. Nitrate concentrations double downstream of He’eia Pool at site S1. Over the same reach (He’eia Pool – S1), phosphate concentrations are reduced by approximately 30%. The decrease in phosphate is possibly due to absorption by soil and clay particles and limited biological uptake. The Izuka et al. discharge measurements (Table 3) suggest an increase in base flow by a factor of 2.5. Therefore, the increase of nitrate could possibly be attributed to the influx of Haiku groundwater with a nitrate concentration similar to that measured at Haiku well.

D. REACH 2: S1-S2 (Figure 2). During the study, nitrate and phosphate removal by He’eia Wetland was consistently high. Table 5 shows that the nitrate and phosphate concentrations of water entering He’eia Wetland were consistently greater than that exiting the wetland. All samples were collected during low base flow, which is prevalent during most of the year, except in the winter months.

He’eia Wetland has an area of approximately 80 ha with a mean average depth of less than 1 m. Based on visual inspection of this freestanding continuously flooded wetland zone, the residence time of He’eia Stream water in the wetland zone is about 1 month. Calculation of actual residence time is not possible due to data limitations.

Possible mechanisms for retention of dissolved nitrate and/or phosphate within He’eia Wetland include uptake by algae, uptake by vegetation, and denitrification. Within He’eia Wetland, microscopic single-celled and filamentous algae are present. Free-floating forms comprise the phytoplankton, which are best developed in the large pond at the lower end of the wetland. The algae were observed macroscopically as a brownish discoloration of the water. The algae are primary producers that use the energy in sunlight to convert available nutrients, oxygen, and carbon dioxide into biomass (AECOS, 1998).

During the growing season, which is year round in Hawai’i, plants absorb inorganic nitrogen and phosphorus. Coupled with a long residence time present in wetland zones, this provides excellent conditions for nitrate and phosphate removal. High concentrations of nitrate and phosphate remain in contact with root hairs longer due to high residence times in wetland zones, and are readily available for growing plants in the wetland zone. *Honohono grass*, the dominant vegetation in He’eia Wetland, takes up available nitrogen and phosphorus in specific ratios. Nitrate and phosphate are taken up until either one is not available. The limiting nutrient then puts a “cap” on uptake by vegetation. Nitrate seems to be the limiting nutrient in He'eia Wetland, although both nitrate and phosphate are reduced to very low concentrations in the wetland.

The main factor contributing to nitrate removal in He'eia Wetland is probably denitrification. The equation for denitrification is:

$$\mathbf{4NO_{3-} + 5CH_2O + 4H + \rightarrow 2N_2 + 5CO_2\,(g) + 7\,H_2O}$$

Efficient removal of nitrate by denitrification, i.e. up to 25% of total nitrogen transport, can occur only at base flow (Jansson, 1992). Denitrification requires anoxic environments that are found in wetland soils. Most wetlands are characterized by hydric soils, which have physical and chemical characteristics reflecting repeated and prolonged saturation at or near the soil surface. Denitrification occurs when oxygen transport is greatly reduced by water in the substrate. Oxygen depletion in saturated soils is caused by roots of plants as well as microbes and other soil organisms using oxygen in respiration. This leads to a complete loss of oxygen and in some cases a substantial accumulation of reduced substances.

Nitrate is converted to NO, N_2O, and N_2 in the process of denitrification (Schlesinger, 1997). In this anoxic environment, denitrification rates are increased when the availability of carbon and nitrate is high, as well as when warm temperatures are present (Schlesinger, 1997). All these factors are present in He'eia Wetland probably accounting for the high removal rate of nitrate (Table 5).

E. REACH 3: S2-S3 (Figure 2). From sampling site S2 to site S3, He'eia Stream enters a large mangrove forest. The mangrove community borders the entire He'eia Fishpond and coastline near He'eia State Park, extending inland along the bank of He'eia Stream to the adjacent He’eia Wetland (Figure 3). This forest which is approximately 80 years old comprises about 1 acre of marshland.

Mangroves are usually situated in nutrient-limited coastal lowlands (Dubinsky, 2000). This is also the case in He’eia Watershed, where the mangrove forest is located adjacent to He’eia Wetland water discharge. Mangroves situated on the coast must compete with marine organisms for available nutrients in the water column. Mangroves have a symbiotic relationship with cyanobacteria in both the substrate and canopy level of the mangrove community. The cyanobacteria fix available nitrogen from the atmosphere and make it available for plant uptake. Figure 6 shows the average nitrate concentrations from site S2 to S3. Average nitrate concentrations rose 0.14 μM within REACH 3 (Figure 2). This increase in nitrate concentrations may reflect nitrogen fixation in the mangrove community. In Guadeloupe, French West Indies, a tropical mangrove community was shown to fix nitrogen biologically at a rate of 42.3 g N/m^2/yr by cyanobacteria growing epiphytically on black mangroves (*Avicennia germinans*) (Sheridan, 1991). This symbiotic nitrogen fixation has been demonstrated in many forest ecosystems (Hicks and Silvester, 1985).

Phosphate concentrations decrease from 0.21 μM to 0.12 μM within REACH 3 (Figure 6). This is probably due to uptake by the mangrove community.

F. REACH 4: S3-S4 (Figure 2). Average phosphate concentrations do not change within Reach 4. Slight variations were measured for specific sampling dates (Table 5), probably due to salinity changes from tidal fluctuation within the stream channel. Phosphorus and nitrogen are used by phytoplankton in forming organic matter. The average composition for marine plankton, given in terms of the Redfield ratio, is

$C_{106}N_{16}P_1$ (Redfield et al., 1963). This is an idealized ratio and the actual marine phytoplankton nutrient utilization ratios can vary from 5N:1P to 16N:1P (Ryther and Dunstan, 1971), depending upon the availability of nutrients in the water and the species of phytoplankton.

The average nitrate concentrations are reduced from 0.22 μM to 0.19 μM. Nitrogen is used by phytoplankton for growth. Another possible reason for the decrease in nitrate concentrations could be due to tidal mixing with coastal waters with lower nitrate concentrations.

G. REACH 5: S4-B1 (Figure 2). Rivers serve as nutrient sources for estuaries due to land weathering and pollution. Phytoplankton, particularly diatoms and algae, are the organisms most often responsible for the removal of dissolved nutrients from estuarine surface water. Table 5 shows site S4 and site B1's silica concentrations. Silica concentrations decrease greatly within this short reach. This can be attributed to the growth of diatoms, which incorporate silica, phosphate, and nitrate.

Phosphate concentrations are decreased from 0.12 μM in He'eia river mouth to 0.09 μM at site B1, approximately 30 m from the river mouth in Kane'ohe Bay. Phosphate is taken up by phytoplankton as it is made available from He'eia river mouth. Phosphate removal from estuaries can also occur by inorganic adsorption of phosphate on particles and subsequent burial in sediments.

Nitrate concentrations increase within this reach (Table 5). There are many possible sources of added nutrients to estuarine waters. Regeneration of nutrients from the breakdown of internally produced biogenic debris can increase the concentration of nitrate within estuary waters. This occurs by bacterial action within the water column as the debris settles out and on the bottom (benthic regeneration) either at the surface of the sediments or from within the sediments (Berner and Berner, 1987). Coastal upwelling and onwelling of nutrient-enriched marine bottom water can also be an important source of nutrients to estuarine waters, but is not an important process in the proximal area of Kane'ohe Bay. Nitrate can also be added to estuaries by fixation of N_2 from the atmosphere by blue-green algae and photosynthetic bacteria. Seitzinger (1991) found that upon mixing with seawater, an increase in pH in the Potomac River estuary caused a release of phosphorus from sediments, stimulating a bloom of nitrogen fixing blue-green algae. At the pH and redox potential of seawater, nitrification occurs rapidly in estuarine waters (Stanley and Hobbie, 1981).

Table 5. Phosphate and Nitrate Concentrations (μM) for Each Sampling Site and Averages.

Nitrate Concentrations (μM)

Date	**5/3/00**	**6/5/00**	**7/2/00**	**7/30/00**	**8/27/00**	**9/10/00**	**Average NO_3**
Pool	5.08	4.28	3.74	3.74	4.04	3.8	**4.11**
S1	11.6	10.63	7.68	8.22	7.8	9.54	**9.25**
S2	0.26	0.15	0	0	0	0.07	**0.08**
S3	0.64	0.21	0	0.16	0.15	0.15	**0.22**
S4	0.41	0.12	0.15	0.17	0.12	0.15	**0.19**
B1	0.19	0.42	0.22	0.28	0.12	0.15	**0.23**

Phosphate Concentrations (μM)

Date	**5/3/00**	**6/5/00**	**7/2/00**	**7/30/00**	**8/27/00**	**9/10/00**	**Average PO_4**
Pool	0.69	0.7	0.79	0.74	0.76	0.68	**0.73**
S1	0.57	0.59	0.56	0.46	0.45	0.51	**0.52**
S2	0.22	0.18	0.24	0.15	0.25	0.22	**0.21**
S3	0.1	0.11	0.1	0.14	0.13	0.11	**0.12**
S4	0.15	0.08	0.16	0.08	0.12	0.1	**0.12**
B1	0.09	0.06	0.1	0.1	0.1	0.06	**0.09**

CONCLUSIONS

Results of this study indicate that He’eia Wetland could effectively reduce overall nitrate and phosphate in He’eia Stream waters before they enter Kane’ohe Bay. Nitrate and phosphate concentrations were reduced 99% and 60%, respectively, after stream waters passed through the wetland. He’eia Wetland also reduced the sediment transport of PCBs within He’eia Stream. PCB concentrations were decreased from 245.29 μg/kg to 7.72 μg/kg. Although pollutant retention values cannot be translated to other areas due to local physiographical, hydrological and hydrochemical conditions, it is evident that He’eia Wetland is a trap for pollutants entering from stream waters. Natural wetlands are passive low maintenance systems that are useful in decreasing the concentrations of pollutants entering coastal waters.

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