# MAMALA BAY STUDY

# ECOSYSTEM RESPONSE STUDY: EFFECTS OF SEWAGE DISCHARGES AND STREAM RUNOFF ON PHYTOPLANKTON COMMUNITIES AND WATER QUALITY IN MAMALA BAY

**PROJECT MB-9**

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# 1 EXECUTIVE SUMMARY

Water quality at 10 recreational beaches in Mamala Bay and in the nearshore ocean were monitored over a period of 12 months in 1993-1994 to determine the impact of sewage discharges and non-point source pollution on conditions in the bay. Analyses of the effluent from the Sand Island and Honouliuli sewage treatment plants revealed that the sewage contained high concentrations of ammonium and silicate, about 1100 and 900 mM, respectively. The $\delta^{15}N$ of the biologically available nitrogen in the sewage was 7-10‰, which is higher by several parts per thousand than the $\delta^{15}N$ of marine nitrogen in Mamala Bay. These fingerprints proved useful in detecting sewage effluent in the water and identifying places where nitrogen derived from sewage had been incorporated into organisms.

Bioassay experiments with sewage effluent revealed that the effluent stimulated phytoplankton growth, the maximum response being about an 80% increase in photosynthesis after 24 hours. Photosynthesis was stimulated by less than 10% at added ammonium concentrations less than about 30 nM. Pigment profiles revealed that diatoms showed the greatest response to added sewage. None of the pigment profiles obtained from recreational beaches or from the nearshore ocean resembled the profiles obtained when Mamala Bay water was enriched with sewage.

Water quality on the 10 recreational beaches was in most cases quite high, with the exception of Keehi Lagoon Beach Park. Water quality at this beach was clearly impacted by stream runoff. Impacts of sewage were apparent at only one beach, Fort Kam Beach Park. The impacts in that case were from the Fort Kam sewage treatment plant, a secondary plant which discharges effluent containing high concentrations of nitrate and phosphate. The lowest nutrient, chlorophyll, and particulate nitrogen and carbon concentrations were measured at beaches from Diamond Head to Sand Island, with Sand Island Beach Park having the lowest particulate nitrogen and second lowest chlorophyll and particulate carbon concentration of any of the 10 beaches. The water quality at Sand Island Beach Park is noteworthy, since it is closer to the Sand Island

sewer outfall than any of the beaches and has been identified by the modeling work in MB-5 as the beach most likely impacted by sewage effluent. It would appear, therefore, that water quality at none of the beaches we sampled was significantly impacted by sewage from the Sand Island or Honouliuli sewage treatment plants.

Effluent from the Sand Island and/or Honouliuli treatment plants was easily detected in nearshore ocean monitoring because of the high silicate and ammonium concentrations associated with the effluent. In most cases the effluent was detected at a depth of 60 m, but on two of six sampling dates, the effluent was apparent at shallow depths of 10-20 m. Water impacted by freshwater derived from streams was easily distinguished from sewage-polluted water by the fact that in the former case ammonium concentrations were low and nitrate concentrations high. Silicate concentrations associated with nearshore waters impacted by sewage or stream water were typically in the range 5-20 mM, substantially higher than the typical marine silicate concentration of about 2 mM. Increases in surface water turbidity in the nearshore ocean were found off Pearl Harbor and the Ala Wai Canal but not near the Sand Island or Honouliuli sewer outfalls.

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## 2 INTRODUCTION

Discharges of wastewater from point sources and runoff from non-point sources are believed to be the principal causes of water quality problems in Mamala Bay. The objectionable characteristics of these discharges are numerous and include pathogens, heavy metals, pesticides, nutrients, biological oxygen demand, sediment and suspended solids, and general trash. Certainly among the most important of these objectionable characteristics is the high concentration of nutrients found in both point and non-point source discharges. Inorganic nitrogen concentrations in the discharges from the Sand Island and Honouliuli sewage treatment plants are 0.9-1.2 millimolar (mM), more than 1000 times background concentrations in the offshore ocean. Nitrogen concentrations in land runoff are 30-40 times lower, but are more than adequate to cause serious eutrophication problems in a confined body of water.

The rationale for including a study of the effect of these point and non-point discharges on the biological community in Mamala Bay as a component of the overall Mamala Bay Study is several-fold. First, there is the obvious fact that these nutrient additions may alter the normal productivity, biomass, and composition of the algal community. Such effects can have serious consequences for other organisms in the ecosystem, the example of Kaneohe Bay being a case in point (Smith et al., 1981). Second, the chemical characteristics of the discharged water, including nutrient concentrations, salinity, and stable isotope ratios, can collectively provide a useful tracer of the impact and fate of the discharges. Concentrations of ammonium in the sewage effluent, as already noted, are about three orders of magnitude higher than ambient concentrations in the mixed layer of the offshore ocean. Silicate concentrations in both stream runoff and sewage effluent on Oahu are also about 1000 times background concentrations in the ocean. Perhaps more intriguing and potentially useful is the fact that the ratio of the stable nitrogen isotopes $^{15}N$ and $^{14}N$ often differ substantially between sewage effluent, stream runoff, and marine waters (Wada and Hattori, 1991). Thus the extent to which sewage effluent and stream runoff are driving production in the waters of

Mamala Bay may be elucidated by an examination of the $^{15}N/^{14}N$ ratio of organisms in the bay.

## 2.1 Scope of Work

The work performed on this project can be broken down into three categories. The first category of work involved bioassay experiments in which effluent from the Sand Island and Honouliuli sewage treatment plants was added to seawater taken from a control station off Diamond Head. The impact of the sewage was judged in terms of its effect on the photosynthetic rates of the microalgal community, the composition of the microalgal community, and the total numbers of heterotrophic bacteria in the water. The second category of work involved monitoring of water quality on 10 recreational beaches from Diamond Head Beach Park to Barbers Point Beach Park. Water quality characteristics that were monitored included temperature, salinity, inorganic nutrient concentrations (silicate, phosphate, ammonium, and nitrate plus nitrite), particulate carbon (PC), particulate nitrogen (PN), chlorophyll *a* (chl *a*), carotenoid pigment concentrations, and the $\delta^{15}N$ of the PN (a measure of the $^{15}N/^{14}N$ ratio of the PN)[1]. The third category of work involved monitoring of offshore water quality characteristics horizontally along a transect from Diamond Head to Barbers Point along the approximate depth contour (isobath) of the sewer outfalls and vertically at selected depths along onshore-offshore transects from the major non-point sources discharging into Mamala Bay. Water quality characteristics that were monitored included temperature, salinity, water clarity, subsurface irradiance, microalgal biomass, inorganic nutrient concentrations, and photosynthetic rates.

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[1] The $\delta^{15}N$ is defined as $\left[\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{standard}} - 1\right] \times 1000$, where the standard is atmospheric $N_2$.

## 2.2 Objectives

The specific objectives of this project were as follows:

1. To determine the effect of enriching water from Mamala Bay with sewage effluent from the Sand Island and Honouliuli sewage treatment plants on the biomass, composition, and productivity of the phytoplankton community and on the $\delta^{15}N$ of particulate matter.

2. To determine the survival of bacteria in sewage effluent from the Sand Island and Honouliuli sewage treatment plants when the sewage is diluted by factors to be expected in the field during the first 24 hours after the sewage is discharged.

3. To carry out field sampling along the approximate isobath of the sewage discharges to determine whether the discharges are having a discernable effect on dissolved inorganic nitrogen and phosphate concentrations when these nutrients are measured by techniques sensitive at the nanomolar level.

4. To determine the biomass and composition of the phytoplankton community in the outflow from Pearl Harbor and the Ala Wai Canal and the $\delta^{15}N$ of the particulate matter in these outflows.

5. To determine the biomass and composition of the phytoplankton community and the $\delta^{15}N$ of particulate matter at recreational beaches in Mamala Bay and to determine, based on pigment and $\delta^{15}N$ analyses, to what extent effluent from the sewage outfalls and discharge from streams may be affecting water quality at these beaches.

6. To characterize water quality in terms of nutrient and chlorophyll concentrations at recreational beaches from Diamond Head to Barbers Point and to determine whether and to what extent water quality on these beaches is being affected by sewage discharges and stream runoff.

7. To characterize water quality in terms of nutrient and chlorophyll concentrations and light transmission at various locations in Mamala Bay, including the approximate isobath of the sewer outfalls and to determine whether and to what extent water quality on these beaches is being affected by sewage discharges and stream runoff.

### 2.3 Project Organization

Dr. Edward Laws (University of Hawaii Oceanography Department) and Dr. David Ziemann (Oceanic Institute) were the principal investigators on this project. The co-principal investigators were Dr. Robert Bidigare (University of Hawaii Oceanography Department) and Dr. Brian Popp, (University of Hawaii Geology and Geophysics Department). Dr. Laws was responsible for coordinating the overall project and specifically for coordinating and directing the bioassay experiments and the beach sampling. Dr. Ziemann was responsible for coordinating and directing the offshore field work. Dr. Laws was responsible for the inorganic nutrient analyses and the $^{14}C$ work, and for the temperature, salinity, and particulate carbon and nitrogen measurements in the beach surveys. Dr. Bidigare was responsible for the pigment analyses and flow cytometry work. Dr. Popp was responsible for the stable isotope analyses. Dr. Ziemann was responsible for the fluorometric work and for the light, salinity, and temperature measurements in the offshore field work. Other participants in the project included Lytha Conquest and Robert Young, research associates at Oceanic Institute, David Hashimoto, a technician at the University of Hawaii, and Deborah Schulman and Deborah Avent, graduate students in the University of Hawaii Oceanography Department.

# 3 METHODS

## 3.1 Task Summary

The tasks to be completed as a part of this research were as follows:

1. Carry out bioassays to determine the response of the Mamala Bay phytoplankton and bacterial communities to sewage enrichment

2. Monitor water quality at ten recreational beaches from Diamond Head to Barbers Point to determine whether any impacts from stream runoff and/or sewage discharges could be detected, and if so the magnitude of the impact

3. Monitor water quality within Mamala Bay at selected stations along the approximate isobath of the sewer outfalls and along transects extending out from the mouths of Pearl Harbor and the Ala Wai Canal.

## 3.2 Task Methodology

### 3.2.1 Sewage Bioassay Experiments

Bioassays were carried out using surface water collected from the Diamond Head buoy, which is located 1 km offshore of the Diamond Head lighthouse. The water was collected in acid-cleaned 20-liter plastic carboys using a Boston Whaler at about 3 p. m. local time. Upon return to the laboratory, the water was dispensed into twenty-eight 300 ml BOD[2] bottles. Four of the bottles received no nutrient additions. The remaining 24 bottles were enriched with filtrate from the effluent of either the Sand Island or Honouliuli sewage treatment plants. The effluent was in each case a 24-h composite sample obtained from the City and County of Honolulu Sand Island laboratory on the same day as the bioassays. The sewage was filtered through precombusted glass fiber

[2] BOD = biochemical oxygen demand

GF/F filters. The particulate material on the filters was analyzed for particulate carbon (PC) and particulate nitrogen (PN) using a Perkin-Elmer model 2400 elemental analyzer. In addition, the PN was analyzed for $\delta^{15}N$ using either a Finnigan MAT 252 or Delta-S mass spectrometer. The filtrate was analyzed for inorganic nutrient concentrations (phosphate, nitrate + nitrite, ammonium + ammonia, and silicate) using colorimetric methods on a Technicon AutoAnalyzer. Concentrations of total dissolved nitrogen (DON) and total dissolved phosphorus (DOP) were determined by ultraviolet oxidation of the filtrates followed by colorimetric analysis of the inorganic nitrogen and phosphorus. Salinity was measured using an Extech Oyster conductivity meter calibrated with Copenhagen seawater. A summary of the sewage effluent analyses is shown in Table 3.1. Ammonium accounted for almost all the dissolved inorganic nitrogen in the sewage effluent, and the concentrations were rather reproducible at 900 mM (micromolar) and 1300 mM in the Sand Island and Honouliuli effluent, respectively. It was therefore not difficult to estimate the degree of dilution of the sewage effluent necessary to produce a target ammonium enrichment in the BOD bottles. The six target enrichment concentrations were either 12.5, 25, 50, 100, 200, and 400 nanomolar (nM) or 25, 50, 100, 200, 400, and 800 nM.

Following addition of the appropriate amount of sewage effluent, the BOD bottles were transferred to the roof of the Marine Science Building, where they were placed in incubators which simulated both the intensity and spectral characteristics of submarine light at either 100%, 33%, 15%, or 8% of surface irradiance. Light intensity within the incubators was controlled with a combination of neutral density filters and blue and blue-violet Rohm and Haas plexi-glass filters (Laws *et al.*, 1990). Temperature within the incubators was maintained with flowing tap water. Seven BOD bottles were placed in each incubator, one control and six treatments containing sewage filtrate equivalent to either 12.5-400 or 25-800 nM added ammonium. In addition, a BOD bottle enriched with 10 milliliters (ml) of unfiltered sewage effluent was placed in each incubator for purposes of monitoring bacterial numbers.

Table 3.1. Summary of results of analyses of effluent from Sand Island and Honouliuli sewage treatment plant effluents.

Nutrient concentrations and concentrations of particulate C and particulate N are micromolar. $\delta^{15}N$ is expressed as per mil. Salinity is given in practical salinity units (psu or grams salt per thousand grams of water).

| | Sand Island | Honouliuli |
|---|---|---|
| Phosphate | 54 ± 8 | 72 ± 3 |
| Nitrate + nitrite | 5.7 ± 8.1 | 7.7 ± 2.8 |
| Ammonium + ammonia | 857 ± 115 | 1302 ± 58 |
| Silicate | 698 ± 59 | 1081 ± 21 |
| Total dissolved N | 1094 ± 61 | 1684 ± 153 |
| Total dissolved P | 58 ± 9 | 74.3 ± 3.4 |
| Dissolved organic N | 231 ± 179 | 376 ± 95 |
| Dissolved organic P | 3.6 ± 1.2 | 2.7 ± 2.6 |
| Particulate C | 2670 ± 219 | 3162 ± 760 |
| Particulate N | 474 ± 334 | 379 ± 85 |
| PC/PN | 6.3 ± 2.5 | 7.1 ± 0.2 |
| $\delta^{15}N$ of PN | 1.9 ± 3.1 | 1.8 ± 3.5 |
| $\delta^{15}N$ of biologically available dissolved N | 6.9 ± 5.8 | 10.1 ± 2.2 |
| Salinity | 4.4 ± 0.2 | 0.7 ± 0.1 |

At sunrise on the following morning, additions of $^{14}C$ labeled bicarbonate were made to all of the BOD bottles, with the exception of those used for monitoring bacterial counts. About $10^6$ becquerels[3] (Bq) of $^{14}C$ were added to each BOD bottle. The bottles were incubated from sunrise to sunset, at which time the contents of each bottle were filtered onto a GF/F filter. The filters were placed in liquid scintillation vials, treated

[3] One becquerel = 1 disintegration per second.

with 1.0 ml of 10% HCl to drive off any residual inorganic carbon, and the activity retained on the filters determined by liquid scintillation counting on a Searle Analytic Delta 300 liquid scintillation counter using ACS (Amersham) as a fluor (Laws *et al.*, 1990). Total inorganic $^{14}C$ activity in the bottles was measured by the addition of 0.5 ml of water to 0.2 ml of a 1:1 solution of phenethylamine:methanol (Iverson *et al.*, 1976). Photosynthetic rates were calculated using the equations in Strickland and Parsons (1972), assuming the inorganic carbon concentration in the seawater to be 2.3 millimolar (mM).

Heterotrophic bacterial counts in the bottles amended with unfiltered sewage effluent were determined initially and after 24 h (sunset to sunset) using a Coulter EPICS 753 flow cytometer.

In addition to the 24 h incubations to determine the short-term impact of the sewage effluent on photosynthetic rates and bacterial numbers, one-week incubations were conducted to determine the $\delta^{15}N$ of the biologically available dissolved nitrogen in the sewage effluent and to determine the impact of sewage enrichment on the composition of the phytoplankton community. For these experiments, 100 ml of sewage filtrate were added to each of two clear polycarbonate bottles containing 900 ml of Diamond Head water. One bottle was incubated without further nutrient additions and the cells harvested by filtration after one week for pigment analysis. The second bottle was enriched with the mixture of trace metals, vitamins, and phosphate recommended for IMR medium (Eppley *et al.*, 1967). The phosphate concentration produced by this enrichment was about 50 mM and the resultant ratio of dissolved inorganic N to dissolved inorganic P about 2 on a molar basis. The enrichment thus assured that the phytoplankton would strip the water of nitrogen before significantly depleting the phosphate concentration, since the ratio of N to P in phytoplankton is about 16 and virtually never falls outside the range 3-30 on a molar basis (Ryther and Dunstan, 1971). After one week all available nitrogen had been stripped from the water, and the phytoplankton cells were harvested by filtration and the particulate material collected on the filter (GF/F) analyzed for $\delta^{15}N$ as previously described.

In addition to the one-week incubations conducted with sewage effluent filtrate, similar bioassays were conducted with stream runoff and groundwater to determine the $\delta^{15}N$ of the biologically available dissolved N. The streams that were sampled included Kalauao Spring, Aiea Stream, the Manoa-Palolo drainage canal, Waiawa Stream, Manaiki Stream, Waimalu Stream, Waikela Stream, and the surface lens of the Ala Wai Canal. The groundwater samples were taken from two wells in the Ewa plain. For the stream water assays, several liters of water were collected and transferred to clear polycarbonate bottles, which were then enriched with IMR concentrations of trace metals, vitamins, and phosphate. The natural phytoplankton community in the streams was allowed to grow until all available nitrogen had been stripped from the water. In the case of the groundwater, 200 ml of groundwater were added to 800 ml of Diamond Head water, and the mixture enriched with IMR concentrations of trace metals, vitamins, and phosphate. The Diamond Head phytoplankton community was then allowed to grow until all available N had been stripped from the water.

### 3.2.2 Beach Sampling Experiments

Samples were collected at the ten beaches shown in Fig. 3.1 on a monthly basis from August 1993 to July 1994. The samples were collected from just below the surface in acid-cleaned 20-liter plastic carboys at a distance from the shoreline where the water column was one meter deep. The temperature of the water was recorded immediately using a thermometer calibrated to 0.1 $^{\circ}C$ and the conductivity measured with an Extech Oyster conductivity meter. Upon return to the laboratory, aliquots of the water were filtered through GF/F filters for further analysis. The filtrates were used to determine inorganic nutrient concentrations as previously described. Samples for PC and PN analysis were collected on precombusted GF/F filters and processed as described above. Samples for chl *a* and carotenoid pigment analysis were collected on GF/F filters and placed in liquid nitrogen prior to extraction. The pigments were extracted by placing the filters in approximately 5 ml of acetone for 12 h. The filters were then ground using a Wheaton tissue grinder and the filter residue removed by centrifugation as described in Strickland and Parsons (1972). The extracted pigment concentrations were then

determined on a Varian 5000 high performance liquid chromatograph (HPLC) as described by Laws *et al.* (1990).

### 3.2.3 Offshore Field Work

Six hydrographic cruises were performed between December, 1993 and December, 1994. Cruises consisted of horizontal transects approximately along the 60 m depth contour between Diamond Head and Barbers Point and vertical profiles at stations generally located at depths of 20, 60, and 120 m. Typical horizontal transect tracks and the locations of the vertical profile stations are shown in Fig. 3.2.

Hydrographic profiles of temperature, salinity, and beam transmissometry to a maximum depth of 100 m were conducted with an Applied Microsystems CTD12 system fitted with a 25 cm beam transmissometer (CTTD). The CTTD was fitted with internal RAM and operated in a stand-alone mode. The CTTD was programmed to record data at two second intervals for all vertical profiles, and data were downloaded to a portable computer at the completion of each cast.

Vertical profiles of *in vivo* fluorescence were performed to a maximum depth of 60 m with a submersible pump system. The system consisted of a 110 volt submersible pool pump, portable generator, 60 m of two-centimeter inside-diameter opaque plastic hose, and assorted fittings. The flow from the pump went to a Turner Designs Model 10 digital fluorometer interfaced to a portable computer. The fluorometer recorded a data point every two seconds. The depth associated with each fluorometer data point was estimated from the volume flow, the volume of the pump and hose, and careful recording of the times of deployment, arrival at depth, retrieval, etc. Chlorophyll *a* values were calculated from a linear regression between paired extracted chl *a* and in vivo fluorescence samples.

Horizontal transects for temperature, salinity, beam transmissometry and *in vivo* fluorescence were performed with the Applied Microsystems CTTD and the Turner fluorometer. The CTTD was fitted with flow-through cells which enabled the collection

of temperature, salinity and transmission while on deck. The pump was positioned approximately 20 m behind the boat at a depth of 2-3 m. Flow was split and directed to the CTTD and fluorometer. Data were collected at ten-second intervals on portable computers.

Vertical profiles of natural (solar induced) fluorescence were made to a maximum depth of 100 m with a Biospherical Instruments PNF300 profiling natural fluorometer. This system measures photosynthetically active radiation (PAR) at the surface and at depth, upwelling natural fluorescence, and temperature. The system provided profiles of these parameters as well as calculating extinction coefficients, chlorophyll, and productivity (Chamberlain *et al.*, 1990).

Horizontal transects and vertical profiles of phytoplankton physiological conditions were performed in December, 1994 with a prototype fast repetition rate fluorometer (FRRF) (Greene *et al.*, 1994). The FRRF was set up in parallel with the Turner fluorometer on the submersible pump system and collected data at five-second intervals. Changes in fluorescence measured by the FRRF provide an estimate of the physiological state of the phytoplankton and phytoplankton productivity rates.

Water samples for analysis of chemical and biological parameters were collected by Niskin bottle during the December 1993 cruise and with the submersible pump system for all subsequent cruises. Samples were transferred to polyethylene bottles and chilled in ice until analyzed in the lab. Samples were split, with one fraction filtered onto Nucleopore membrane filters for analysis of extracted chlorophyll, and a second fraction filtered onto tared GF/F glass microfibre filters for determination of total suspended solids. The other fraction was analyzed (unfiltered) for dissolved nutrients (nitrate + nitrite, ammonium, total nitrogen, phosphate, total phosphorus, and silicate) and turbidity. All analyses were performed using accepted oceanographic techniques for low concentration samples (Table 3.2).

Large-volume (2 liter) samples were collected at selected stations for analysis of phytoplankton pigments as described in section 3.2.2.

Table 3.2 Methodologies for water quality analyses performed during offshore surveys.

| Water Quality Parameter | Collection and Analysis |
|---|---|
| Salinity | Laboratory salinometer |
| Nutrient Analyses | Technicon AutoAnalyzer II |
| Total Nitrogen | D'Elia *et al.* (1977) |
| Ammonium | Solorzano (1969) |
| Nitrate + Nitrite | Technicon Inc. (1977) |
| Total Phosphorus | Grasshoff *et al.* (1983) |
| Phosphate | Murphy and Riley (1962) |
| Silicate | Strickland and Parsons (1972) |
| Chlorophyll | Turner Designs fluorometer<br>Strikland and Parsons (1972) |
| Turbidity | Turner Designs nephalometer<br>APHA Standard Methods (1992) |
| Suspended Solids | Filtration, Cahn electrobalance<br>APHA Standard Methods (1992) |

# 4 RESULTS

## 4.1 Bioassay Results

Figures 4.1 and 4.2 summarize with respect to production and growth the responses of the phytoplankton and heterotrophic bacterial communities to sewage enrichment. Average photosynthetic rates were depressed at 100% irradiance and peaked at a simulated incubation depth of 26 m (15% surface irradiance). There was very little response of the phytoplankton to sewage enrichment at 100% irradiance, but at lower irradiances the response was described rather well by an equation of the form

$$Y = 100 + \frac{80X}{250 + X}$$

where Y is the photosynthetic rate expressed as a percent of the control value and X is the concentration of added ammonium.

Heterotrophic bacterial numbers in sewage enriched seawater increased from initial values at all irradiances. The increase was about a factor of 3 in samples incubated at 8-33% surface irrdiance and a factor of 2.5 for the samples incubated at 100% surface irradiance.

The $\delta^{15}N$ of the biologically available dissolved N in the sewage averaged 7-10 per mil, about 5-8 per mil higher than the $\delta^{15}N$ of the PN in the sewage (Table 3.1). The $\delta^{15}N$ of the biologically available dissolved N in stream water and groundwater averaged $2.4 \pm 2.7$ per mil and $10.4 \pm 0.7$ per mil, respectively.

## 4.2 Beach Monitoring Results

Figures 4.3 to 4.21 summarize the results of the beach monitoring work. Salinities and silicate concentrations varied in a systematic manner between the 10 beaches (Fig. 4.3 and 4.4). Both were relatively constant at Diamond Head, Queens Surf, Fort Derussy, Ala Moana, and Sand Island beach parks. The lowest salinities and highest

silicate concentrations were found at Keehi Lagoon and Fort Kam beach parks. Salinities then increased and silicate concentrations decreased moving west from Ewa Beach to Barbers Point. There was a highly significant negative correlation (r = -0.90) between median silicate and salinity concentrations at the 10 beaches (Fig. 4.5). A regression line fit to the data extrapolates to a silicate concentration of 306 mM at zero salinity. This figure is comparable to values reported for freshwater streams on Oahu (Smith *et al.*, 1981). Because of the low silicate concentration in seawater (~2 mM) near the Hawaiian Islands, even a small amount of freshwater mixed with seawater can significantly raise the silicate concentration of the mixture. Because of this fact, silicate concentrations in the ocean near Oahu are a useful tracer of the presence of freshwater derived from groundwater.

Chlorophyll *a* concentrations were by far the highest at Keehi Lagoon Beach Park (Fig. 4.6). The second and third highest chl a concentrations were at the mouth of the Ala Wai Canal (1.4 mg $l^{-1}$) and at Ala Moana Beach Park (Fig. 4.6). Keehi Lagoon, the Ala Wai Canal, and the lagoon at Ala Moana Beach Park are all confined bodies of water, and in the first two cases are directly impacted by stream runoff. The lowest median chl a concentration was found at Sand Island Beach Park, which is the beach closest to the Sand Island sewer outfall. Ewa Beach and Oneula Beach had the highest chl a concentrations of the beaches directly exposed to the ocean.

Particulate carbon and nitrogen concentrations were highest at Keehi Lagoon Beach Park, with Ewa Beach and Oneula Beach having the second and third highest concentrations (Fig. 4.7 and 4.8). Sand Island had the lowest median particulate nitrogen concentration and the second lowest particulate carbon concentration.

The C/N ratios of the particulates ranged between 12 and 22 by weight (Fig. 4.9). The lowest values were found at the mouth or within enclosed bodies of water - Ala Moana, Keehi Lagoon, and Fort Kam beach parks. The high value at Ewa Beach may reflect the presence of seaweed fragments in the water. Seaweed of the genus *Gracilaria* is abundant at Ewa Beach.

In order to explore the temporal variability of particulate nitrogen concentrations on the beaches, we divided the sampling dates into wet, intermediate, and dry categories based on the median salinities at the ten beaches (Fig. 4.10). Based on this criterion, wet days were defined to be April through June 1994; intermediate days were September through December, 1993. Dry days were August 1993 and January through March 1994. The relationship between median particulate nitrogen and median salinity on wet, intermediate, and dry days is shown in Fig. 4.11. The particulate nitrogen concentrations were about 50% higher on wet days compared to dry days, with days of intermediate salinity having intermediate particulate nitrogen concentrations. The implication of this analysis is that particulate nitrogen concentrations on the beaches are impacted by freshwater runoff and are generally higher on days when the salinity is depressed due to the presence of freshwater.

The $\delta^{15}N$ of the suspended particulates in the water column at the beaches generally increased from east to west, i.e., from Diamond Head to Barbers Point Beach Park (Fig. 4.12). The lowest values, 3.5-4.5 per mil, were found at Diamond Head, Queens Surf, Fort Derussy, Ala Moana and Sand Island beach parks. Based on the salinity and silicate concentrations measured at these beaches, they appear to be the ones least impacted by freshwater. The $\delta^{15}N$ values generally increased from Keehi Lagoon to Barbers Point, and all values exceeded 5 per mil. It seems clear that Keehi Lagoon Beach Park is heavily impacted by fresh water, but if stream runoff was the source of much of the nitrogen in the water in Keehi Lagoon, our bioassay results would imply that the $\delta^{15}N$ at Keehi Lagoon should be low rather than high. Considering its location, it seems unlikely that the water at Keehi Lagoon Beach Park is being impacted by sewage from either the Sand Island or Honouliuli sewage treatment plants. Given the highly eutrophic condition of the lagoon and the very muddy nature of the sediments at the bottom of the lagoon, it does seem likely that there is a significant amount of denitrification occurring in Keehi Lagoon. Since denitrification discriminates against $^{15}N$, the nitrogen left behind is enriched in $^{15}N$, and this may account for the elevation of the $\delta^{15}N$ in Keehi Lagoon. The $\delta^{15}N$ of 6.5 at Fort Kam Beach Park is probably due to its proximity to the Fort Kam

sewage treatment plant, assuming that the biologically available nitrogen in the effluent from the Fort Kam plant has a $\delta^{15}N$ comparable to that of the Sand Island and Honouliuli sewage treatment plants, i.e., 7-10 per mil. The elevated $\delta^{15}N$ values at Ewa Beach, Oneula Beach, and Barbers Point could be due either to groundwater or to sewage. Fortunately the chemical signatures of groundwater in the Ewa area and sewage from the Sand Island and Honouliuli treatment plants are quite different. The sewage has very high ammonium and silicate concentrations, a phosphate concentration of about 60 mM, and a nitrate concentration of 6-7 mM (Table 3.1). Groundwater in the Ewa area has a silicate concentration of several hundred micromolar, a nitrate concentration of about 700 mM, and very little ammonium or phosphate (Dames and Moore, 1986). An examination of the silicate and $\delta^{15}N$ values for Ewa, Oneula, and Barbers Point beach parks (Fig. 4.13) reveals that there were two months in which both silicate and $\delta^{15}N$ values were high, December 1993 and May 1994. The phosphate concentrations measured at these three beaches during those two months were the second and third lowest recorded during this study (Fig. 4.14). The ammonium concentrations were also below average during those two months (Fig. 4.15). Nitrate concentrations, however, were above average (Fig. 4.16). In fact, the December nitrate concentrations were the second highest recorded during the study. These observations do not support the hypothesis that the high $\delta^{15}N$ values at Ewa, Oneula, and Barbers Point beach parks were caused by sewage effluent from the Sand Island and Honouliuli treatment plants reaching the shoreline. Rather, they suggest that the high $\delta^{15}N$ values reflect the influence of groundwater seepage. The lack of a sewage influence is further suggested by the fact that there is a distinctly negative correlation between ammonium concentrations and $\delta^{15}N$ on these beaches (Fig. 4.17) and by the results of the pigment analyses (see following).

When data from all ten beaches were analyzed, median concentrations of ammonium (Fig. 4.18) were found to be roughly 4 times the concentrations of nitrate (Fig. 4.19) and phosphate (Fig. 4.20). The lowest median ammonium concentration, highest phosphate concentration, and second-highest nitrate concentration were found at Fort Kam Beach Park. The high phosphate concentration is not surprising considering

the proximity of the beach to the Fort Kam sewage treatment plant. The Fort Kam plant is a secondary treatment facility which uses the activated sludge process, and almost all the inorganic nitrogen in its effluent is nitrate or nitrite.[4] This fact probably accounts for the high nitrate concentrations at Fort Kam Beach Park. The drawdown of ammonium probably reflects the stimulation of microbial production by the phosphate in the sewage effluent and the fact that phytoplankton prefer ammonium over nitrate as a source of inorganic nitrogen (McCarthy *et al.*, 1977). With the exception of the phosphate concentrations at Queens Surf and Fort Kam, all the phosphate concentrations were remarkably uniform and fell within the range 0.10-0.15 mM. The reason for the unusually low phosphate concentration at Queens Surf beach is unclear, but may be due to the fact that it is arguably the beach least impacted by freshwater (see Fig. 4.3 and 4.4).

In order to explore the possible association between ammonium, nitrate, and phosphate concentrations and freshwater, we have plotted in Fig 4.21-4.23 the relationships between these nutrients and silicate. In the case of ammonium (Fig. 4.21), the correlation is negative and highly significant ($p < 0.01$). If sewage effluent were a significant source of ammonium on these beaches, one would expect the correlation to be positive, because the silicate and ammonium concentrations in the sewage effluent are comparable (Table 3.1). It would appear from this analysis that the freshwater which impacts water quality on these beaches has a lower concentration of ammonium than the nearshore seawater. In fact the nitrate concentrations in stream water on Oahu are roughly 10 times the ammonium concentrations (Laws and Atkinson, 1994). Hence one would expect streams to have a much greater impact on nitrate concentrations than ammonium concentrations.

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[4] The effluent from the Fort Kam plant contains 359 μM nitrate + nitrite, 13 μM ammonium, and 55 μM total phosphorus (personal communication to E. Laws from Dwayne at 808-474-3704).

As expected, there is a positive correlation between nitrate and silicate concentrations (Fig. 4.22). The correlation is significant at $p = 0.08$ based on a two-tailed test or $p = 0.04$ based on a one-tailed test. The implication is that the nitrate concentration in the freshwater impacting these beaches is greater than the nitrate concentration in the seawater. The marine nitrate concentration, estimated from the regression line at a silicate concentration of 2 mM, is about 0.1 mM. The freshwater nitrate concentration, assuming the freshwater to be sewage effluent, can be estimated by extrapolating the regression line to a silicate concentration of about 900 mM (Table 3.1). The freshwater value estimated in this way is 16.3 mM, which is about 2.5 times the nitrate concentrations in the sewage effluent.

Phosphate concentrations were also found to be positively correlated with silicate concentrations. The correlation coefficient is significant at $p = 0.10$ based on a two-tailed test or $p = 0.05$ based on a one-tailed test. The implication is that the phosphate concentration in the freshwater impacting these beaches is greater than the phosphate concentration in the seawater. The marine phosphate concentration, estimated from the regression line at a silicate concentration of 2 mM, is about 0.105 mM. The freshwater phosphate concentration, again assuming the freshwater to be sewage effluent, is estimated to be 8.6 mM, which is about 15% of the phosphate concentration in the sewage effluent. The implication of these calculations is that the freshwater which is impacting these beaches is not sewage effluent.

The carotenoid pigment profiles (Fig. 4.24-4.26) were tested for similarity by calculating the correlation coefficient between each pair of profiles, taking the normalized concentrations of one profile as X and the normalized concentrations of the second profile as Y. The profiles were then assigned to groups based on the arbitrary criterion that the correlation coefficient between all pairs of pigment profiles in a group be $\geq 0.87$, the critical value of the magnitude of the product-moment correlation coefficient at $p = 0.01$ for $n = 7$. The resultant groups are as follows:

Group 1: Keehi Lagoon, Diamond Head, Queens Surf, Fort Derussy, Ala Moana

Group 2: Ala Moana, Sand Island, Ewa Beach, Oneula Beach

Group 3: Ala Wai Canal

Group 4: Fort Kam

Group 5: Barbers Point

Group 6: Sewage-enriched Diamond Head buoy water

The correlation coefficients between the beach profiles in groups 1 and 2 are shown in Tables 4.1 and 4.2, respectively.

Table 4.1 Correlation coefficients between pigment profiles of beaches in group 1.

| | KL | DH | QS | FD | AM |
|---|---|---|---|---|---|
| KL | | 0.98 | 0.97 | 0.95 | 0.87 |
| DH | | | 0.99 | 0.99 | 0.93 |
| QS | | | | 0.99 | 0.91 |
| FD | | | | | 0.95 |

Table 4.2 Correlation coefficients between pigment profiles of beaches in group 2.

| | AM | SI | EB | OB |
|---|---|---|---|---|
| AM | | 0.88 | 0.93 | 0.93 |
| SI | | | 0.91 | 0.97 |
| EB | | | | 0.95 |

The Ala Moana profile correlated almost equally well with beaches in both groups 1 and 2. None of the profiles contained more than small amounts of zeaxanthin and prasinoxanthin. Prasinoxanthin is diagnostic for prasinophytes and zeaxanthin for cyanobacteria. These two algal groups apparently contributed little to the biomass of microalgae at any of the beaches. The pigments which proved useful in distinguishing the profiles were therefore fucoxanthin, chlorophyll *b*, 19'-butanoyloxyfucoxanthin, 19'-hexanoyloxyfucoxanthin, and peridinin. Peridinin is diagnostic for dinoflagellates, and in the absence of prasinophytes, chlorophyll *b* is diagnostic for chlorophytes (Letelier *et al.*, 1993). Fucoxanthin, 19'-butanoyloxyfucoxanthin, 19'-hexanoyloxyfucoxanthin are all found in chrysophytes, prymnesiophytes, and diatoms, but in differing ratios, and to a first approximation fucoxanthin may be taken as diagnostic of diatoms, 19'-butanoyloxyfucoxanthin as diagnostic of chrysophytes, and 19'-hexanoyloxyfucoxanthin as diagnostic of prymnesiophytes.

The following is a summary of the relative importance of the dominant diagnostic carotenoids in the six algal groups:

Group 1: chl *b* > fucoxanthin ~ 19'-hexanoyloxyfucoxanthin

Group 2: fucoxanthin > chl *b* > 19'-hexanoyloxyfucoxanthin

Group 3: peridinin > chl *b* > 19'-hexanoyloxyfucoxanthin ~ 19'-butanoyloxyfucoxanthin ~ fucoxanthin

Group 4: fucoxanthin > 19'-hexanoyloxyfucoxanthin ~ 19'-butanoyloxyfucoxanthin

Group 5: 19'-hexanoyloxyfucoxanthin ~ fucoxanthin

Group 6: fucoxanthin > chl b > 19'- butanoyloxyfucoxanthin

Groups 1 and 2, which account for 8 of the 10 beaches, are dominated by the same three algal groups, diatoms, chlorophytes, and prymnesiophytes. Chlorophytes are most important in group 1, and diatoms are most important in group 2. The microalgal communities at the other two beaches, Fort Kam and Barbers Point, had significant numbers of diatoms and prymnesiophytes, but at Fort Kam there were substantially more chrysophytes than at Barbers Point. The Ala Wai Canal (group 3) was unique in having large numbers of dinoflagellates. The microalgal community that developed in Diamond Head water enriched with sewage was dominated by diatoms, with chlorophytes and chrysophytes running a close second. The fact that this profile stood in a group by itself suggests that sewage is not significantly impacting the microalgal communities at any of the beaches we studied.

### 4.3 Offshore Field Results

Vertical and horizontal trends in the levels of temperature, salinity, dissolved nutrients, natural fluorescence, chlorophyll, and turbidity were measured during the six sampling cruises. The data presented here are only a small portion of those collected and represent those data which support general trends and conclusions regarding the relative impacts of point and non-point source discharges on water quality and phytoplankton communities in Mamala Bay.

#### 4.3.1 Dissolved Nutrients

Figure 4.27 presents concentrations of ammonium and nitrate in all water samples plotted as a function of silicate concentration. Each data point is identified by the depth (m) at which it was taken. Figure 4.27A shows the presence of two different water types

in addition to the typically low nutrient nearshore oceanic water: water collected at surface stations (1, 2, and 5 m) with silicate levels from 5-20 mM and ammonium levels less than 1 mM; and deep (15-60 m) samples with silicate levels between 2 and 10 mM and ammonium levels between 1 and 9 mM. Figure 4.27B shows that in general the high silicate, low ammonium surface waters were also those highest in nitrate. These data suggest that at the times the surveys were performed, the plumes from the wastewater treatment plant (WWTP) discharges were generally located between 20 and 60 m depth and were distinguishable by their high ammonium, high silicate signature, while nearshore surface samples were characteristic of waters receiving groundwater inflow with a low ammonium, high silicate signature.

These characteristic nutrient patterns were also seen at stations located near the potential point and non-point sources. Figures 4.28A-C present the concentrations of ammonium, nitrate, and turbidity plotted against station, with individual data points identified by the sample depth. High ammonium levels were usually seen only in the deep (20-60 m) samples at stations near the Sand Island WWTP (stations 1, 2, and 3) and the Honouliuli WWTP (stations 14, 15, and 16). High nitrate levels were seen at the surface stations off the Ala Wai Canal (station 4) and Pearl Harbor (station 9). Occasional high nitrate levels were seen at 20 m at stations throughout Mamala Bay (Stations 2, 8, 12, 16, and 17) and deeper at stations 12 and 17. High turbidity levels were observed almost exclusively at nearshore shallow stations (4 and 9).

### 4.3.2 Salinity, Turbidity, and Chlorophyll Profiles

Vertical profiles of temperature, salinity, transmissometry, and chlorophyll on six cruises showed very different water column structure between cruises. Vertical profiles of temperature, salinity, turbidity, and chlorophyll for 60 m stations (Diamond Head, Ala Wai Canal, Sand Island, Pearl Harbor, Honouliuli, midway between Honouliuli and Barbers Point, and Barbers Point) for September and December 1994 are presented in Fig. 4.29 and 4.30. The September cruise occurred during a period of light winds, while the December cruise occurred at the end of a two-week period of strong trade winds. The

lack of wind mixing in September is reflected in the strong vertical gradients, particularly in temperature, while the deep mixed layer and lack of gradients in December reflect the previous strong mixing regime.

Strong subsurface structure in turbidity and chlorophyll was evident throughout the year. Strong subsurface peaks in turbidity were seen at the 60 and 120 m Honouliuli stations in September (Fig. 4.31). Weaker subsurface turbidity maxima were seen in the vertical profiles at 60 and/or 120 m stations at Honouliuli in February and December, 1994 (Fig. 4.32), and at Sand Island in February, May, August, September (Fig. 4.31), and December, 1994 (Fig. 4.32). The turbidity peaks in September were generally associated with salinity minima (Fig. 4.33), which suggests these features may be related to the WWTP discharge. No salinity minima were seen in December (Fig. 4.34).

In December higher levels of turbidity were observed throughout the water column at the 20 m and 60 m stations at Pearl Harbor and Honouliuli (Fig. 4.32). These conditions may represent the presence of the Honouliuli WWTP plume rising to the surface in the vertically uniform water column[5] or may reflect the previous period of vigorous wind mixing and resuspension of fine sediments from the bottom.

There were general patterns of increasing chlorophyll concentration with depth which did not reflect the patterns in turbidity and salinity. In waters around the Hawaiian Islands, an accumulation of chlorophyll occurs at the pycnocline (the region of maximum density change), the result of the processes of wind mixing, phytoplankton growth, sinking, nutrient uptake and changes in cellular chlorophyll content at low light. This accumulation is termed the deep chlorophyll maximum. In offshore waters the maximum is found between 60 and 120 m depth, with peak chlorophyll concentrations exceeding 0.5 mg $l^{-1}$ (Bienfang and Szyper, 1981). Thus the observed chlorophyll distributions may

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[5] Chemical analyses, however, showed no elevated levels of ammonium or silicate, which would be characteristic of WWTP discharges.

be a reflection of this general oceanographic feature rather than a response to the WWTP discharges.

### 4.3.3 Chlorophyll *a*: Turbidity Relationships

Wastewater treatment plant discharges contain materials (coproporphyrins) which fluoresce in the same spectral region as chlorophyll and thus would be detected by the fluorometer which was set up to detect chlorophyll fluorescence. Since the wastewater discharge contains a variety of particulate material which does not fluoresce, one would expect that the ratio of chlorophyll to turbidity would be different for natural populations of phytoplankton than for wastewater discharges. Outflow from estuaries, containing both phytoplankton and mixed terrigenous and organic particles, would have a chlorophyll:turbidity ratio different from either natural nearshore phytoplankton or WWTP discharges.

Vertical profiles of the chlorophyll:turbidity ratio for Sand Island and Honouliuli stations for September and December are presented in Fig. 4.35. In September, a period of strong vertical gradients, a deep chlorophyll:turbidity maximum was observed at 50-60 m depth at the deep stations (stations 3 and 15). The upper 30 m of the water column was well mixed and exhibited low (<0.1) ratio values. In contrast, the vertical profiles in December, a period of weak or no gradients, were vertically uniform at all Sand Island stations and over the upper 40 m at the deep Honouliuli station (15), with levels similar to or slightly higher than those observed in the upper water column in September. Stations 13 and 14 at Honouliuli, however, showed elevated chlorophyll:turbidity ratios throughout the water column, with values similar to those observed at the 60 m depth in September.

### 4.3.4 Solar Induced Fluorescence

Vertical profiles of temperature and the ratio of solar induced fluorescence to underwater light measured by the PNF300 for the deep stations at Sand Island, Pearl Harbor, and Honouliuli in September and December, 1994 are presented in Fig. 4.36 and

4.37. The ratio of natural fluorescence to underwater light provides a normalized estimate of the fluorescence response of particulate material in the water column. In September the profiles show the development of strong layers of fluorescent material located just under the surface mixed layer. The shapes and depths of these fluorescent layers are similar to the layers observed in the chlorophyll:turbidity ratio plots. However, the December vertical profiles of fluorescence to light show the layers are less well developed and are not related to any physical gradient in the water column.

### 4.3.5 Chemical Constituents of the Water

Measurements of the chemical constituents of the water samples provide an indication of the water source. The concentrations of chlorophyll, ammonium, nitrate, phosphate, and silicate from water samples collected at 20 and 60 m depths at the three deep stations in August and December are presented in Table 4.3. Low concentrations of chlorophyll (~0.1-0.2 mg $l^{-1}$) were measured in most cases, but there were peaks at 60 m of 0.27 and 0.30 mg $l^{-1}$ at Pearl Harbor and Honouliuli, respectively, in December, and at 20 m of 0.27 mg $l^{-1}$ at Sand Island in August.

Table 4.3 Nutrient and pigment concentrations measured at deep stations during August and December, 1994 cruises.

| Month | Station | Depth (m) | Chl (mg/l) | $NH_4^+$ (mM) | $NO_3^-$ (mM) | $PO_4^{3-}$ (mM) | Si (mM) |
|---|---|---|---|---|---|---|---|
| August | Sand Island | 20 | 0.266 | 0.32 | 0.01 | 0.07 | 1.76 |
| | | 60 | 0.174 | 1.91 | 0.05 | 0.18 | 2.83 |
| | Pearl Harbor | 20 | 0.194 | 0.02 | 0.01 | 0.05 | 1.23 |
| | | 60 | 0.208 | 0.04 | 0.02 | 0.12 | 1.72 |
| | Honouliuli | 20 | 0.208 | 0.74 | 0.03 | 0.12 | 2.64 |
| | | 60 | 0.200 | 0.16 | 0.05 | 0.06 | 1.72 |
| December | Sand Island | 20 | 0.111 | 0.01 | 0.02 | 0.12 | 1.67 |
| | | 60 | 0.111 | 0.05 | 0.01 | 0.07 | 1.47 |
| | Pearl Harbor | 20 | 0.096 | 0.09 | 0.01 | 0.07 | 1.54 |
| | | 60 | 0.267 | 0.06 | 0.03 | 0.11 | 1.91 |
| | Honouliuli | 20 | 0.059 | 0.05 | 0.01 | 0.12 | 1.64 |
| | | 60 | 0.300 | 0.07 | 0.03 | 0.12 | 1.95 |

These measurements reflect those concentrations seen in the continuous vertical profiles performed with the CTTD and the PNF. As would be expected in oceanic water, the concentrations of ammonium, nitrate, and phosphate waters were generally low, often in the range 10-100 nM, and most silicate concentrations fell in the range 1.7 ± 0.2 mM. One notable exception to this pattern was the 60 m Sand Island results for August, where ammonium, phosphate, and silicate were all elevated. This result suggests the presence of sewage, presumably from the Sand Island outfall. The implication, based on the silicate data in Table 3.1, is that this water contained Sand Island effluent diluted by roughly a factor of 698/(2.83 - 1.7) ≅ 618.[6]

### 4.3.6 Trends in Water Mass Characteristics

Horizontal transects of temperature, salinity, turbidity, and chlorophyll along the 60 m isobath from Diamond Head to Barbers Point in September (Fig. 4.38) and December 1994 (Figure 4.39) showed patterns which may have reflected the advection of water masses with different characteristics from the adjacent Moanalua Bay and outflow from Pearl Harbor.

In September the horizontal transects show a characteristically cooler, higher salinity water mass containing elevated levels of turbidity and chlorophyll at the Diamond Head station. Temperature and salinity return to more typical offshore conditions and remain constant from just west of Diamond Head to midway between Pearl Harbor and Honouliuli, but evidence of the Ala Wai Canal discharge is seen in elevated turbidity and chlorophyll levels west of the Ala Wai Canal. Strong depressions in temperature and salinity along with elevated turbidity and chlorophyll mark the outflow from Pearl Harbor[7]. The strong depressions in temperature and salinity and the associated increased turbidity and chlorophyll to the west of Honouliuli appeared to be a

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[6] 1.7 corrects for the background silicate concentration in the seawater.

[7] A distinct change in surface color could be seen from boatside during the transect and traced to its source at the mouth of Pearl Harbor.

second water mass from Pearl Harbor. The presence of strong vertical gradients in temperature suggest that in September the physical structure of the water column was sufficiently different between the upper surface layer and deeper water that the initial dilution and mixing of the plume with deep water resulted in a plume whose density was not low enough to cross the density barrier of the thermocline. Evidence of a subsurface plume presumably associated with sewage during the September cruise is clearly apparent in Fig. 4.42. The conclusion that the subsurface LuChl/UPAR maximum in Fig. 4.42 was caused by sewage is supported by the ammonium and silicate data in Table 4.3.

The characteristics of the subsurface features of the December vertical profiles suggest that they are manifestations of the deep chlorophyll maximum layer rather than discharge plumes. Chlorophyll levels were typical of the deep maximum, and neither silicate nor ammonium concentrations were elevated above background levels.

### 4.3.7 Carotenoid Pigment Analysis

Carotenoid pigment profiles from the August and September 1994 cruises are shown in Fig. 4.40. On these cruises the water column was stratified, and as noted there is strong evidence of a sewage plume centered at a depth of about 60 m. The pigment profiles from 20 m most strongly resemble the Group 1 beach profiles, with chl *b* being the dominant carotenoid and 19'-hexanoyloxyfucoxanthin of secondary importance. There is more 19'- butanoyloxyfucoxanthin than in the typical Group 1 profile, and in this respect the 20 m results most strongly resemble the Ala Moana Beach pigment profile. There was virtually no resemblance between the 20 m profiles and the sewage enriched profile. The 60 m profiles were qualitatively identical, with chl *b* being the dominant carotenoid, followed by 19'-butanoyloxyfucoxanthin, 19'-hexanoyloxyfucoxanthin, fucoxanthin, and peridinin. The 60 m samples distant from the outfalls were taken at stations 6 (off Ala Wai Canal), 8 (Diamond Head), and 11 (off Pearl Harbor). There was little resemblance between the 60 m profiles and the sewage enriched profile. In the latter case there was very little 19'-hexanoyloxyfucoxanthin, and fucoxanthin was the dominant carotenoid. The implication of this analysis is that while

the sewage plume was present, it was too dilute to significantly impact the composition of the phytoplankton community.

# 5 CONCLUSIONS

The results of this study clearly show that sewage effluent, when mixed with water from Mamala Bay, has a stimulatory effect on phytoplankton and heterotrophic bacteria. The effect on phytoplankton photosynthetic rates is about a 60% increase after 24 h at a dilution factor of 1000. At a dilution of 10,000 the stimulation of photosynthesis amounts to 20-25% after 24 h. Heterotrophic bacterial counts increased by about a factor of 3 after 24 h when sewage effluent was mixed with Mamala Bay water in a ratio of 1:99.

Although the sewage discharges are undoubtedly having some impact on water quality and the biological community in Mamala Bay, there is virtually no evidence to indicate that water quality or the phytoplankton community at recreational beaches is being impacted by sewage. The data collected in this study do indicate, however, that stream runoff and groundwater seepage impact water quality at some recreational beaches. There is also good evidence that effluent from the Fort Kam sewage treatment plant impacts water quality at Fort Kam Beach Park. The relevant evidence with respect to these points is as follows:

1. The lowest chl *a* concentration on any of the recreational beaches was found at Sand Island Beach Park, which is located closer to the Sand Island sewer outfall than any other recreational beach. If the sewage were rising to the surface and moving onshore a significant percentage of the time, one would expect, based on the bioassay results, to see an increase in chl *a* at Sand Island Beach Park. Clearly this was not the case.

2. By far the highest chl *a* concentrations measured at recreational beaches were recorded at Keehi Lagoon Beach Park, which is heavily impacted by runoff from Moanalua and Kalihi Streams. The second-highest chl *a* concentrations were found at the mouth of the Ala Wai Canal, which is heavily impacted by runoff from the Manoa-Palolo drainage canal and Makiki Stream. It is clear from this study that stream runoff can and does have

a significant impact on water quality at some recreational beaches and other shoreline areas.

3. The particulate nitrogen concentrations at the recreational beaches were highest on days when the salinity was lowest and lowest when the salinity was highest. This suggests that freshwater is the cause of elevated particulate nitrogen concentrations, either because the freshwater contains higher particulate nitrogen concentrations than the ocean and/or because nutrients in the freshwater stimulate the growth of microalgae.

4. The $\delta^{15}N$ of suspended particulate matter on the beaches and the results of bioassays with stream water, groundwater, and sewage effluent suggest that the suspended particulate nitrogen concentrations at beaches from Diamond Head to Sand Island Beach Park are little affected by nitrogen derived from fresh water. Of the beaches studied, Keehi Lagoon Beach Park is the one most impacted by nutrients derived from stream runoff. Both inorganic nutrient concentrations and the $\delta^{15}N$ of suspended particulate matter at Fort Kam Beach Park suggest an impact from nutrients derived from the Fort Kam sewage treatment plant, not a surprising conclusion considering the proximity of the plant. Similar analysis of the data from Ewa, Oneula, and Barbers Point beach parks suggests that groundwater is a significant source of nitrogen for those beaches.

5. The correlation between ammonium and silicate concentrations measured on the recreational beaches is negative, in direct contrast to what would be expected if sewage effluent were the source of a significant portion of the ammonium. Sewage effluent from the Sand Island and Honouliuli treatment plants has a very high concentration of both ammonium and silicate (Table 3.1), the ammonium/silicate ratio being about 1.2 on a molar basis. If ammonium concentrations increased as a result of sewage moving onshore, one would expect the silicate concentration to increase by almost an equal amount. In fact, the two concentrations are negatively correlated with a correlation coefficient of -0.87. Stream water, on the other hand, has a high concentration of silicate (~300 mM) and a low concentration of ammonium (~1 mM). The data suggest that the

increases of silicate concentrations above about 2 mM are associated with inputs of stream water with an ammonium concentration less than that of the nearshore ocean.

6. The correlations between nitrate and silicate concentrations and between phosphate and silicate concentrations measured on the recreational beaches are both positive. Extrapolating the regression lines to the silicate concentration of about 900 mM characteristic of Sand Island and Honouliuli sewage effluent gives a nitrate concentration which is 2.5 times higher than the nitrate concentration in the sewage effluent and a phosphate concentration which is about 7 times lower than the phosphate concentration in the sewage effluent. Thus sewage effluent does not seem to be the cause of increases of nitrate and phosphate on these recreational beaches. The results, however, are consistent with stream water being the cause of elevated nitrate and phosphate concentrations. The nitrate concentration in stream water is 2-3 times higher than the nitrate concentration in sewage and the phosphate concentration in stream water much smaller than the phosphate concentration in sewage.

7. Carotenoid pigment profiles, which can be used to characterize the classes of microalgae in the water, are inconsistent with sewage-enriched seawater contributing in a significant way to the microalgal populations on the beaches. Eight of the ten beaches have microalgal communities dominated by diatoms, chlorophytes, and prymnesiophytes. Sewage enrichment produced an algal community with a pigment profile unlike those found on any of the recreational beaches or in the Ala Wai Canal.

In the nearshore field work, significant differences in water quality were observed both vertically and along horizontal transects from Diamond Head to Barbers Point. The major features observed in vertical profiles were deep (~60 m) increases in turbidity and chlorophyll. Analyses of the chemical and biological composition of these features suggest that they are either the natural oceanographic feature known as the deep chlorophyll maximum or a portion of the wastewater discharge plume trapped at depth by the stratified nature of the water column. The chlorophyll maximum layer was a feature found at all deep stations in September, 1994. This fact suggests that the feature is

widespread rather than localized. Modeling of the plume has suggested that it would travel in a relatively unidirectional manner rather than spreading out as a sheet at depth (see MB-5 report).

During the February, May, and September, 1994 cruises the plumes from the offshore sewer outfalls were identifiable at a depth of 60 m by elevations of ammonium and silicate concentrations above background levels. The degree of dilution implied by the silicate concentrations was at least a factor of 140. Based on chemical analyses, there was no evidence of the sewage plumes in December 1994. During December 1993, however, the plume from the Sand Island outfall was visually evident at the surface near the outfall, and chemical analyses revealed elevated ammonium and silicate concentrations at a depth of 10 m. The degree of dilution implied by the silicate concentration was a factor of 830. During August, 1994, elevated ammonium and silicate concentrations were found at a depth of 20 m over the Honouliuli outfall and at depths of 15 and 20 m over the Sand Island outfall. The degree of dilution implied by the silicate concentrations was at least a factor of 500.

Horizontal transects of physical and biological parameters along the 60 m contour between Diamond Head and Barbers Point consistently showed the influences of non-point source discharges on nearshore water quality. Wide areas of decreased surface water clarity were seen on every cruise. The waters off Diamond Head appear to be impacted by water flowing westward from Moanalua Bay into Mamala Bay. Turbid waters were attributed to discharges from the Ala Wai Canal and Honolulu Harbor. By far the greatest impact on nearshore water quality came from the continuous heavy discharge of high turbidity, chlorophyll-laden water from Pearl Harbor. This highly productive estuary is the recipient of surface runoff and groundwater discharge from a drainage basin exceeding 250 $km^2$ in area. The continuous input of fresh and brackish water to the relatively still water of Pearl Harbor results in a continuous outflow of brackish water at the surface. This discharge, in addition to the effluent from the Fort Kam sewage treatment plant, is moved by the prevailing winds and nearshore currents in

an easterly or westerly direction roughly parallel to the shore, with an offshore extent at least to the 120 m depth contour.

# 6 RECOMMENDATIONS

## 6.1 Recommended Actions

The Commission should recommend that the water quality monitoring program presently undertaken by the City and County of Honolulu be modified to include measurements which will permit discrimination between effects caused by non-point source pollution and discharges from the Sand Island and Honouliuli sewer outfalls. Measurements should be made of ammonium, nitrate + nitrite, phosphate, and silicate concentrations. Although silicate is not considered to be a pollutant, it is a very useful tracer of groundwater or fresh water derived from groundwater in Hawaii. Although measurements of salinity could to some extent serve the same purpose as silicate measurements, the impact of stream runoff, groundwater, and sewage discharges on silicate concentrations is far greater than the impact of the same fresh water sources on nearshore salinity values. In other words, the signal-to-noise ratio is much higher for silicate than salinity. Although nitrate is a very minor component of the inorganic nitrogen in the effluent from the Sand Island and Honouliuli sewage treatment plants, it is a major component of the inorganic nitrogen in stream runoff, groundwater, and the effluent from the Fort Kam sewage treatment plant. This fact allows one to distinguish freshwater derived from the Sand Island and Honouliuli sewage treatment plants from freshwater derived from one of these other sources. Nitrate concentrations in nearshore waters should be routinely measured with the chemiluminescent method developed by Garside (1982), because the concentrations of nitrate + nitrite in most cases are below the limit of detection by colorimetric methods.

Carotenoid pigment analyses should be made by HPLC methods to determine whether the phytoplankton community has been impacted by effluent from the Sand Island or Honouliuli sewage treatment plants. The high silicate, ammonium, and phosphate concentrations in the effluents from these plants stimulates diatoms, chlorophytes, and chrysophytes, with diatoms showing the greatest response. The resulting carotenoid pigment profile is different from the profiles associated with the

natural phytoplankton community in Mamala Bay or with phytoplankton communities which wash out of bodies of water such as the Ala Wai Canal and Pearl Harbor.

$\delta^{15}N$ analyses should be made on suspended particulate matter in conjunction with nutrient analyses on recreational beaches. The $\delta^{15}N$ of the biologically available nitrogen in sewage effluent and groundwater in the Ewa area are high compared to the $\delta^{15}N$ of the biologically available nitrogen in stream runoff. Measurement of the $\delta^{15}N$ can therefore be used to determine the source of the nitrogen incorporated into the food chain. Since the source of the high $\delta^{15}N$ of groundwater in the Ewa area is presumably the fertilizer used by Oahu Sugar Company, it is probable that the $\delta^{15}N$ of groundwater in the Ewa area will decline during the next few years due to the closure of Oahu Sugar. The conclusion reached in this report that the elevated $\delta^{15}N$ values observed at Ewa, Oneula, and Barbers Point beach parks can therefore be tested with a monitoring program. If the cause of the elevated $\delta^{15}N$ is sewage, the $\delta^{15}N$ should remain high.

### 6.2 Future Studies

The results of the work reported here strongly suggest that non-point sources are the major factors contributing to reduced water quality in the nearshore regions of Mamala Bay. We found impacts from estuarine discharges from the Ala Wai Canal, Honolulu Harbor, and Pearl Harbor, as well as advective movement of water from adjacent Moanalua Bay. The scope of the work, however, did not incorporate detailed mapping of the extent and magnitude of the various non-point sources, so no estimates of the relative importance or aerial impact could be made.

If an integrated watershed management plan is developed and undertaken for the Mamala Bay watershed, a study to map the aerial extent and magnitude of the non-point sources affecting Mamala Bay under varying seasonal conditions would be critical to establish baseline conditions against which the success of the watershed management plan could be evaluated. Such a baseline study would incorporate at a minimum two-dimensional mapping of Mamala Bay utilizing the existing towed pump system and instrumentation to measure temperature, salinity, turbidity, and fluorescence, and

potentially the fast repetition rate fluorometer to estimate photosynthetic rates. Water quality samples would be collected underway to determine water quality conditions in ambient and plume areas, as indicated by the real time instrumentation. The water quality measurements should include ammonium, nitrate + nitrite, phosphate, and silicate concentrations, and the concentrations of diagnostic carotenoid pigments. Measurements of discharge flows and loads from major non-point sources would be performed concurrently. The results of these efforts could provide the input and validation data for a two-dimensional or three-dimensional model of Mamala Bay which could be used to examine the potential benefits of proposed watershed management actions.

## 7 REFERENCES

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# 8 APPENDIX

## FIGURES

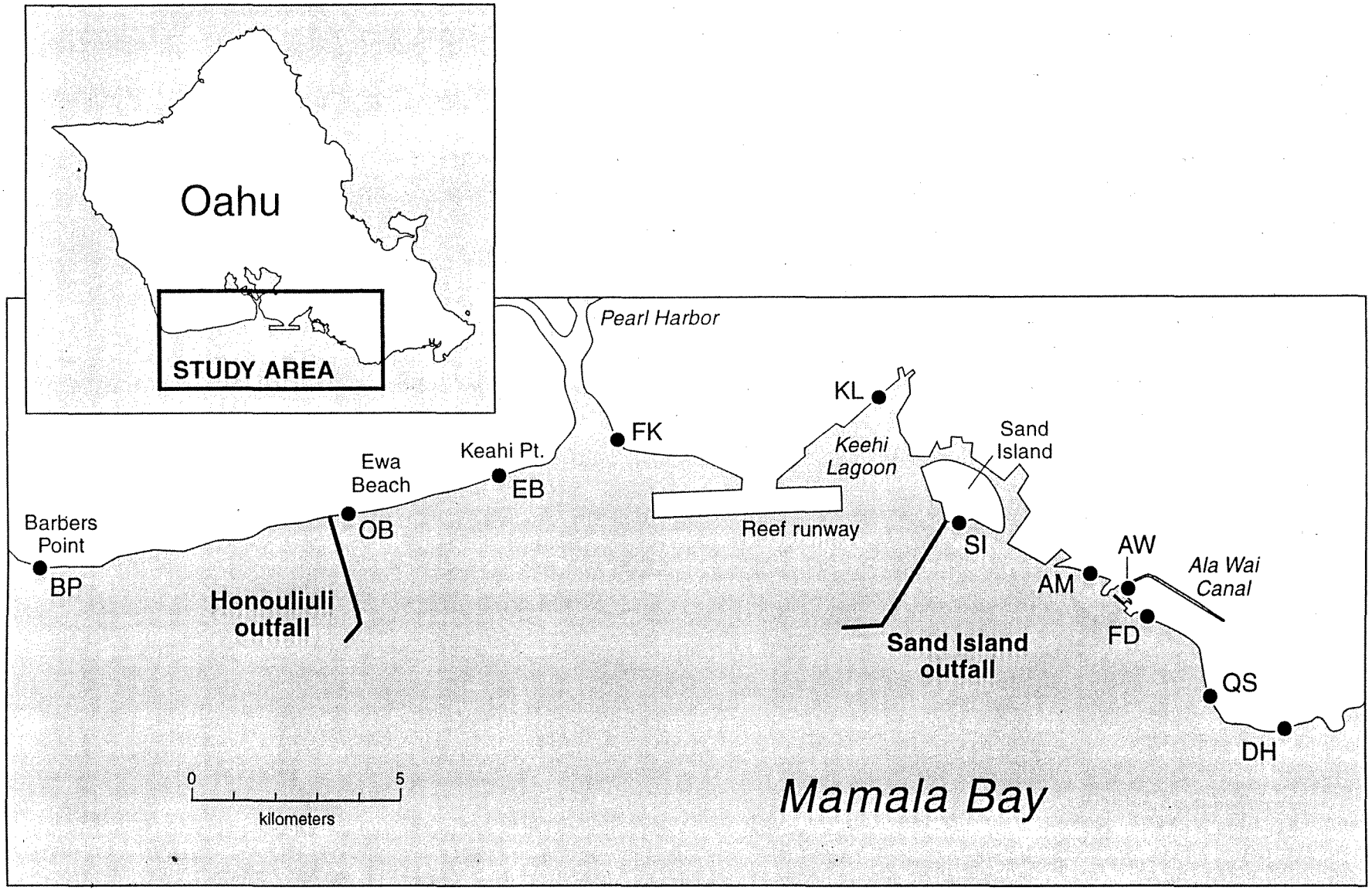


Figure 3.1. Locations of beaches which were sampled on a monthly basis from August 1993 to July 1994. DH = Diamond Head, QS = Queens Surf, FD = Fort Derussy, AM = Ala Moana, SI = Sand Island, KL = Keehi Lagoon, FK = Fort Kam, EB = Ewa Beach, OB = Oneula Beach, BP = Barbers Point. Samples were also collected near the mouth of the Ala Wai Canal (AW).

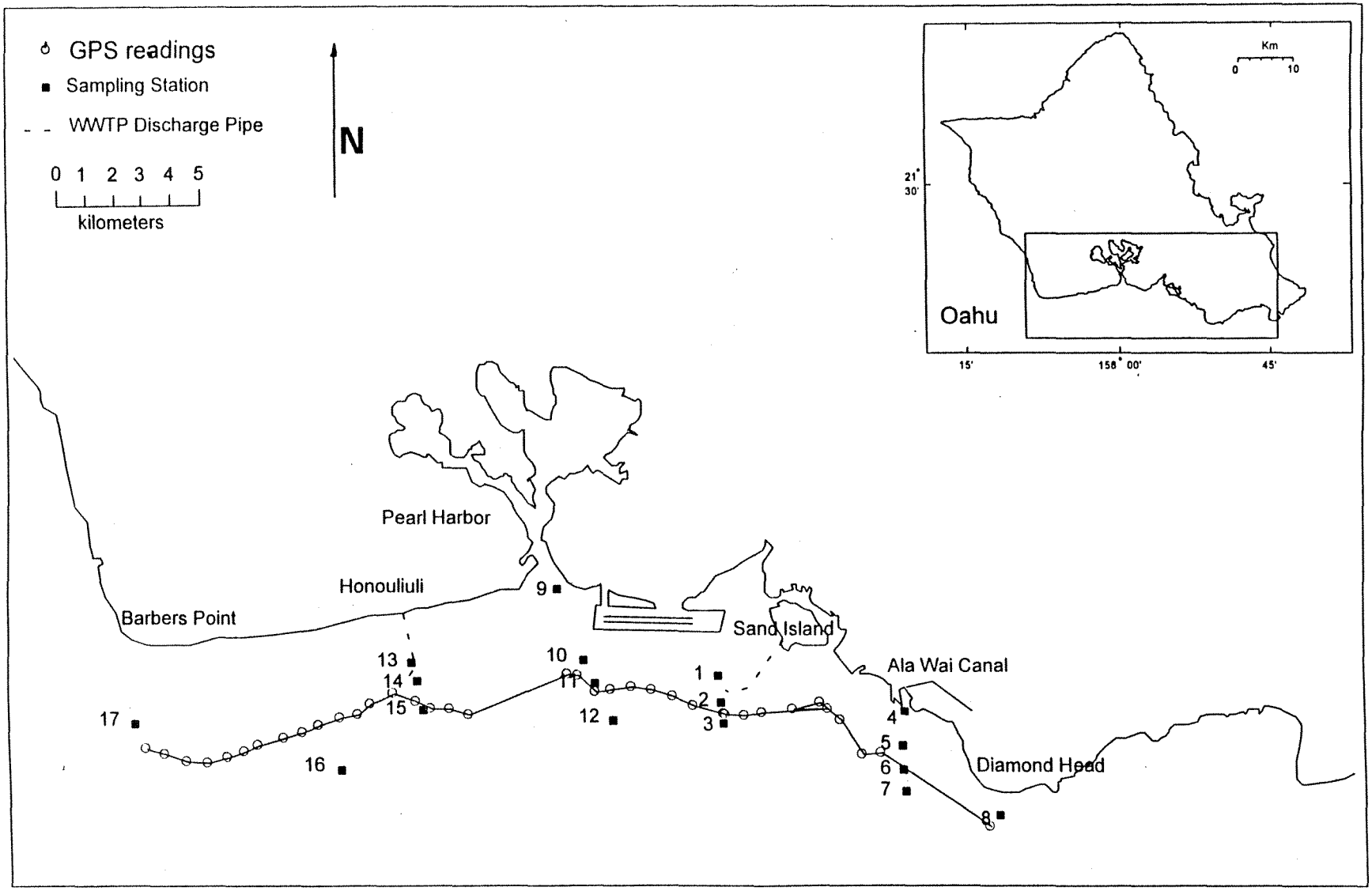


Figure 3.2. Map of Mamala Bay study area showing water quality station locations and typical horizontal transect track.

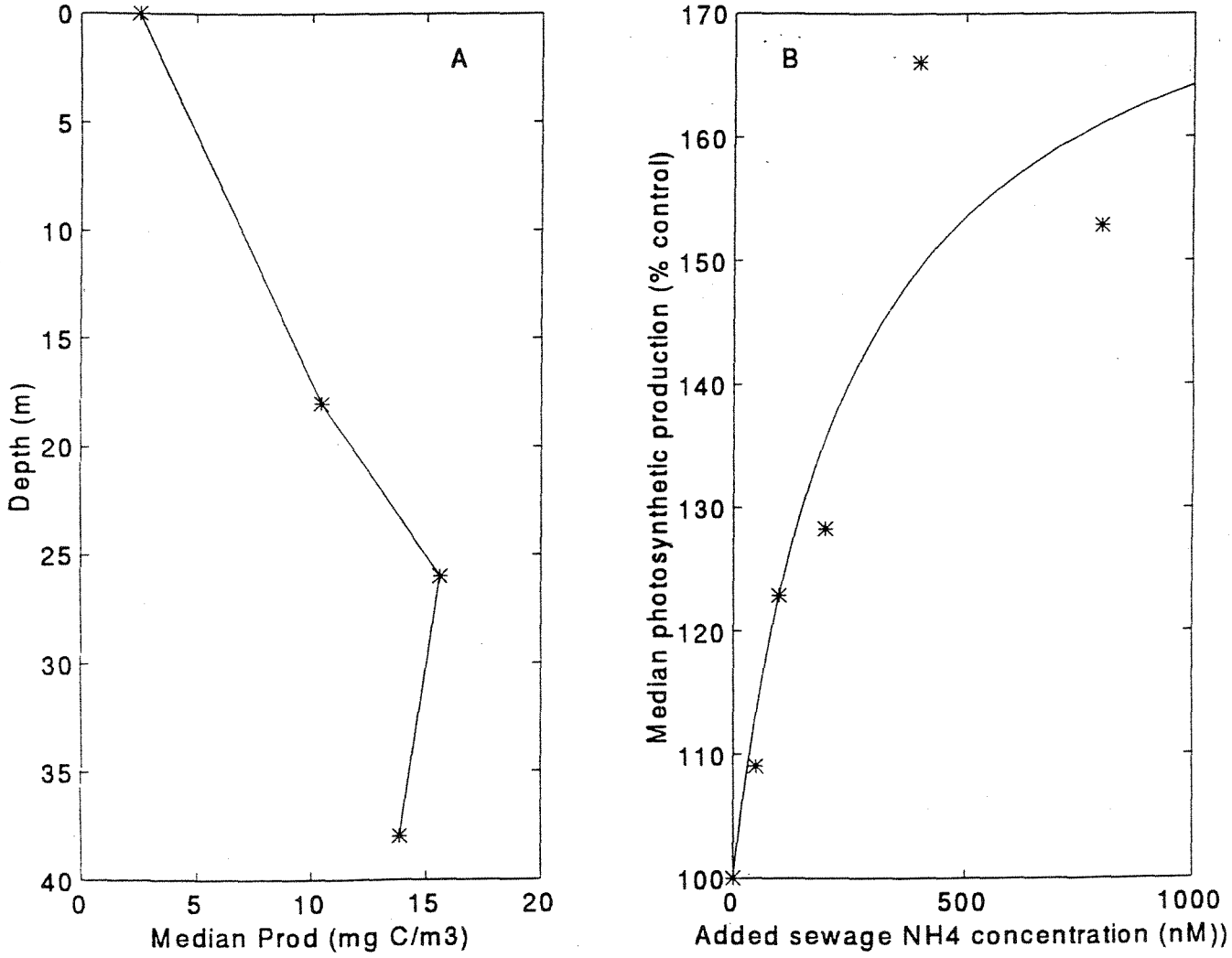


Figure 4.1 (A) Median production of phytoplankton in control and sewage-enriched bottles as a function of simulated depth. (B) Photosynthetic production of phytoplankton community as a function of sewage enrichment quantified in terms of added ammonium. Results are expressed as a percentage of controls, which received no added sewage. Results are median values over all bioassays ($n = 6$) and irradiances less than 100% of surface values ($n = 3$). The smooth curve is the least squares equation $Y = 100 + 80X/(250 + X)$.

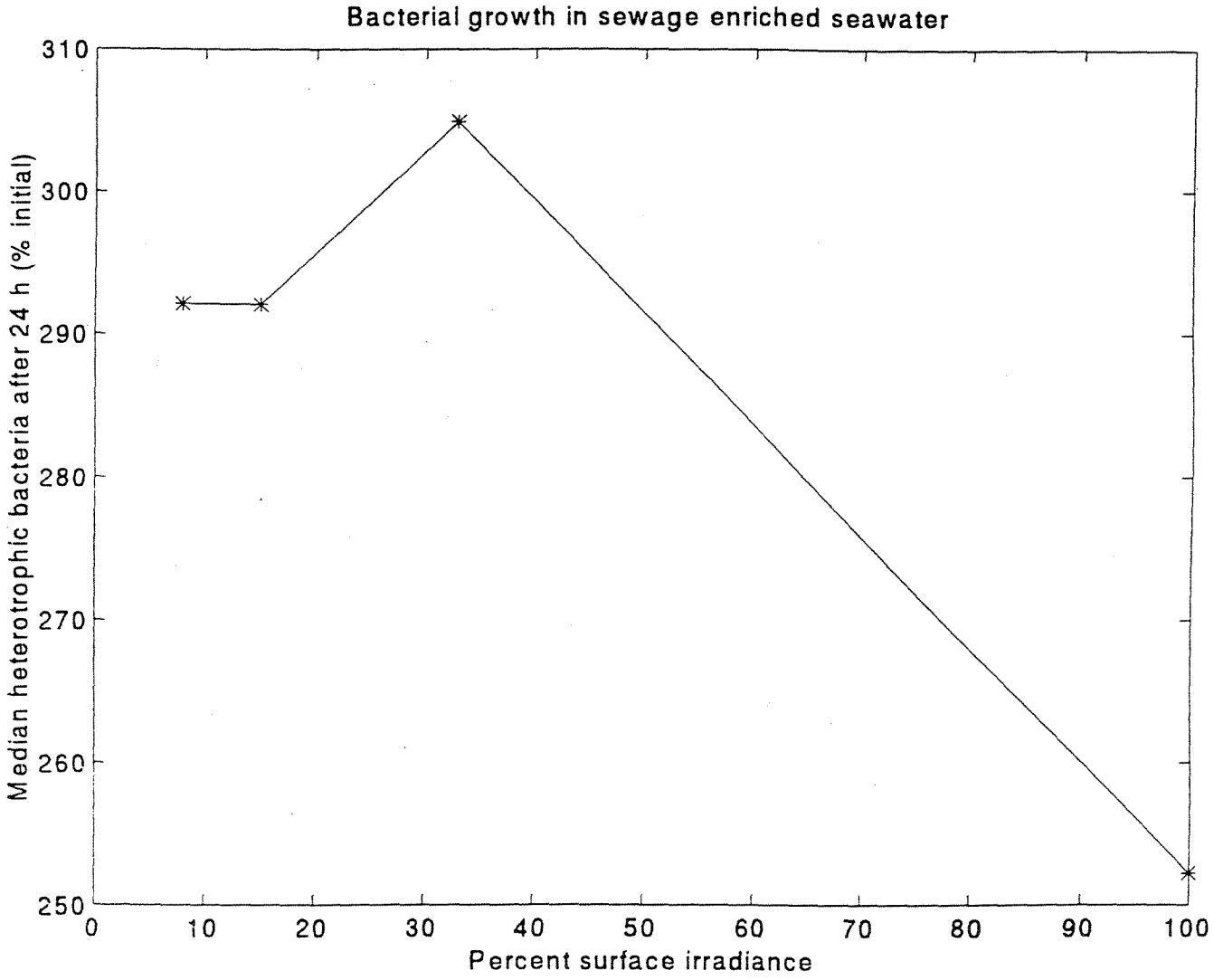


Figure 4.2 Heterotrophic bacterial cell numbers expressed as a percentage of initial heterotrophic bacterial cell numbers in seawater enriched with unfiltered sewage effluent. Each data point is the median percentage of three bioassays.

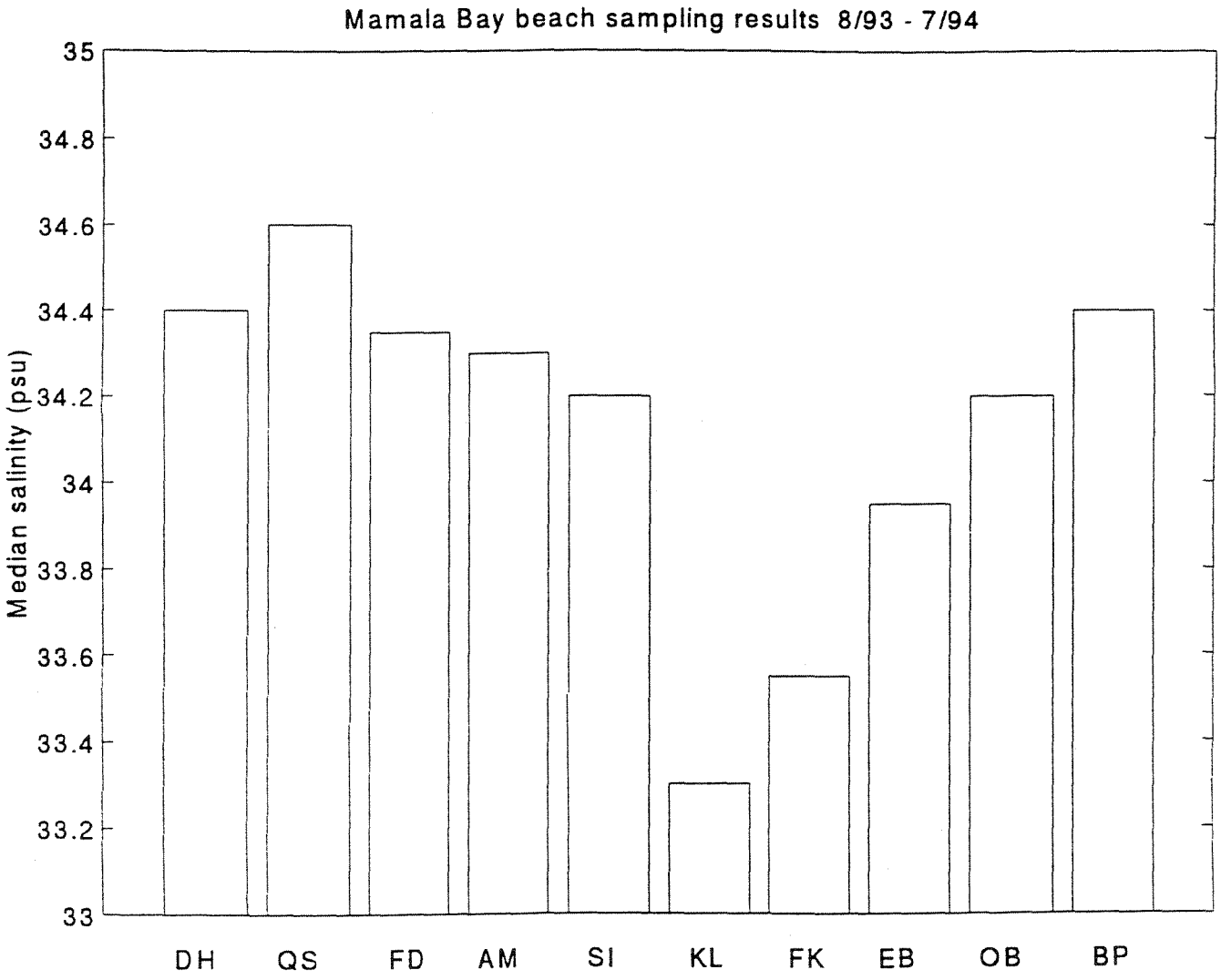


Figure 4.3 Median salinity at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

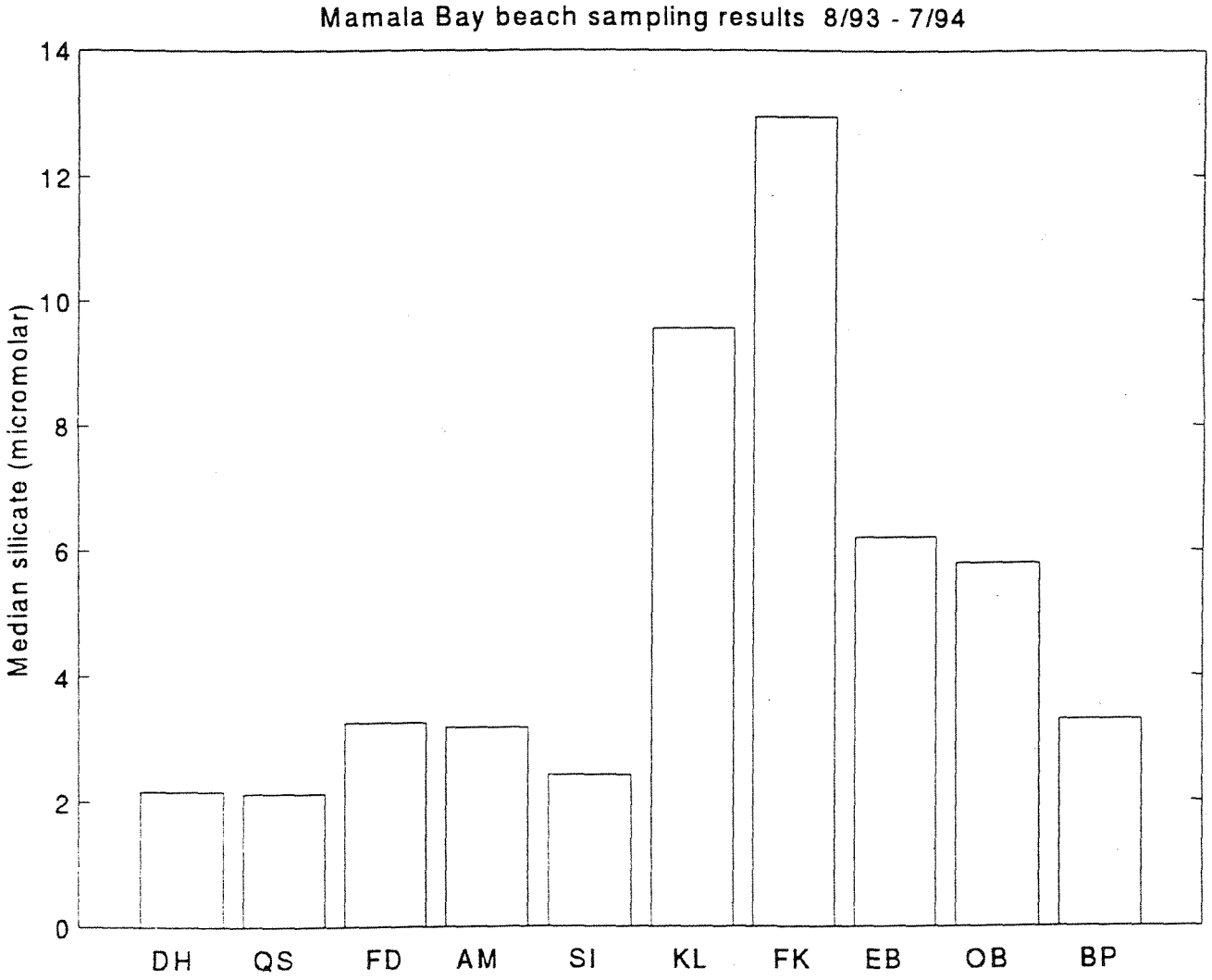


Figure 4.4. Median silicate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

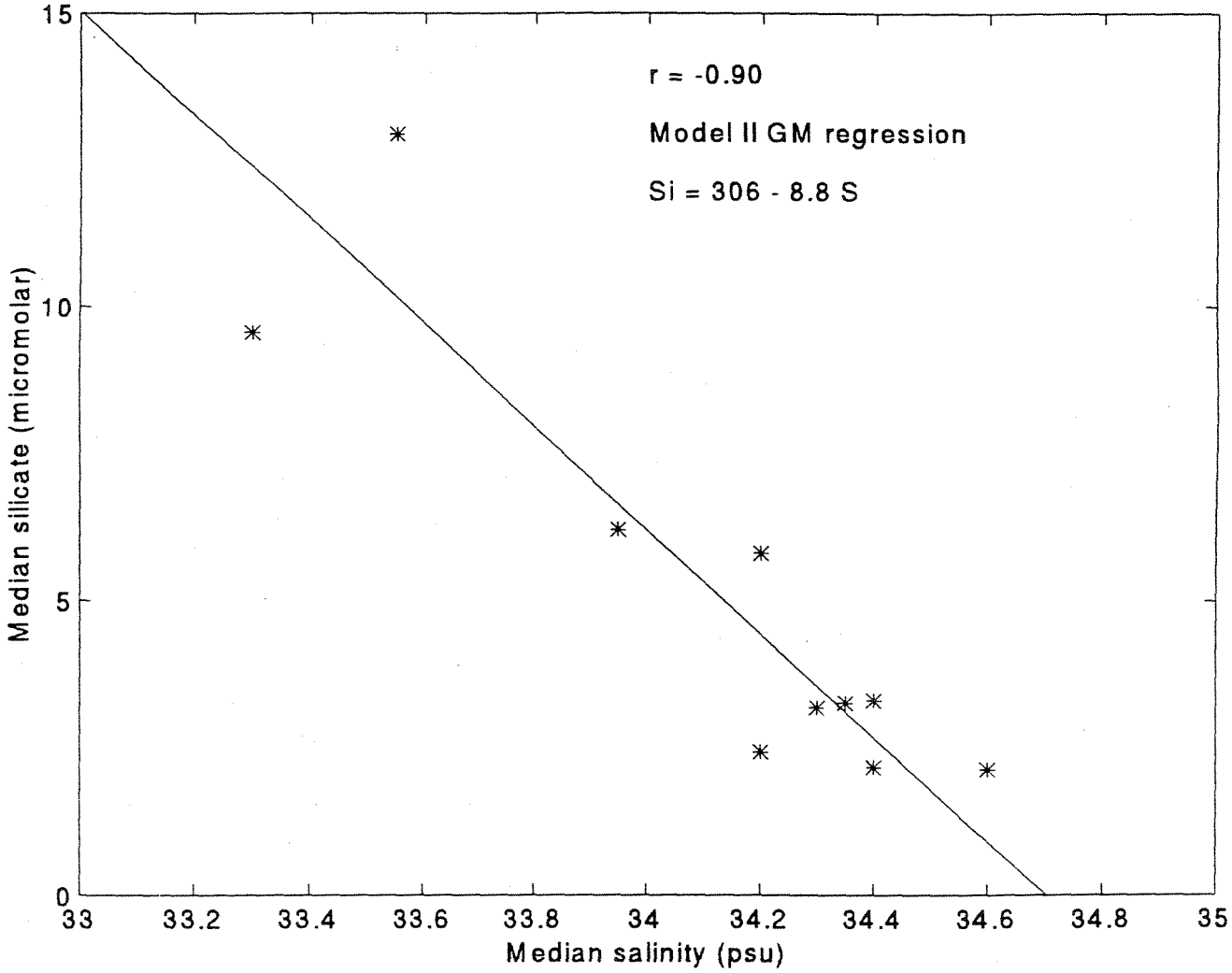


Figure 4.5. Relationship between median salinity and silicate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

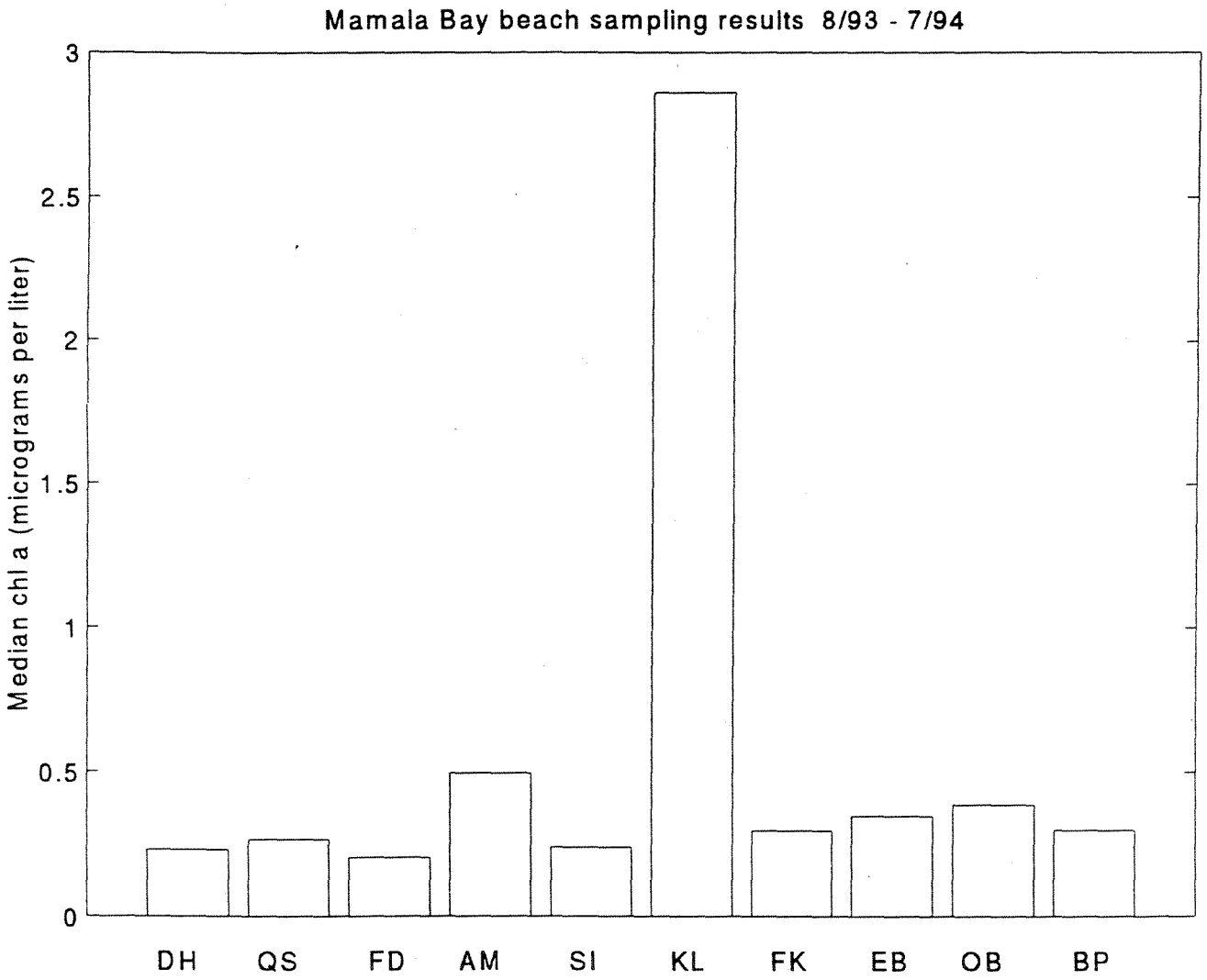


Figure 4.6 Median chl *a* concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

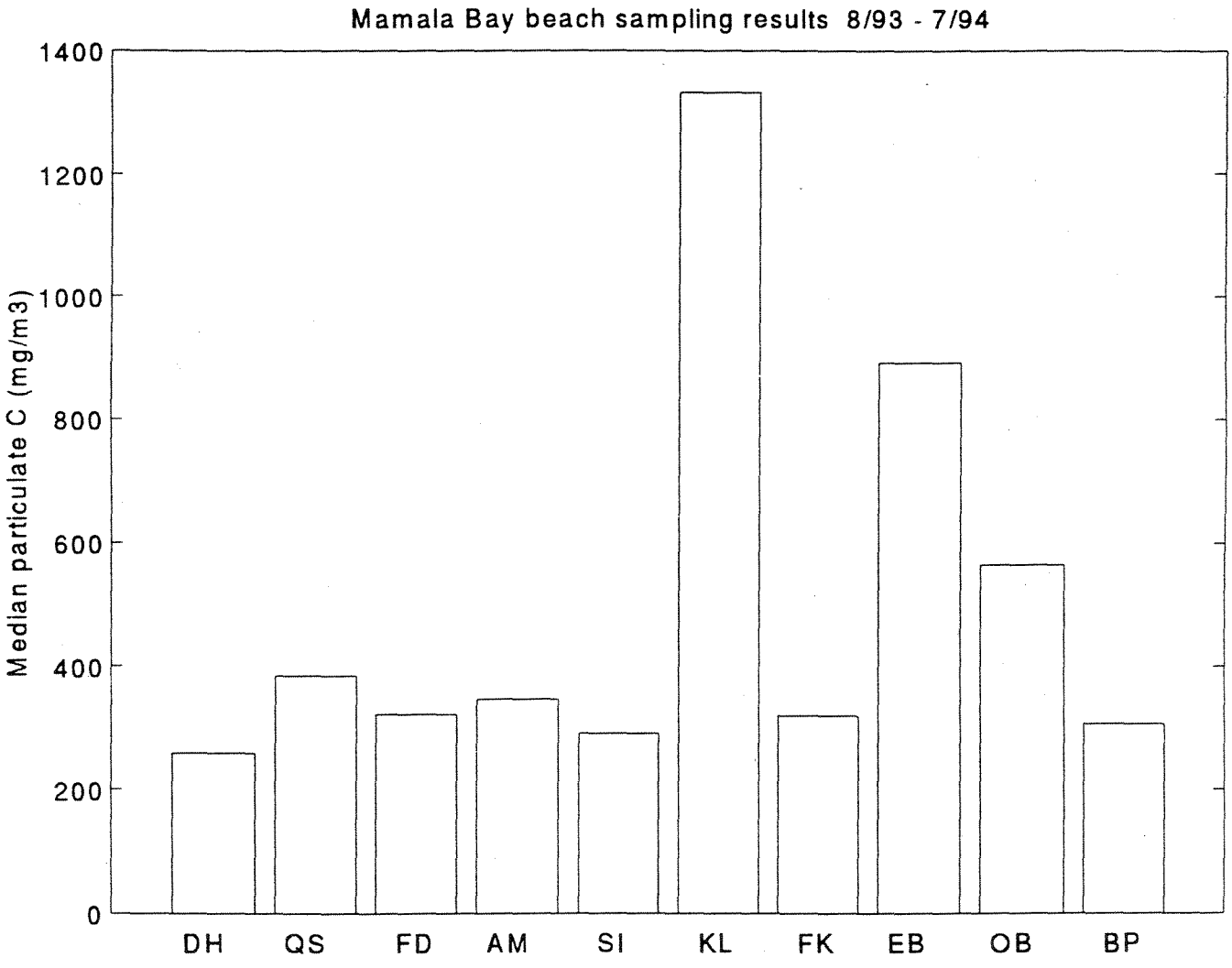


Figure 4.7 Median particulate carbon concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

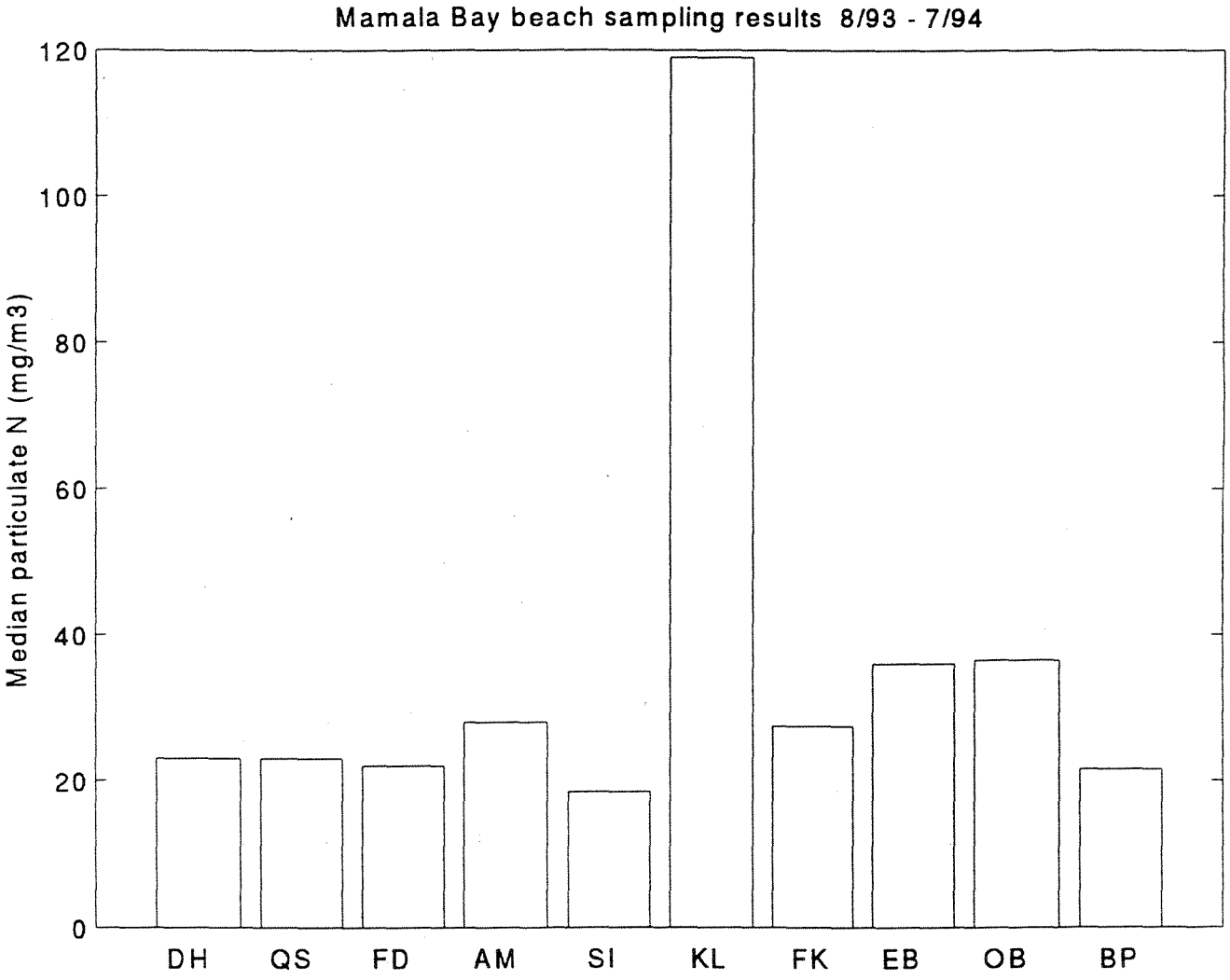


Figure 4.8 Median particulate nitrogen concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

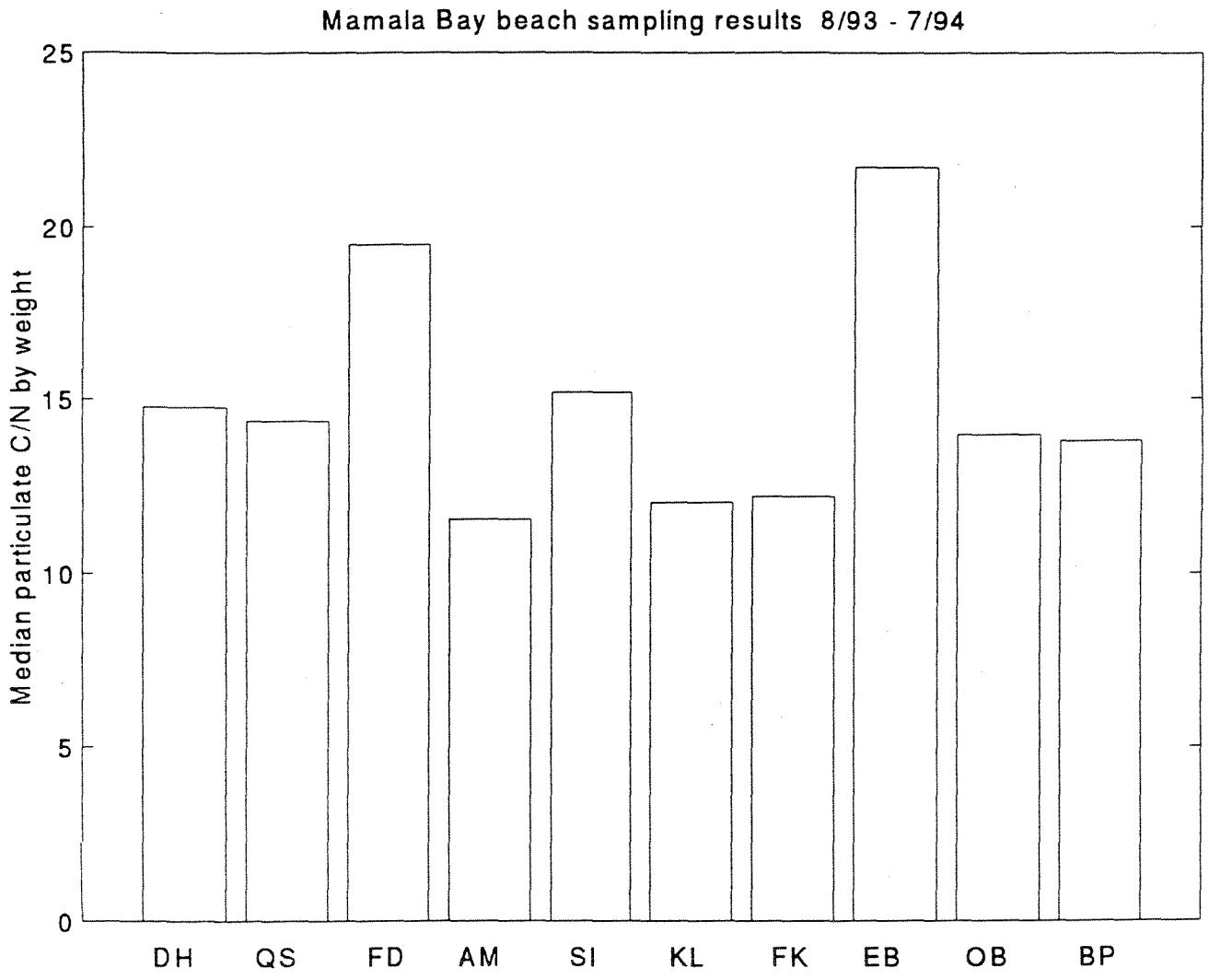


Figure 4.9 Monthly median particulate carbon to particulate nitrogen ratios at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

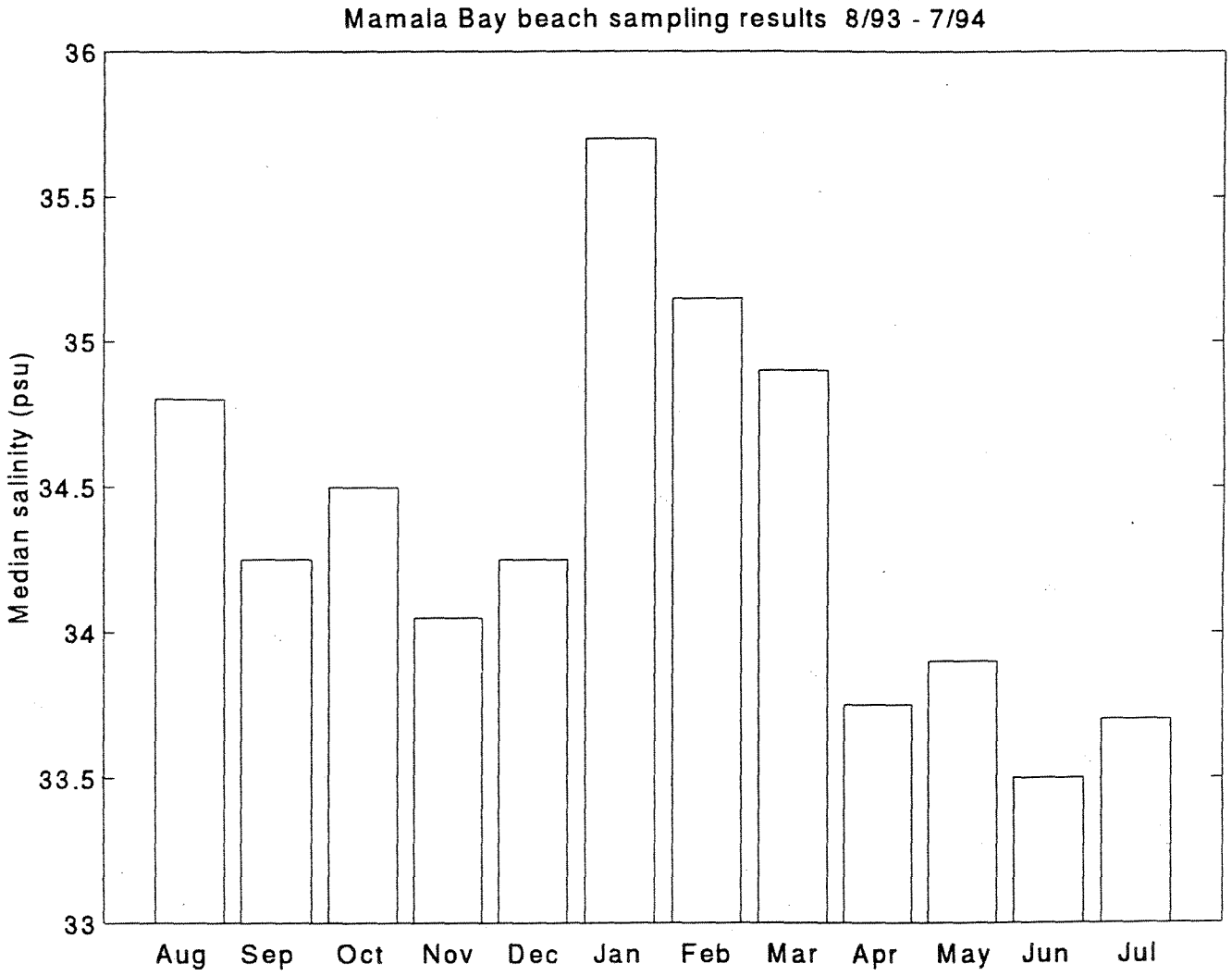


Figure 4.10 Monthly median salinity values at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

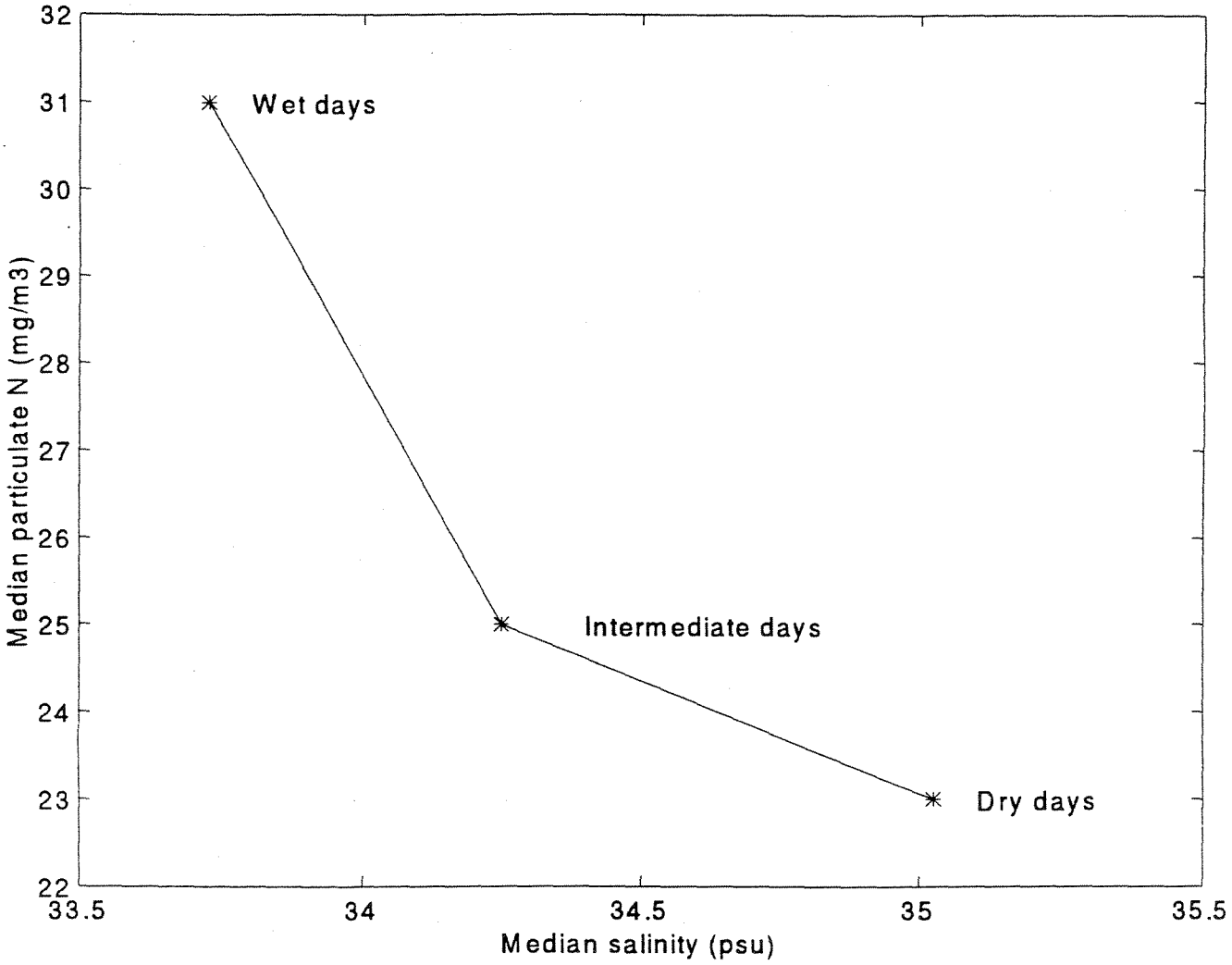


Figure 4.11 Relationship between particulate nitrogen and salinity at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994. Wet and dry days are here taken to be the four days in Fig. 4.10 having the lowest and highest median salinities, respectively.

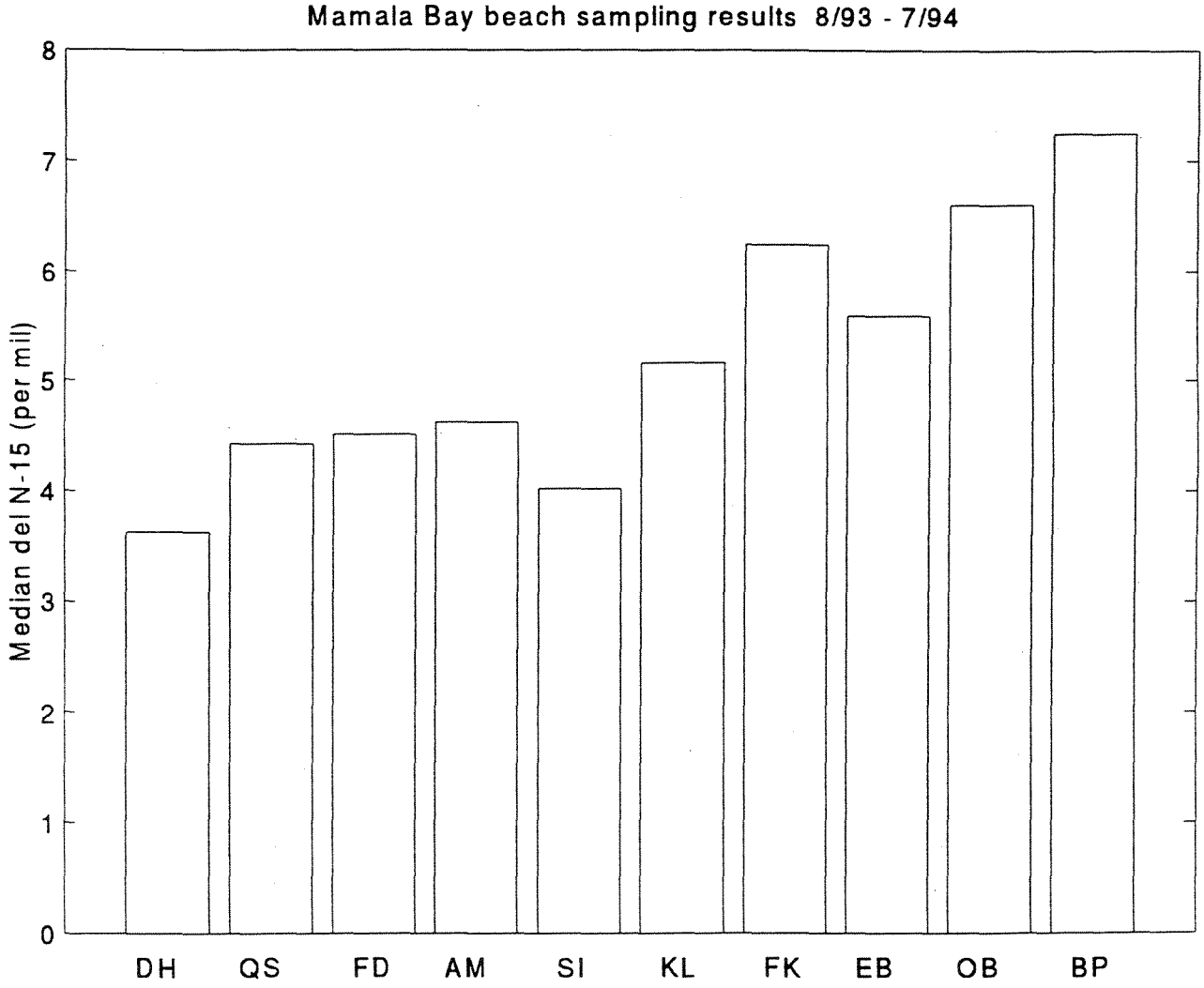


Figure 4.12 Median $\delta^{15}N$ of suspended particulates at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

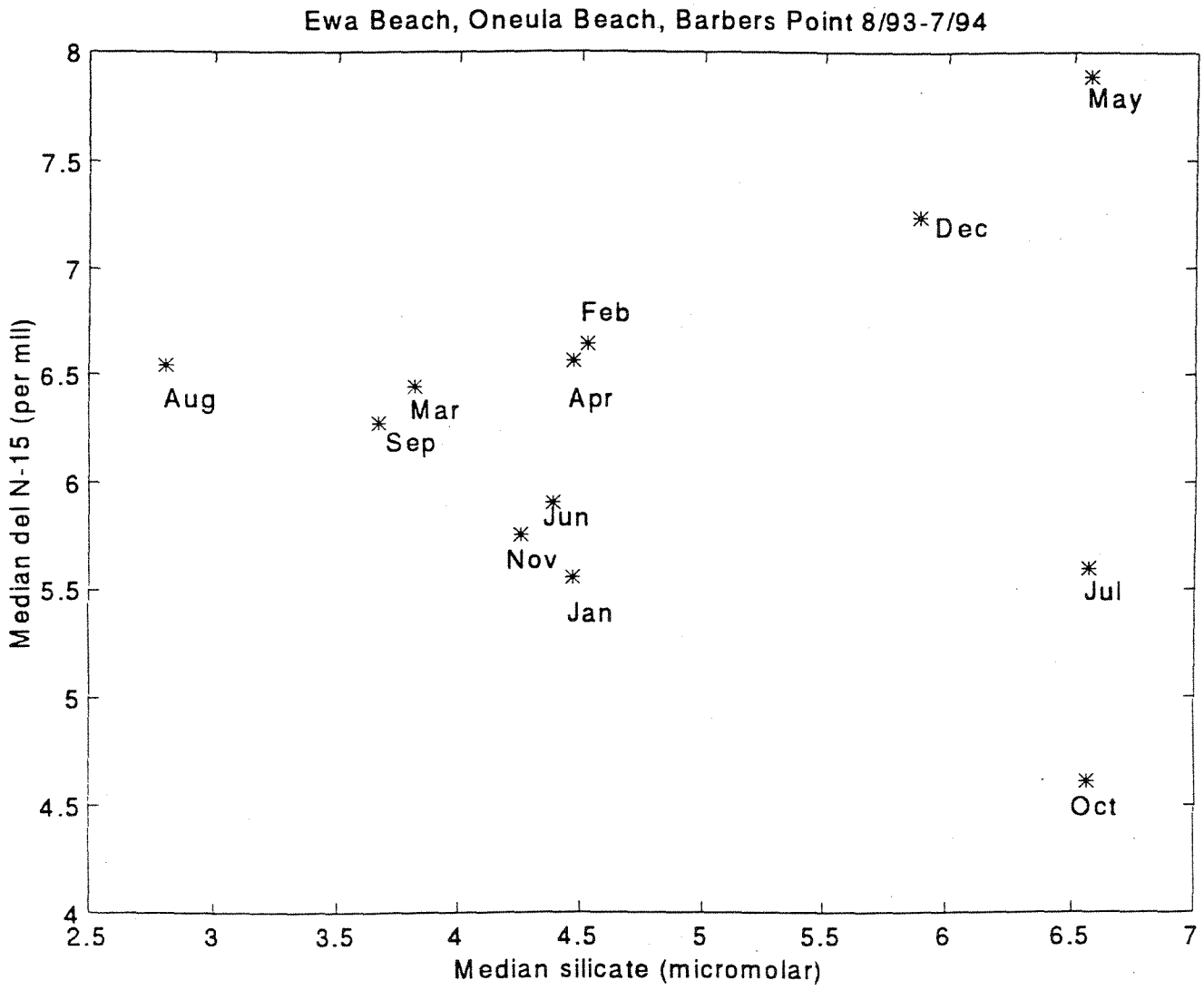


Figure 4.13 Median silicate and $\delta^{15}N$ values for Ewa, Oneula, and Barbers Point beach parks from August, 1993 to July, 1994.

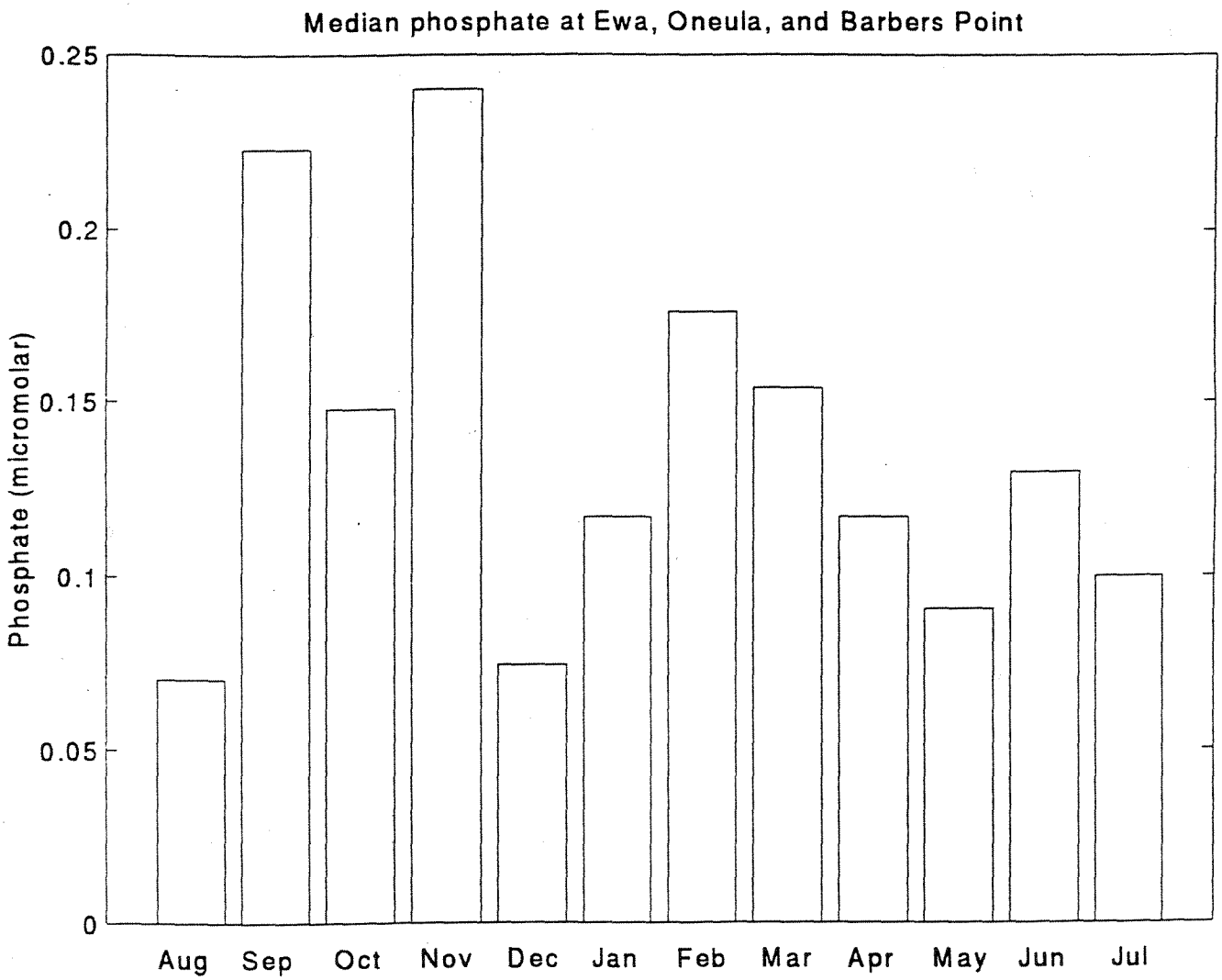


Figure 4.14 Median phosphate concentrations at Ewa, Oneula, and Barbers Point beach parks from August, 1993 to July, 1994.

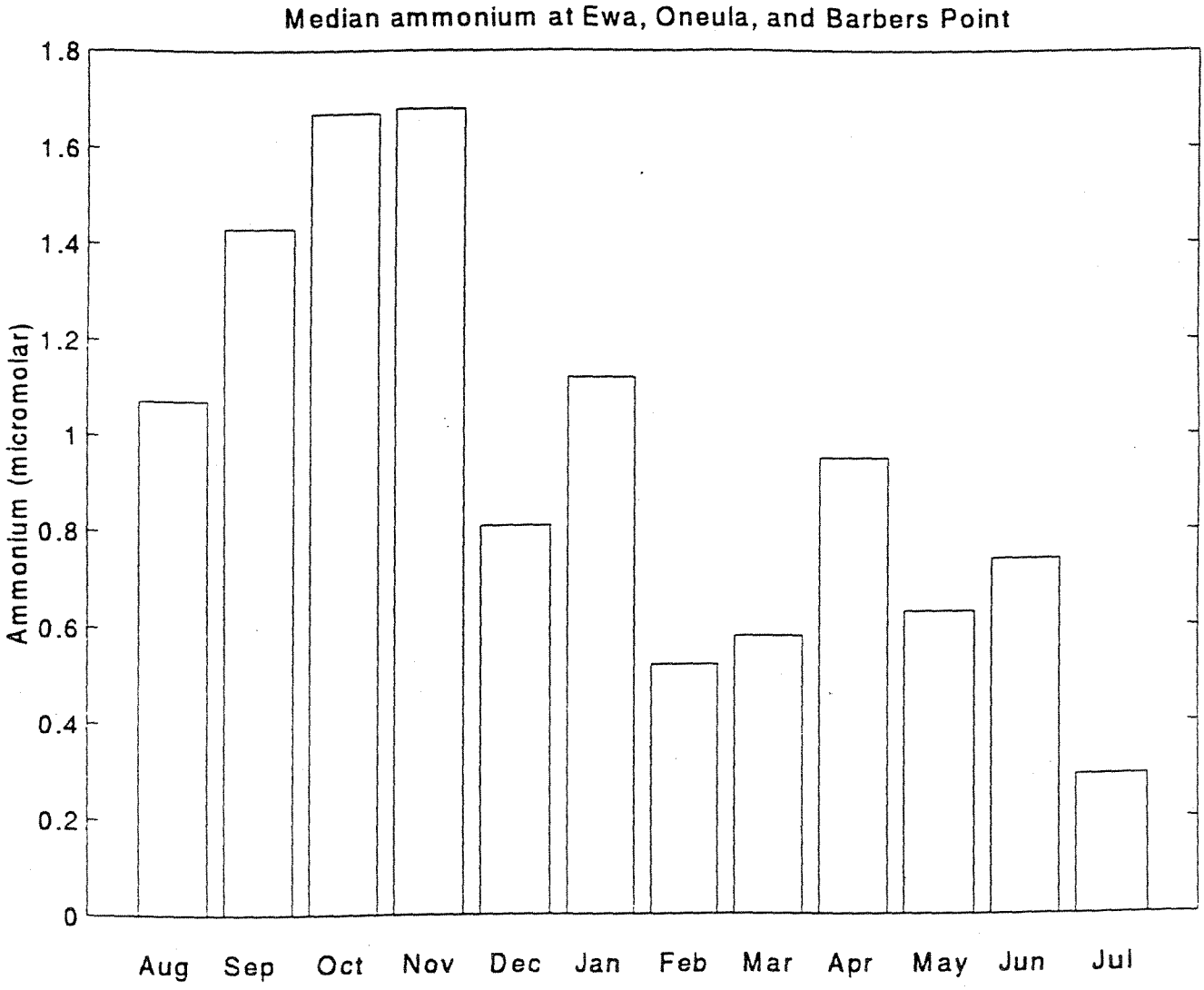


Figure 4.15 Median ammonium concentrations at Ewa, Oneula, and Barbers Point beach parks from August, 1993 to July, 1994.

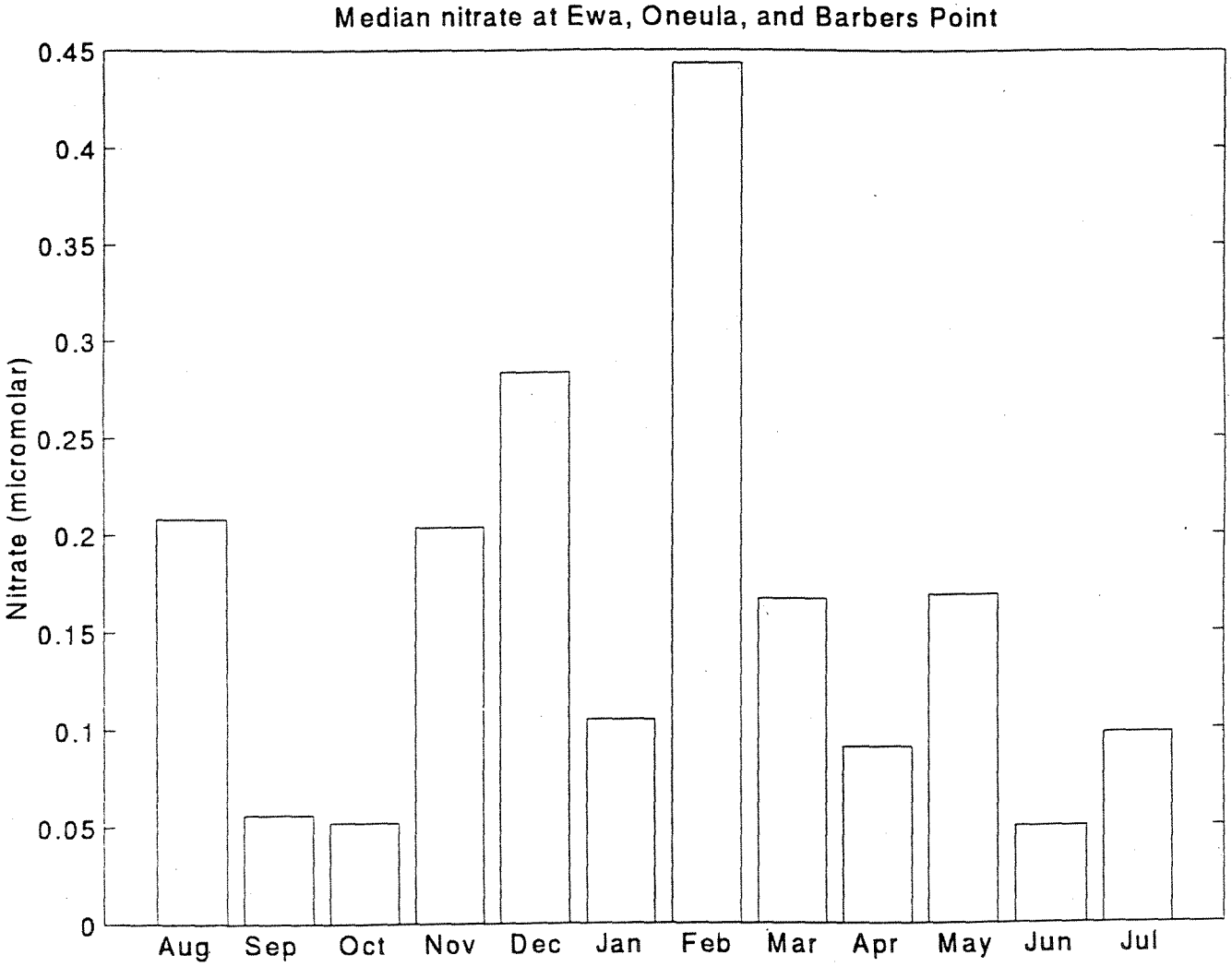


Figure 4.16 Median nitrate concentrations at Ewa, Oneula, and Barbers Point beach parks from August, 1993 to July, 1994.

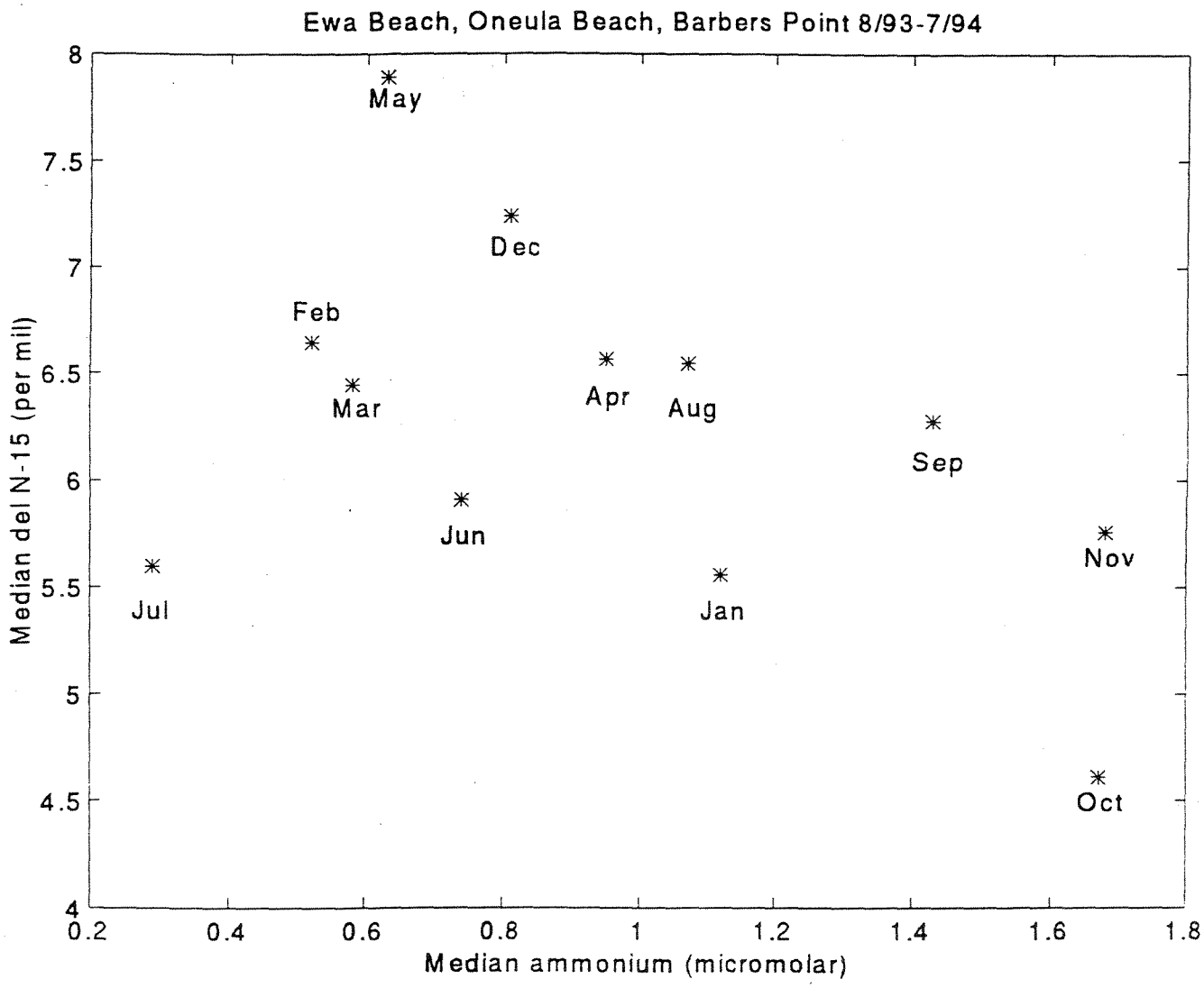


Figure 4.17 Median $\delta^{15}N$ and ammonium concentrations at Ewa, Oneula, and Barbers Point beach parks from August, 1993 to July, 1994.

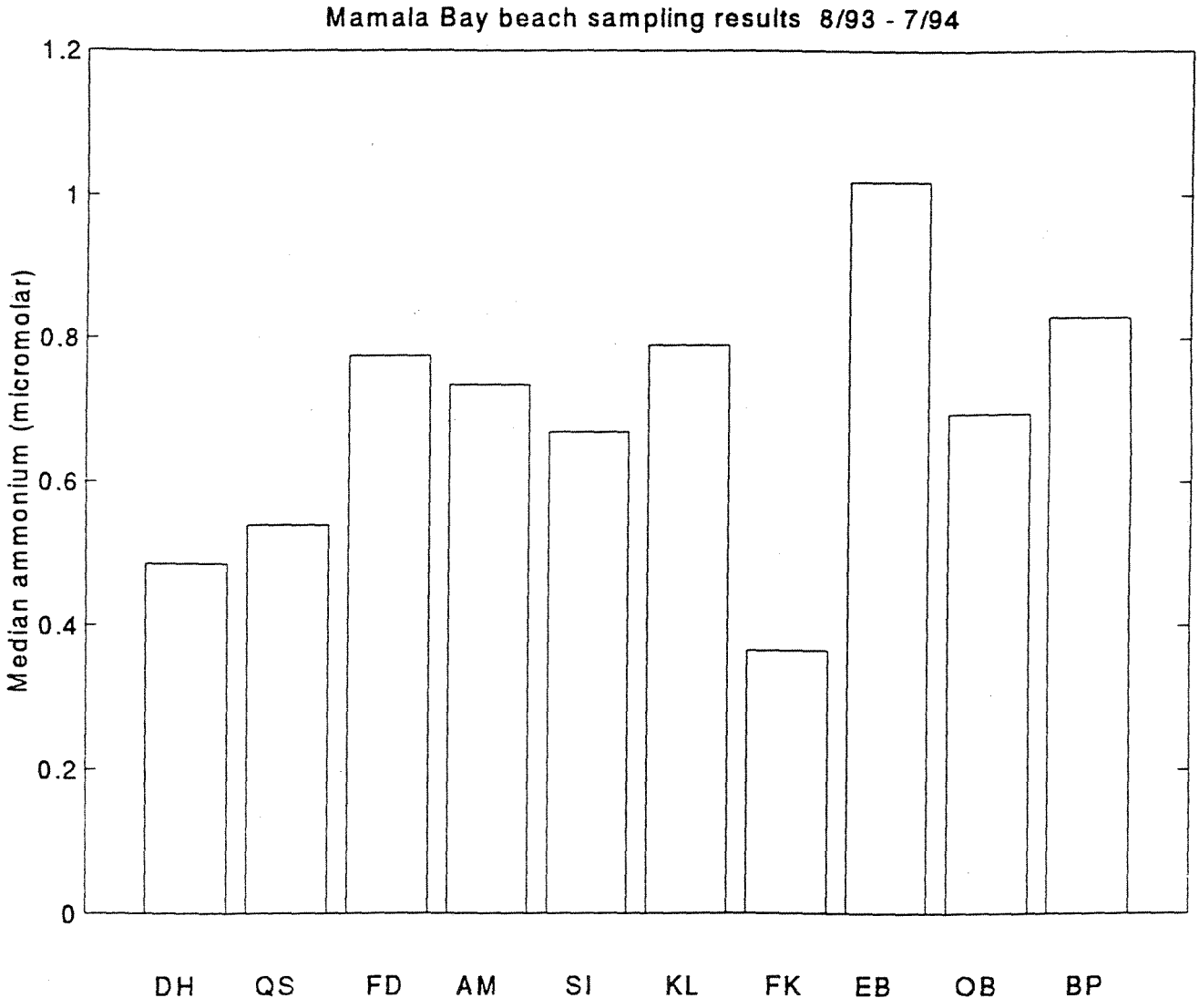


Figure 4.18 Median ammonium concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

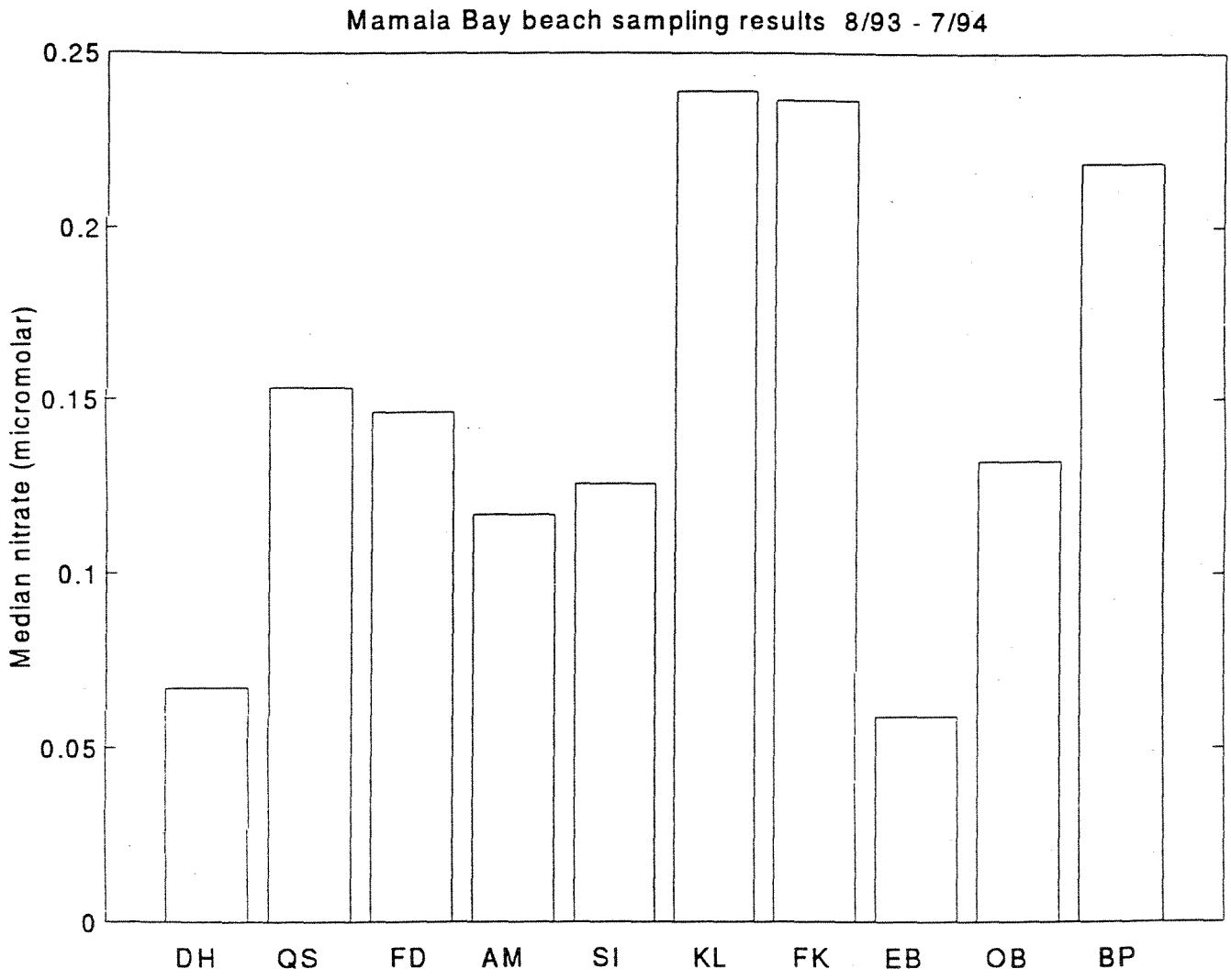


Figure 4.19 Median nitrate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

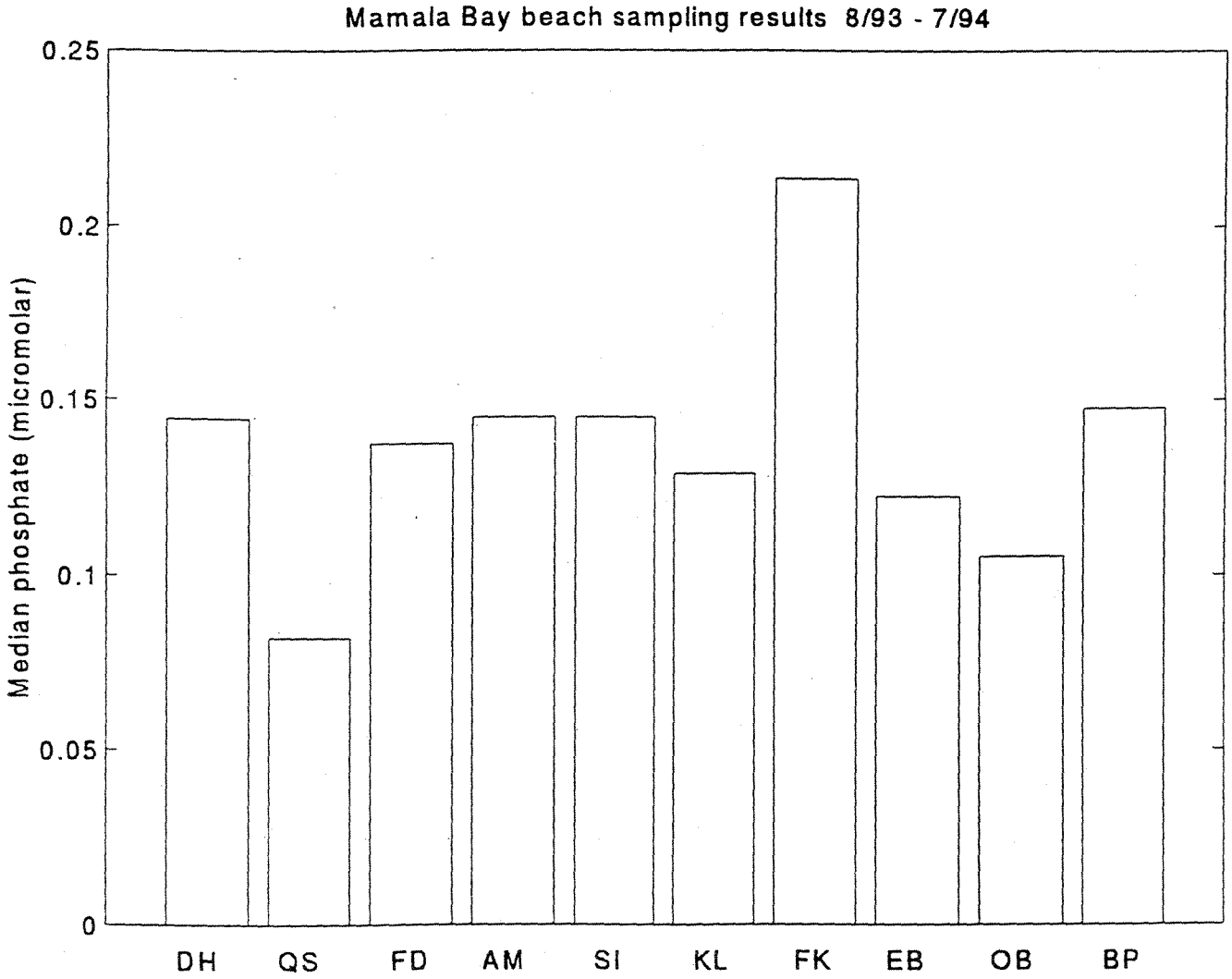


Figure 4.20 Median phosphate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

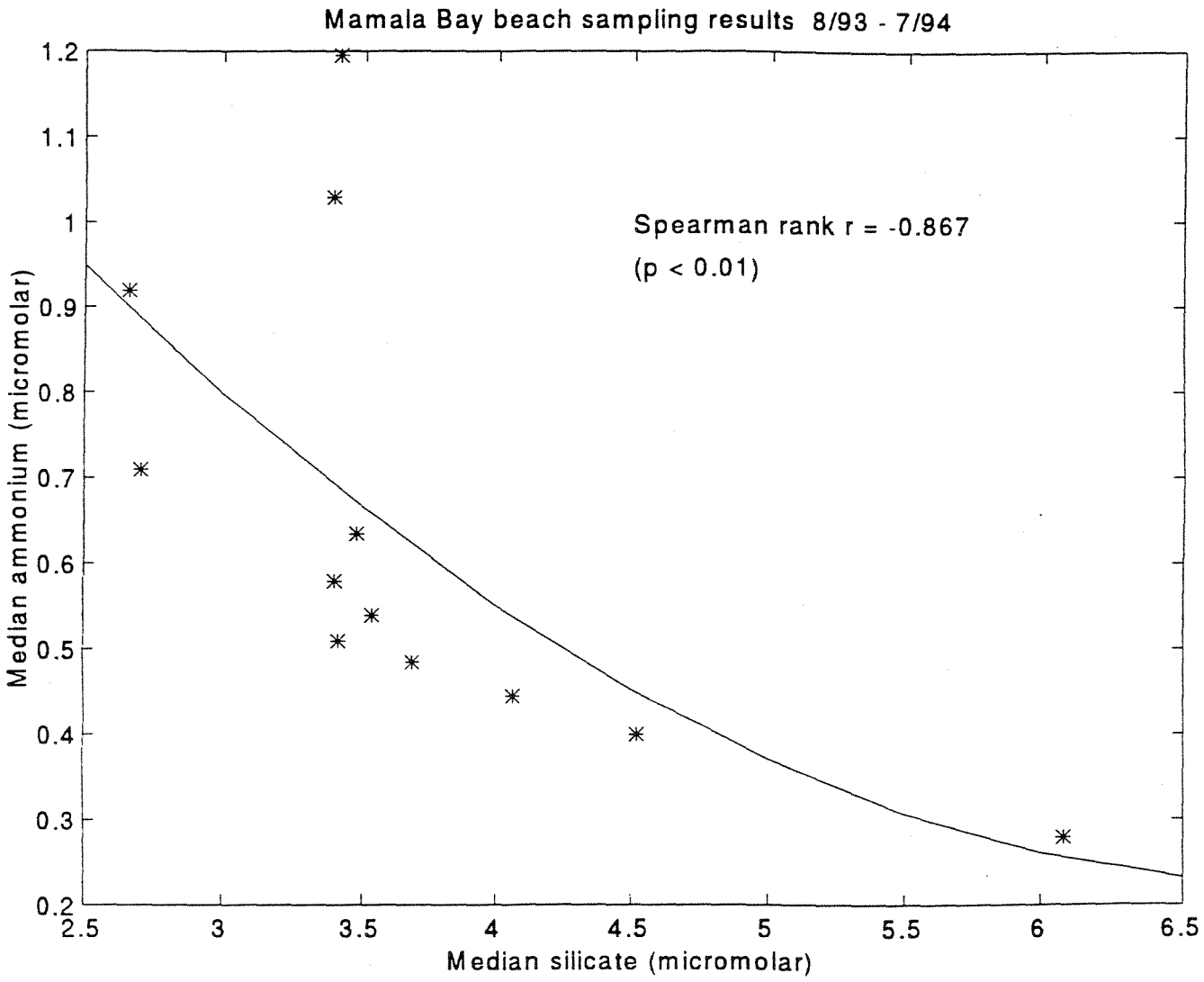


Figure 4.21 Relationship between median ammonium and silicate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994. The smooth curve is a second-order polynomial fit to the data.

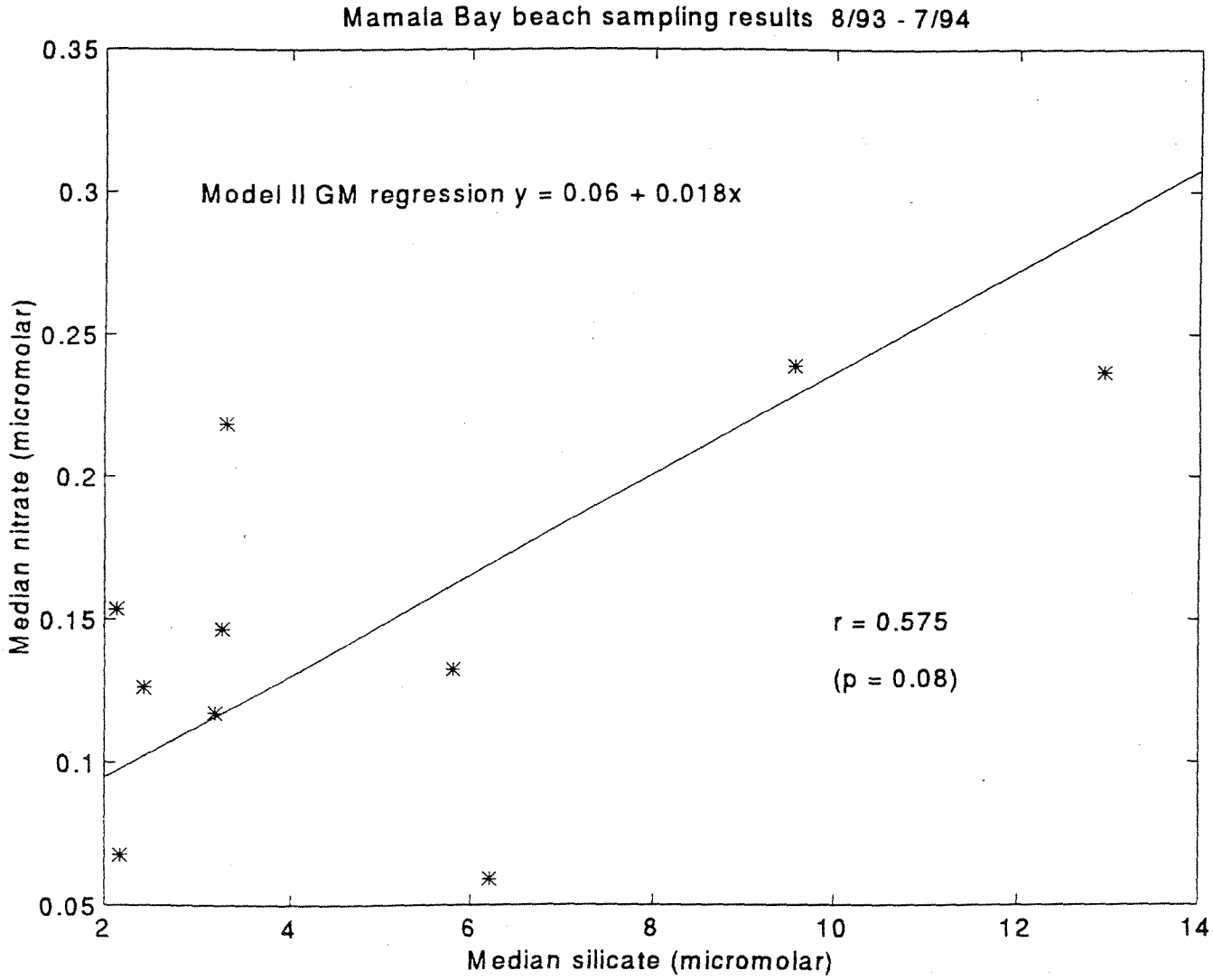


Figure 4.22 Relationship between median nitrate and silicate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

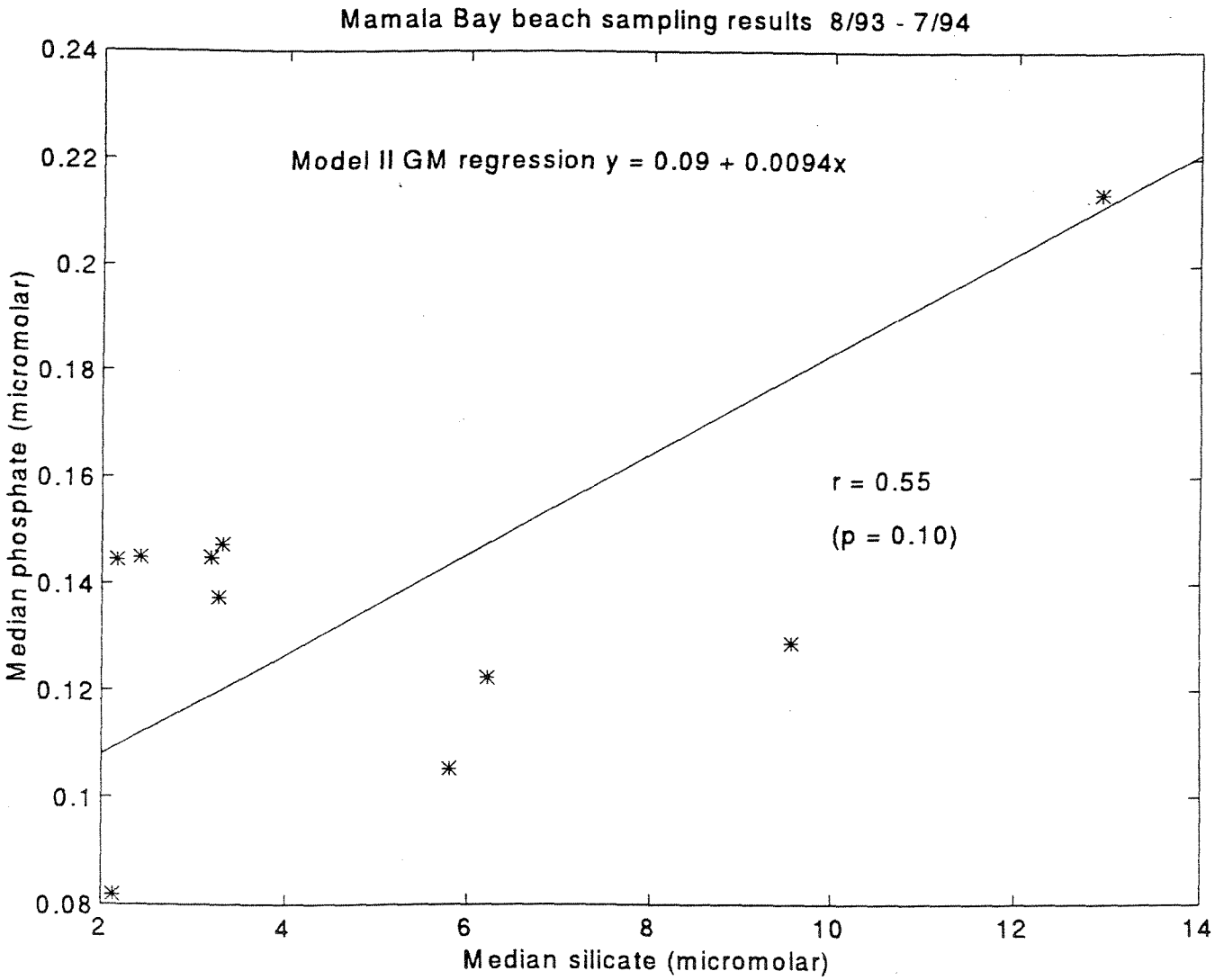


Figure 4.23 Relationship between median phosphate and silicate concentrations at the 10 beaches shown in Fig. 3.1 from August, 1993 to July, 1994.

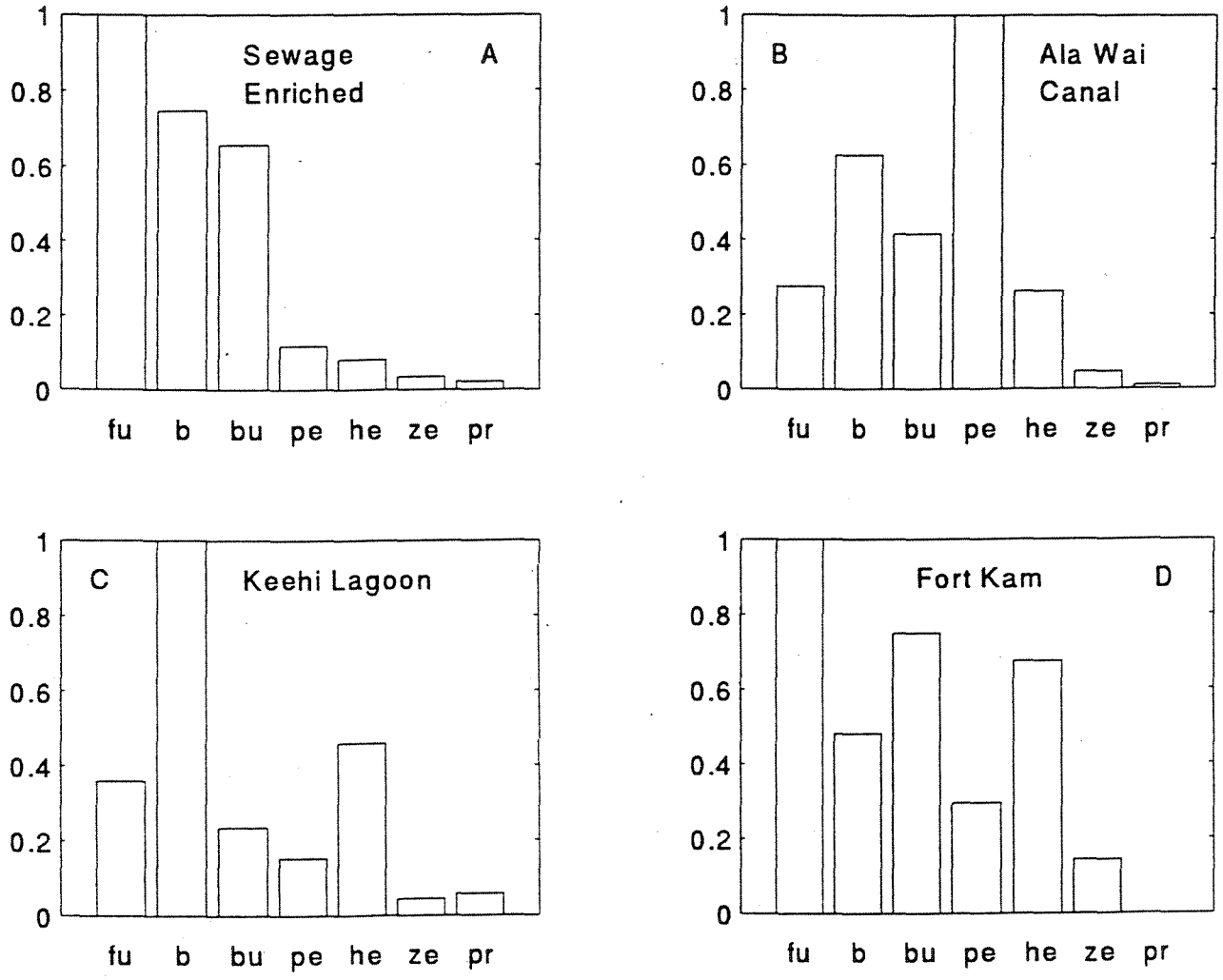


Figure 4.24 Profiles of diagnostic carotenoid pigments in (A) surface water from the Diamond Head buoy enriched with sewage effluent and incubated for one week, (B) mouth of the Ala Wai Canal, (C) Keehi Lagoon, and (D) Fort Kam Beach based on sampling from August, 1993 to July, 1994. The values are median concentrations normalized so that the highest concentration is 1.0.

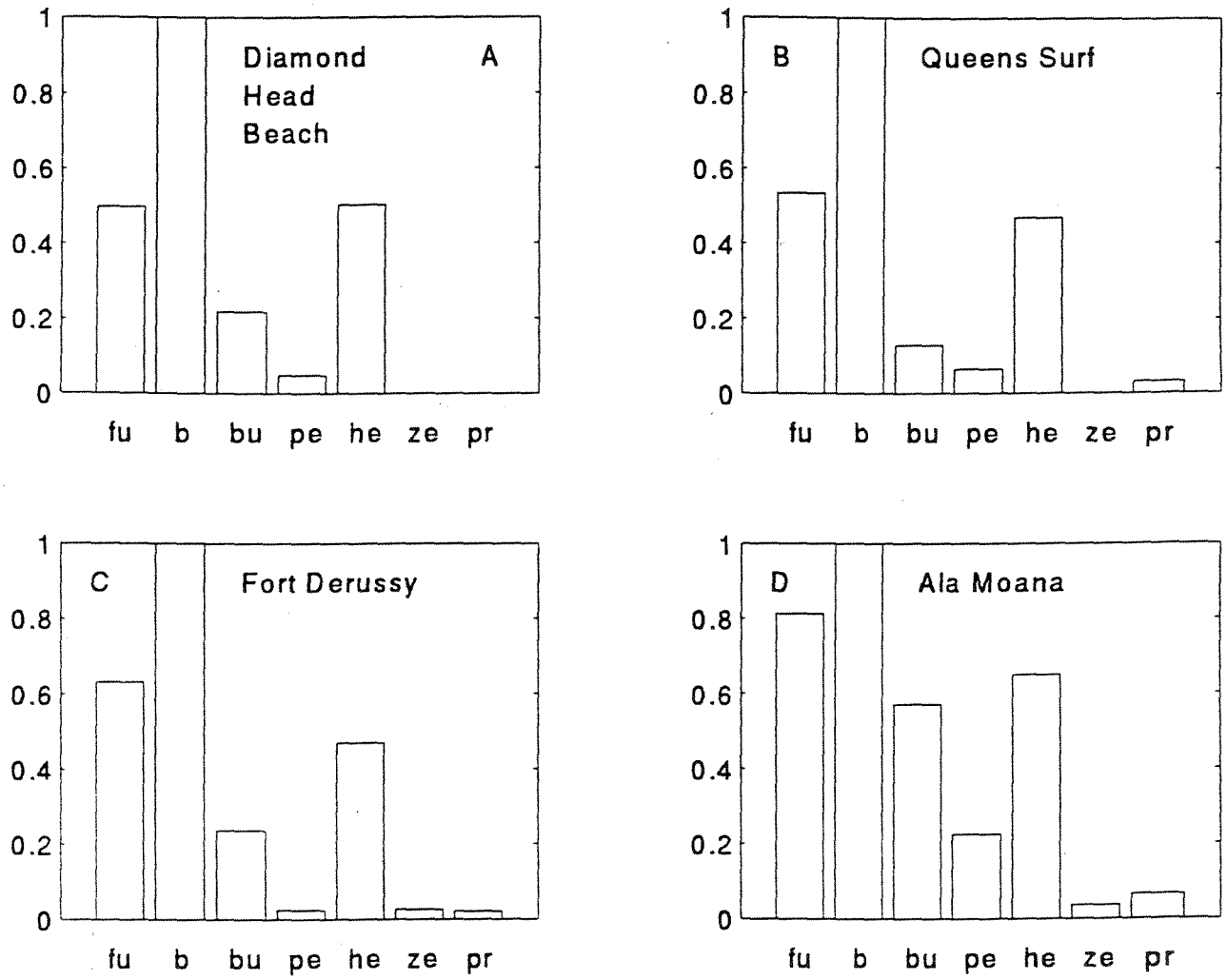


Figure 4.25 Profiles of diagnostic carotenoid pigments in (A) Diamond Head Beach, (B) Queens Surf Beach, (C) Fort Derussy Beach, and (D) Ala Moana Beach based on sampling from August, 1993 to July, 1994. The values are median concentrations normalized so that the highest concentration is 1.0.

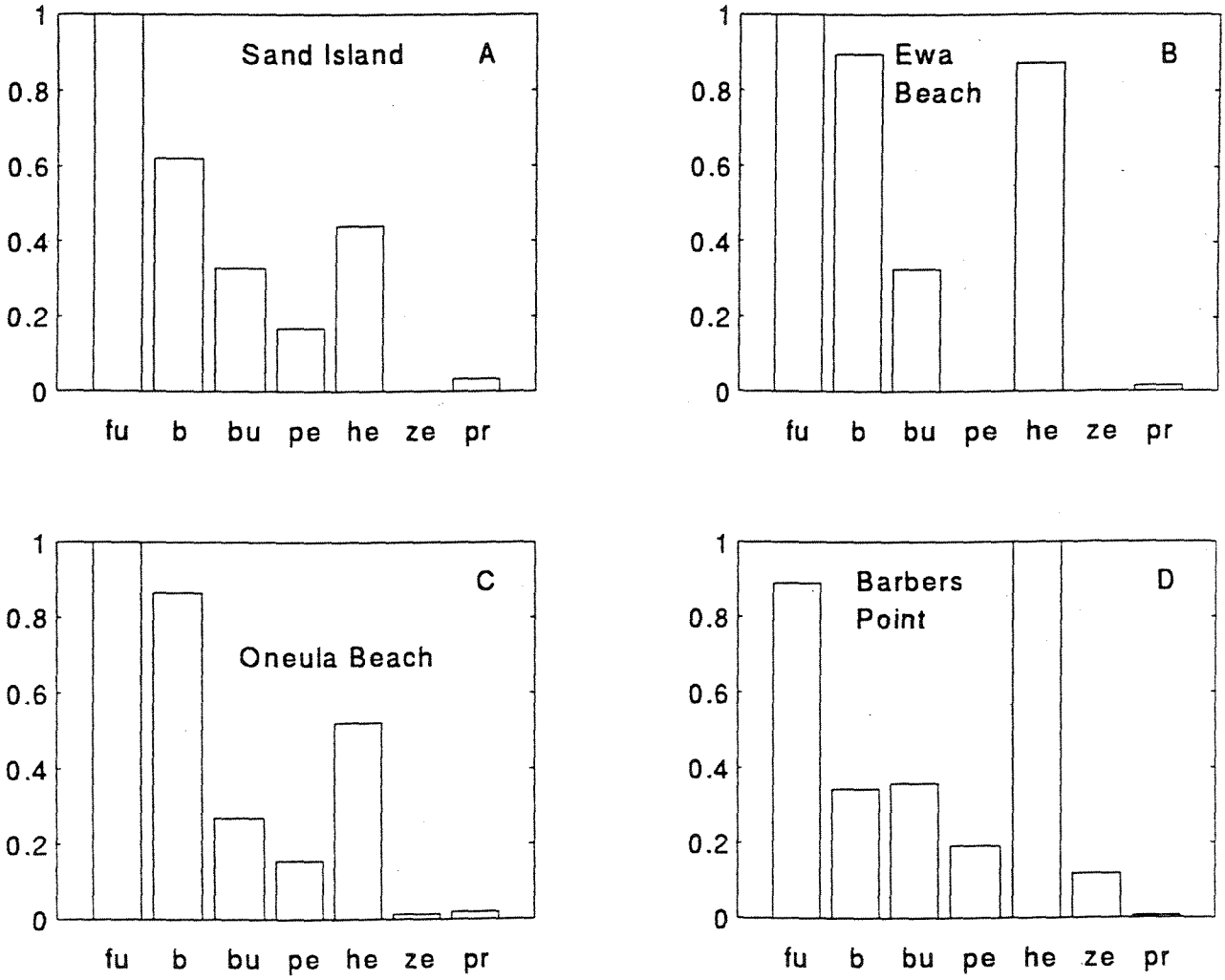


Figure 4.26 Profiles of diagnostic carotenoid pigments in (A) Sand Island Beach, (B) Ewa Beach, (C) Oneula Beach, and (D) Barbers Point Beach based on sampling from August, 1993 to July, 1994. The values are median concentrations normalized so that the highest concentration is 1.0.

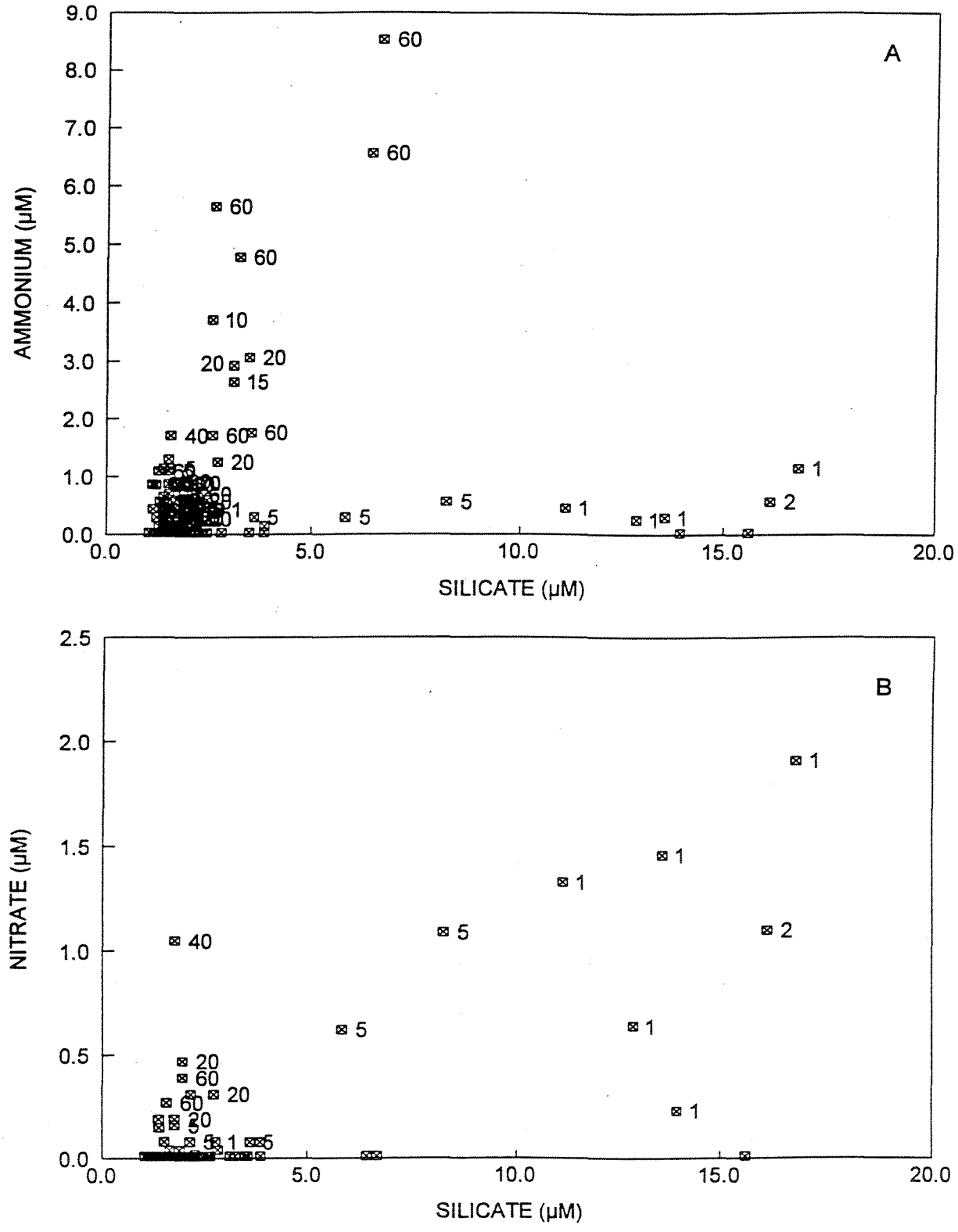


Figure 4.27 Plots of concentrations of ammonium and nitrate as functions of silicate for water quality samples collected on six cruises. Depth (m) of sample collection is indicated for data points.

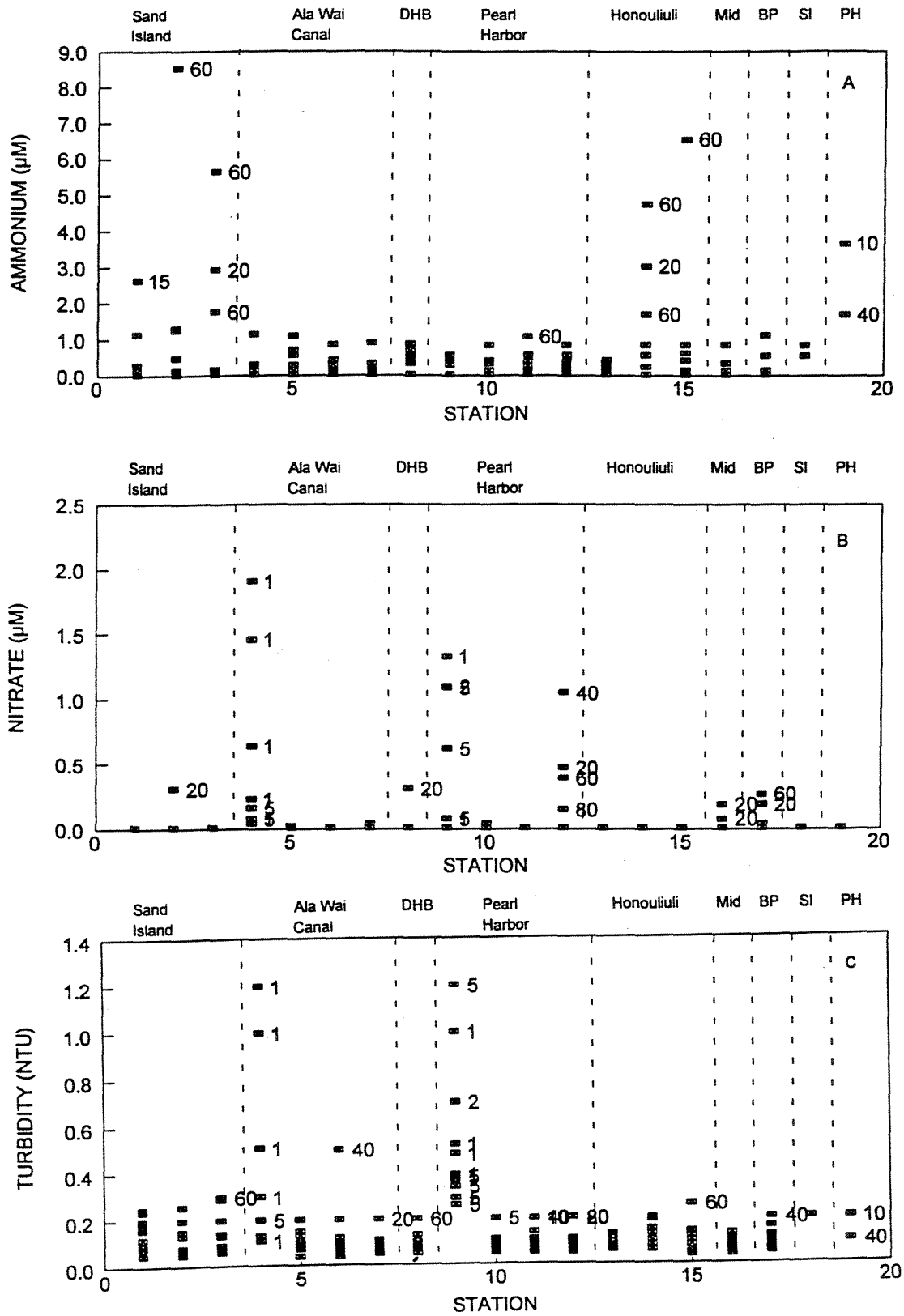


Figure 4.28 Plots of concentrations of ammonium, nitrate and turbidity by station for water quality samples collected on six cruises. Depth (m) of sample collection is indicated for data points.

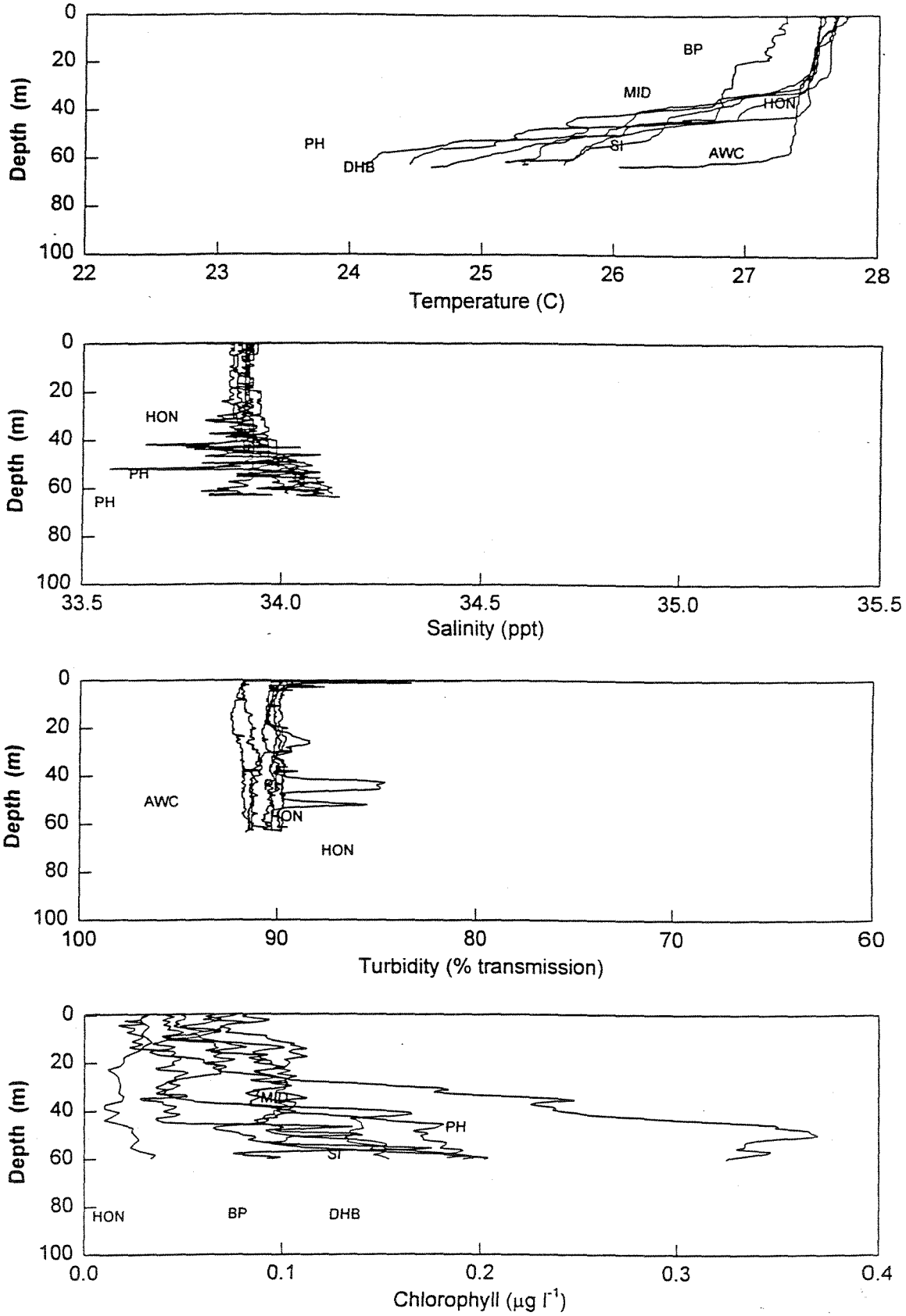


Figure 4.29 Vertical profiles of temperature, salinity, turbidity, and chlorophyll at the 60 m stations in September, 1994.

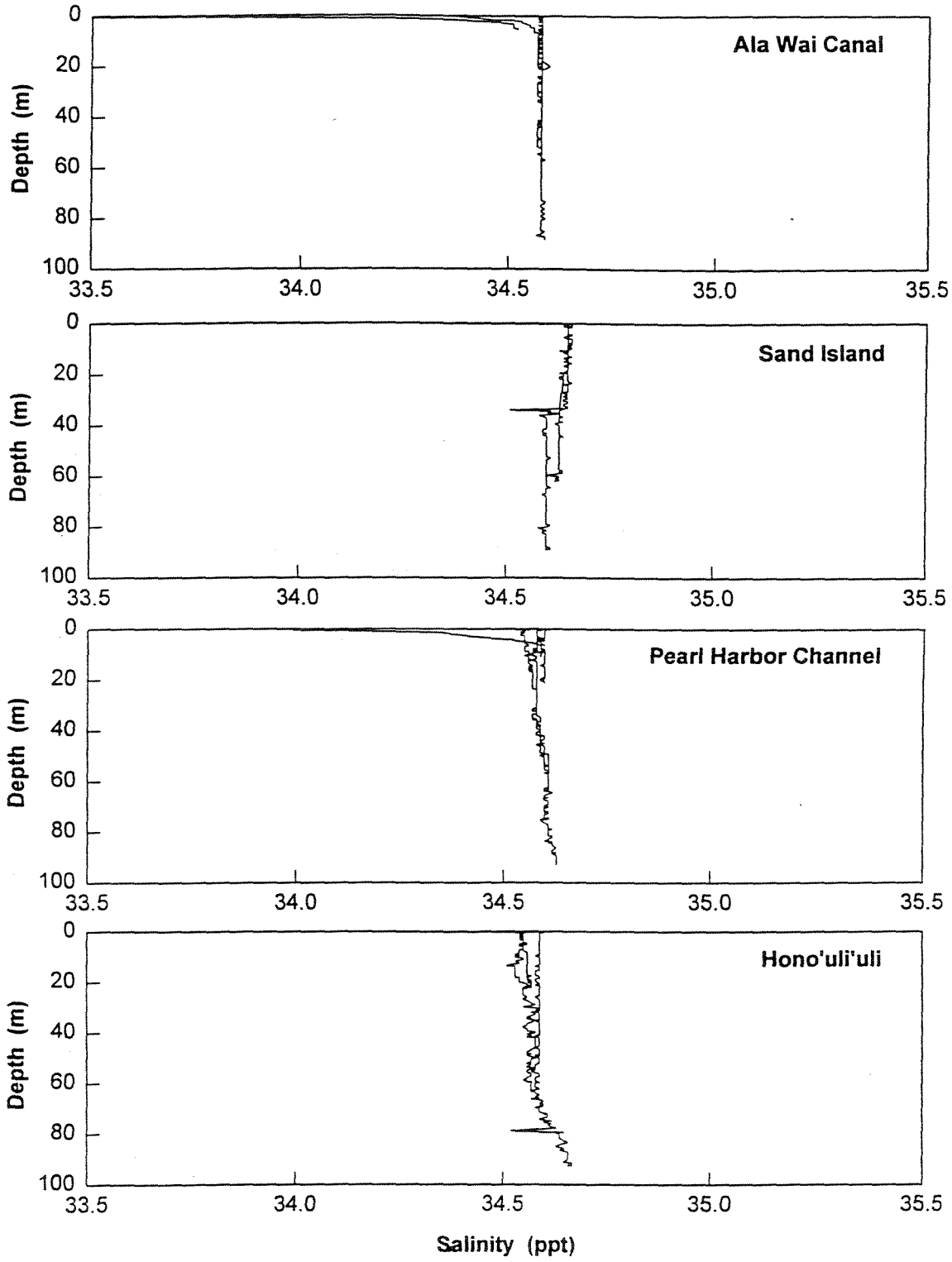


Figure 4.34 Salinity profiles for stations in December, 1994. Bottom depth (m) is indicated for selected stations.

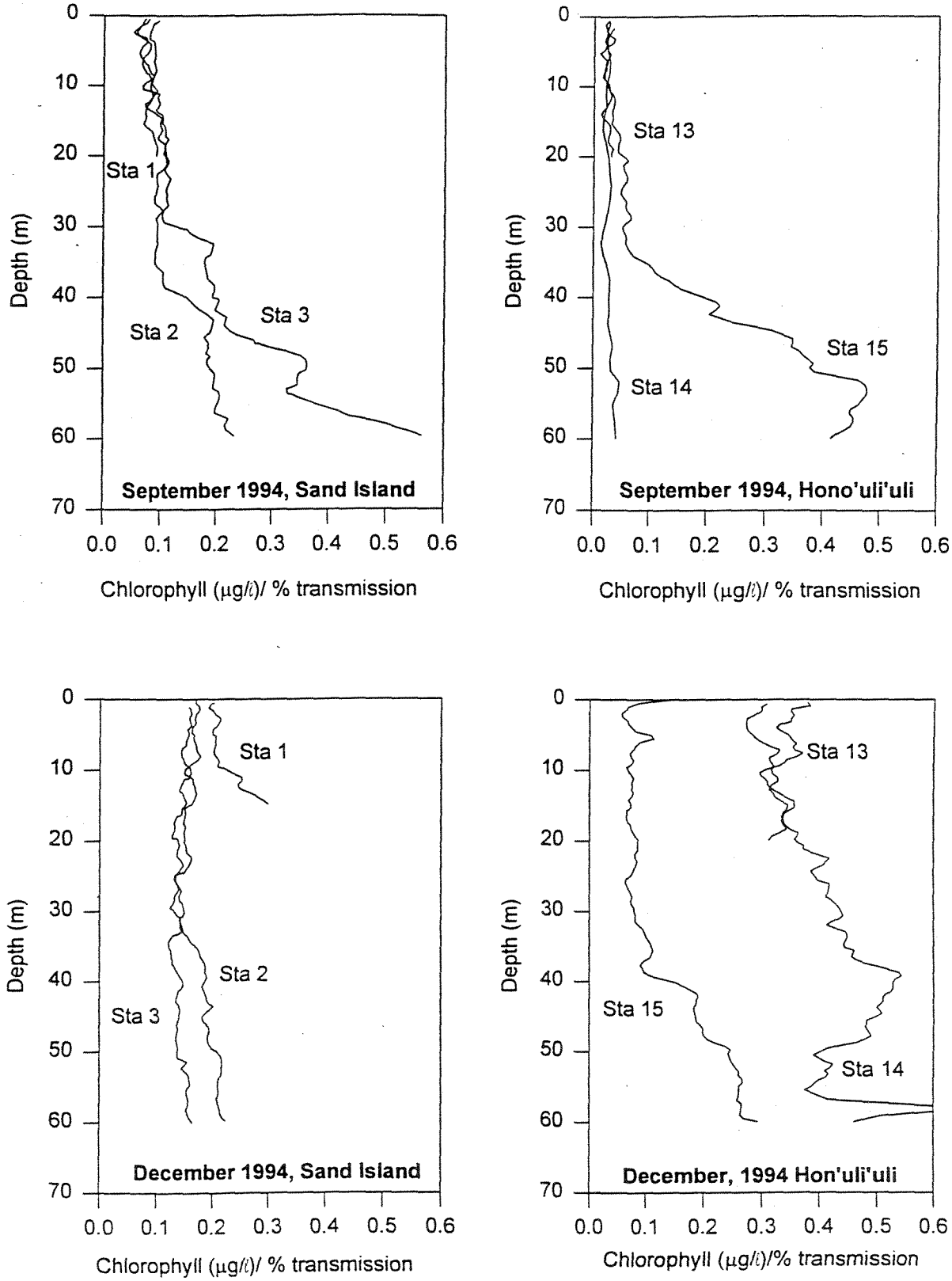


Figure 4.35 Vertical profiles of the chlorophyll:turbidity ratio for Sand Island and Honouliuli stations for September and December, 1994.

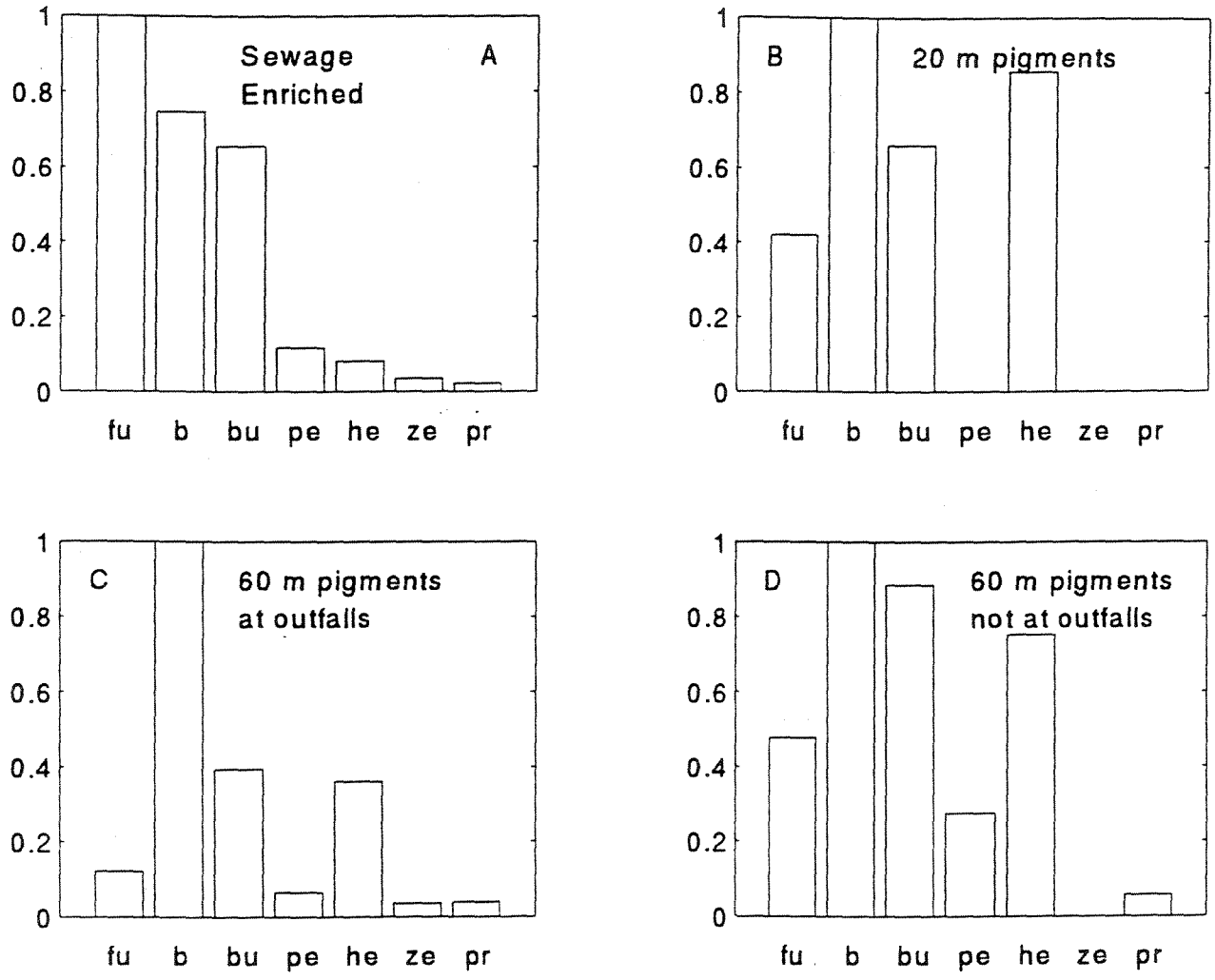


Figure 4.40 Profiles of diagnostic carotenoid pigments in (A) surface water from the Diamond Head buoy enriched with sewage effluent and incubated for one week, (B) nearshore water samples collected from a depth of 20 m, (C) water samples collected from a depth of 60 m at sewer outfalls, and (D) water samples collected from a depth of 60 m at stations other than the outfall stations.