

Quantitative Environmental Benchmarking in a Hydrologically Driven Hawaiian Coastal System

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Introduction Environmental Setting

The study area is a coastal environment located on the western slope of the Hualalai Volcano on the Kona Coast of Hawaii Island, which lies between longitude 154°48'W and 156°04'W and between latitude 18°54'N and 20°17'N (Figure 1). The area is semidesert, receives only 50–75 cm of rainfall year⁻¹, and has high solar irradiance that averages ~250 cal cm⁻² day⁻¹ in the visible region (400–700 nm wavelength) of the spectrum (Laws and Berning, 1991). Upslope to the east, rainfall increases to ~150 cm year⁻¹ at altitudes of 300–600 (Oki et al., 1999).

Geological and Hydrological Setting

The Hualalai substrate consists of porous alkalic basalt, with minor hawaiite and trachyte (Langenheim and Clague, 1987). Due to the high porosity of the lava, there are no surface streams in the area. Groundwater, having high inorganic nutrient concentrations relative to the adjacent seawater, flows from upland areas to the coast, where it discharges as a diffuse subter-

ABSTRACT

The spatial and temporal variability of water quality within aquatic habitats in the *Kaloko-Honokohau* National Historical Park was examined over a 2-year period to quantitatively establish water quality benchmarks against which future data might be compared to test for evidence of anthropogenic impacts. Throughput of low-salinity, high-nutrient groundwater and mixing with high-salinity, low-nutrient seawater caused significant temporal and spatial water quality variability in wells, anchialine pools, and fishponds within the study area. Variable mixing of seawater and freshwater was shown to be the primary determinant of changes in nutrient concentrations in these aquatic habitats, although leaching of basaltic rocks (Si) and biological uptake (N, P) may also influence nutrient concentrations.

The anchialine pool data, which evidenced the least variability, were used as input for a Monte Carlo simulation to identify the percentage change in nutrient concentrations that could be detected at a type II error rate of 5% using a nonparametric Kruskal-Wallis test with a type I error rate of 5%. Percentage changes of 8%, 20%, and 42% in silicate, phosphate, and nitrate + nitrite, respectively, were detectable by this criterion; these values represent sensitivity limits for detecting future changes in concentrations that might occur within this system.

Keywords: groundwater, water quality, nutrients, monitoring, Hawaii

anean flow into the oligotrophic coastal ocean. Diffuse groundwater discharge along the shore is a significant and characteristic hydrological feature of the island (Cox et al., 1969; Fisher et al., 1966; Oki, 1991; Oki et al., 1999, and references therein).

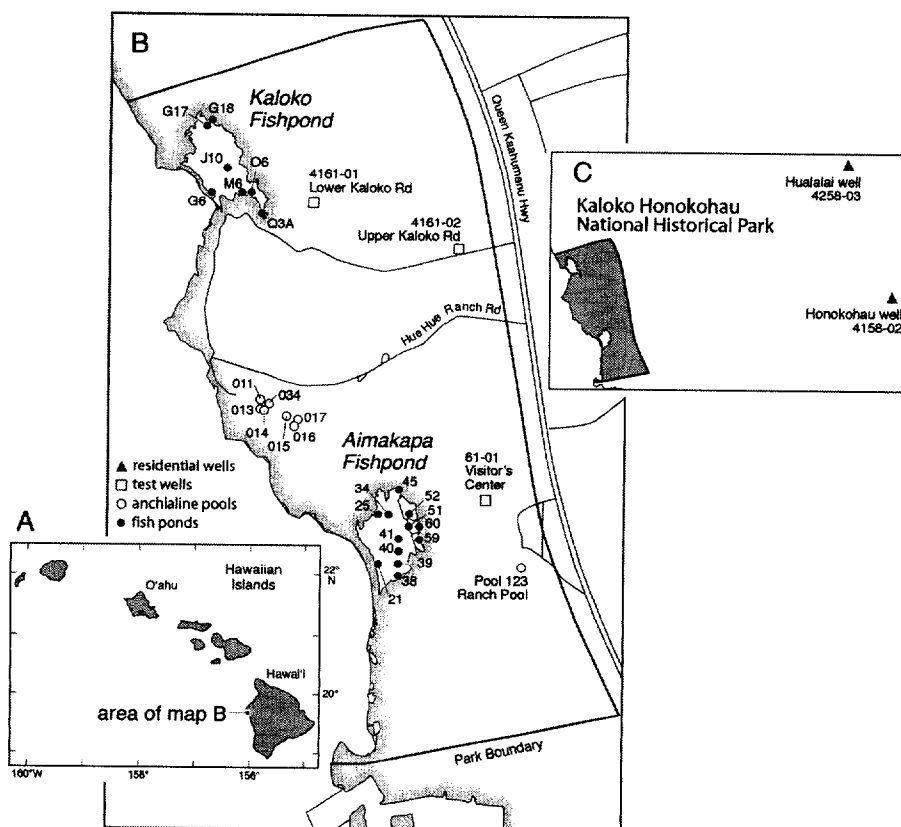
Societal Setting

The study site, the *Kaloko-Honokohau* National Historical Park (KAHO), was established in 1978. It contains two large Hawaiian fishponds with associated wetlands, numerous anchialine pools, and 240 ha of marine waters (Figure 1). Groundwater traversing the area is essential to the park's fishponds and anchialine pools

and wetlands, the latter of which provide breeding and foraging habitat for two endangered waterbirds and other migratory waterfowl. In the past two decades, considerable land surrounding the park has been reclassified from "conservation" to "urban." Various existing and proposed developments adjacent to and upgradient from the study area have caused concern about their possible effects on the quality and quantity of groundwater passing through aquatic habitats within the park. The work described here was intended to provide a quantitative understanding of the characteristics of groundwater currently entering the study area and of water quality within the park's various aquatic habitats. The

FIGURE 1

Location of *Kaloko-Honokohau National Historical Park* and the sites that were sampled in this study.



information resulting from this study has provided benchmarks to which water quality may be compared in future research aimed at determining the impact of nearby land use changes on water quality within the park.

Aquatic Environments

The study area (Figure 1) contains diverse aquatic resources, including a coastal fishpond (Kaloko), a marsh-fishpond complex (Aimakapa), and more than 130 anchialine pools. Anchialine pools are natural depressions in the porous basalt that intersect seaward-flowing groundwater. They have no surface inflows or outflows, but water levels vary with the tides (Brock and Kam, 1997; Maciolek and Brock, 1974). Kaloko fishpond is

an ancient Hawaiian fishpond in the process of being restored. A porous lava rock wall separates the pond from the coastal ocean, and two sluice gates control seawater exchange. Kaloko fishpond receives input from both subterranean groundwater and considerable exchange with surface seawater. The Aimakapa fishpond is bisected by a wall that separates a shallow, marshy, inland basin from a deeper (<2 m) outer basin. It receives groundwater input but has no free exchange with surface ocean waters. Its restricted water exchange has resulted in considerable sediment accumulation, and it functions as an avian nesting habitat. Subterranean connections to both groundwater and the sea cause water levels in these mixohaline pools to rise

and fall with tidal cycles. Anchialine pools represent inland extensions of the oceanic water table and display dampened fluctuations to tidal changes. Water within all these aquatic habitats is a mixture of seaward-flowing groundwater and seawater modulated by tidal cycles. Because of the strengths of the distinctly different marine and freshwater forcing functions, water quality in these aquatic habitats is highly variable. The salient differences in the chemistry of the low-salinity, high-nutrient groundwater and high-salinity, low-nutrient seawater create considerable temporal and spatial water quality variability in the aquatic environments within this study area.

Materials and Methods

Description of Sampling Sites

Samplings sites included two residential wells (4158-02 and 4258-03) upgradient of KAHO and 30 locations within KAHO: three test wells (4161-01, 4161-02, and 4061-01), eight anchialine pools, seven stations within Kaloko Fishpond, and twelve stations within Aimakapa Fishpond (Figure 1). The residential wells were located downgradient of residential housing but upgradient of existing/proposed commercial developments within the park; the test wells were located seaward (i.e., downgradient) of an existing light industrial development and residential housing. The choice of sampling wells was intended to facilitate evaluation of the characteristics of groundwater entering aquatic habitats within the park.

Description of Sampling and Analyses

Field samples were collected 19 times over a period of ~2 years (739 days) from July 23, 2004 to August 1, 2006.

Samples were collected at a variety of tidal stages, and in some cases certain pools were dry at spring low tides (i.e., no sample). Temperature, pH, salinity, and dissolved oxygen (D.O.) were measured with a HydroLab Quanta Water Quality Monitoring System having precision limits of $\leq 0.1^\circ\text{C}$, 0.1, 0.5 practical salinity units (psu), and 0.2 mg/L, respectively. Water quality data included concentrations of ammonium (NH_4^+), nitrate + nitrite ($\text{NO}_3^- + \text{NO}_2^-$), phosphate (PO_4^{3-}), silicate (SiO_4^-), dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), and chlorophyll *a* (chl *a*). Nutrients were measured on filtered samples using a Technicon AutoAnalyzer AAI according to standard methods outlined in Strickland and Parsons (1972), Grasshoff (1983), and Clesceri et al. (1998). Concentrations of total dissolved nitrogen and total dissolved phosphorus were determined via Environmental Protection Agency (EPA) methods 351.2 and 365.4 (Grasshoff, 1983; Ebina et al., 1983) using ultraviolet light digestion of filtrates followed by analyses for nitrate + nitrite and phosphate. Limits of detection for the dissolved nutrients were 0.5 μM DON, 0.05 μM PO_4^{3-} , 0.07 μM NH_4^+ , 0.10 μM DOP, 0.10 μM $\text{NO}_3^- + \text{NO}_2^-$, and 0.5 μM SiO_2^- . Chl *a* was measured fluorometrically using the method outlined in Strickland and Parsons (1972) with a detection limit of 0.01 μg chl *a* L^{-1} and a precision limit of 5%–10% for concentrations ≥ 0.25 $\mu\text{g/L}$.

Statistical Analyses

Statistical analyses of the nutrient data were carried out using MATLAB®. For each nutrient, sampling sites were first tested for differences in median values based on a Kruskal-Wallis (KW) test with a type I error rate (α)

≤ 0.05 . For a situation when *n* random samples have been collected/analyzed from a number of possibly different sets, the KW tests the null hypothesis that all are identical against the alternative that some of the sets tend to supply greater observed values than others (Conover, 1971). For purposes of the KW test, analytical results below the limit of detection were set equal to the limit of detection. Because the statistical test was nonparametric, the numerical value assigned to nondetects is irrelevant as long as it is consistently chosen and somewhere between zero and the limit of detection.

RSD values refer to relative standard deviation and are equal to the ratio of the standard deviation to the mean, expressed as a percentage. Because the frequency of sampling was roughly monthly, temporal variation

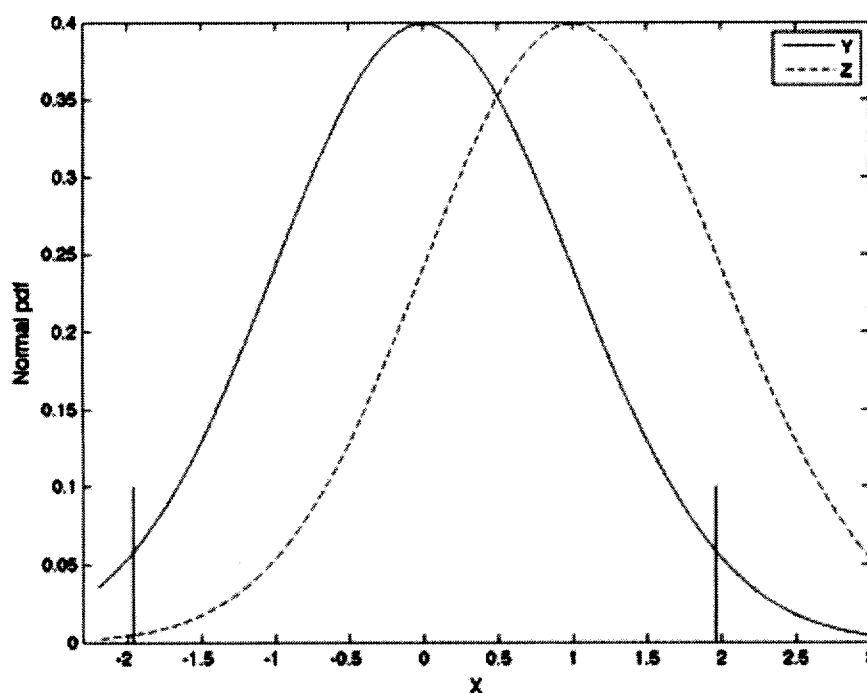
reported here should be understood to represent between-month variability. Runs tests above and below the median (Sokal and Rohlf, 1995) were used to examine time series for evidence of seasonality. For any dataset the minimum number of runs above and below the median is 2 and the maximum number of runs is *N* (if *N* is even) or *N* – 1 (if *N* is odd), i.e., values are alternately above and below the median. The data were judged to evidence seasonality if the number of runs was unusually small.

Type II error rates were calculated on the assumption that a subsequent study of similar extent was carried out. The concept of a type II error is illustrated in Figure 2.

Here two normally distributed random numbers, *Y* and *Z*, each with a standard deviation of 1, have

FIGURE 2

Probability density functions of two normally distributed random numbers, one (*Y*) with an expectation value of 0 and a standard deviation of 1, and another (*Z*) with an expectation value of 1 and a standard deviation of 1. The 95% confidence intervals for *Y* are indicated by the vertical lines at $X = -1.96$ and 1.96.



expectation values of 0 and 1, respectively. A single value from the Z distribution would lie within the 95% confidence interval for the Y distribution if it lies within -1.96 and 1.96 standard deviations from the center of the Y distribution or equivalently between -2.96 and 0.96 standard deviations from the center of the Z distribution. The probability that a single value from the Z distribution would lie between -2.96 and 0.96 standard deviations of the center of the Z distribution is 83%. Thus, if the type I error rate is set at 5%, a single value from the Z distribution would be incorrectly judged to be coming from the Y distribution 83% of the time. The type II error rate in this case is 83%. The same conclusion could be reached using a Monte Carlo approach by drawing many random numbers from the Z distribution and keeping track of the percentage of the time that the numbers fell within the 95% confidence interval of the Y distribution. We used a Monte Carlo approach in our type II error analysis, because it was easy to implement in conjunction with a KW test.

Assuming a subsequent study of similar extent, we generated noise-corrupted datasets that followed a log-normal distribution with mean and variance identical to the mean and variance of the values collected during this study for the three nutrients nitrate + nitrite, phosphate, and silicate. A second log-normal dataset was then generated with an expectation value that differed from the original by a specified percentage. This exercise was repeated 2,000 times, and in each case the two datasets were compared using a KW test to determine whether they would be judged to be different at $\alpha \leq 0.05$. We varied the percentage difference in the expectation values to determine what percentage difference was associ-

ated with a type II error rate of 5%. In other words, given the simulated level of noise, how different did the expectation values have to be before the null hypothesis that the medians were the same was correctly rejected 95% of the time?

Results

Table 1 provides a summary of the range and average values of approximately 6,000 water quality analyses made during this study. For each of the parameters, the RSD values reflect the combined effects of spatial, temporal, and tidal variability within each type of aquatic environment. Runs tests indicated the absence of seasonality for all parameters measured in the ponds and pools, with the exception of temperature and phosphate. Given this result and because in most cases our sampling covered almost exactly 2 years, this suggests that average (mean and median) values for all parameters are unbiased by seasonality. Runs tests also revealed no evidence of seasonality in temperature, salinity, pH, or nutrient concentrations in the test wells.

Temperatures in the wells and pools were ~ 3 – 5°C cooler than the fishponds but were characterized by similar RSD values. Generally, salinity followed the pattern Kaloko > Aimakapa > pools > wells; this sequence directly reflects the relative degree of mixing with oceanic waters. The average salinity in Kaloko fishpond declined from about 26–20 psu during the course of the study due to reconstruction of the fishpond's seawall. The seawall, although porous, significantly reduces water exchange between the fishpond and the ocean.

Despite the three test wells being upgradient and 300–600 m inland

from the pools, the salinity of the pools averaged less than 2 psu above that of the wells (9.8 vs. 8.0 psu, respectively). This result illustrates the inland extent of subterranean seawater penetration. Although the salinity of the residential wells was not measured, it was presumably less than 0.5 psu at the depth of removal for testing, since the secondary drinking water standard for total dissolved solids is 500 mg L^{-1} . With the exception of well water, all water samples were characterized by nearly saturated dissolved oxygen levels and pH values approximating those of seawater.

To test for differences in nutrient concentrations among the wells and pools, concentrations first were normalized to ocean water salinity to filter out differences associated with variable dilution with low-nutrient seawater. Concentrations were normalized using the equation $X_n = [(34X - X_{34}S)/(34 - S)]$, where X is the nutrient concentration in well water with salinity S psu, X_{34} is the concentration of the same nutrient in coastal water with a salinity of 34 psu, and X_n is the normalized nutrient concentration. X_n so calculated is the apparent nutrient concentration in the freshwater ($S = 0$) endpoint if the nutrient concentrations in brackish ($S > 0$) samples reflect nothing more than mixing of freshwater and seawater.

Values of X_{34} were assumed to be 159, 7.2, and $0.82\text{ }\mu\text{M}$ for silicate, nitrate + nitrite, and phosphate, respectively (Brock, 2006; Nance, 2002; Brock and Kam, 1997; Bienfang, 1980). Based on a KW test, the normalized silicate concentrations were lower ($\alpha = 1.4 \times 10^{-10}$), and the normalized concentrations of nitrate + nitrite and phosphate were higher ($\alpha = 1.3 \times 10^{-6}$ and 8×10^{-15} , respectively) in the test

TABLE 1

Summary of water quality characteristics measured during the study period.

	Temperature (°C)	Salinity (psu)	pH	D.O. (mg/L)	D.O. (% sat.)	NO ₃ (μM)	PO ₄ (μM)	NH ₄ (μM)	Si (μM)	DON (μM)	DOP (μM)	Chl <i>a</i> (μg/L)
Kaloko												
Mean	25.0	22.6	8.0	7.3	101	24.9	1.6	4.2	378	32.4	0.4	7.1
Min	18.9	10.5	7.3	3.1	47	0.1	0.14	0.1	54	0.5	0.1	0.09
Max	29.2	33.8	8.5	14.4	200	168	4.2	18.1	612	195	1.2	51
RSD (%)	9.6	27.5	3.5	25.2	24	99	67	75	35	82	75	116
Aimakapa												
Mean	25.5	12.5	8.1	6.0	78	8.1	1.7	5.2	516	32	0.8	9.5
Min	21.5	10.6	7.1	0.25	3	0.1	0.05	0.7	390	0.5	0.1	0.24
Max	32.3	13.8	8.7	11.4	130	90.3	4.5	24.7	640	87	2.3	34
RSD (%)	8.0	5.0	4.4	34.2	34	197	64	91	10	47	55	63
Anchialine pools												
Mean	20.9	9.8	8.0	8.0	94	91	3.9	3.2	566	101	0.2	1.6
Min	18.7	4.8	7.2	4.6	54	36	2.3	0.1	468	3	0.1	0
Max	27.1	15.7	9.1	14.9	187	183	5.3	14.2	643	398	1.8	95
RSD (%)	6.5	15.6	2.6	19.8	21	28	14	85	6	62	140	569
Test wells												
Mean	21.1	7.9	7.8	7.6	88	83	4.5	1.4	690	118	0.2	
Min	19.8	4.9	7.1	4.8	59	41	3.6	0.1	479	2	0.1	
Max	26.7	12.7	8.8	12.6	147	161	5.6	8.6	961	330	4.1	
RSD (%)	6.4	35.6	5.3	17.6	16	30	10	118	19	63	208	
Coastal ocean	25	34	8.1	7.0	103	0.024	0.13	0.20	2.6	4.3	0.24	1.4

The coastal ocean values for nutrients are mean values from the multidecadal database available at www.NELH.org. Due to sampling constraints for the residential wells, hydrological data are available only for the test wells.

wells than in the drinking water wells. Note that an alpha of 1 in 10^{-10} means is that if we performed the same sort of test many times and rejected the null hypothesis only when alpha was less than one in 10^{-10} or smaller, we would be wrong on average only once every ten billion times.

Normalized silicate and nitrate + nitrite concentrations were not significantly different among the anchialine pools (KW test, $\alpha = 0.47$ and 0.22 , respectively), and there was no signifi-

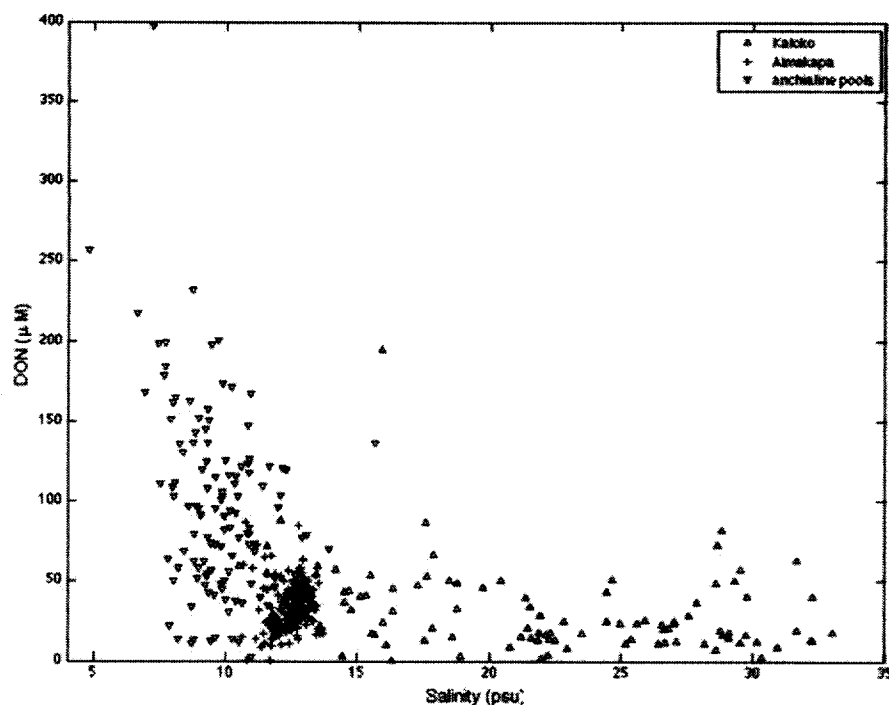
cant difference in normalized phosphate concentrations among seven of the eight anchialine pools. The normalized phosphate concentration in one atypical, inland pool (123) was significantly lower ($\alpha = 0.0007$) than phosphate concentrations in the other seven pools. This manmade basin was larger and deeper than other anchialine basins, and it was the only pool supporting both macrophytic aquatic algae and an overgrowth of terrestrial flora. In general then, the nutrient char-

acteristics of the various wells were similar, as were those of the anchialine pools, excepting pool 123.

Concentrations of oxidized inorganic nutrients followed the general pattern wells > pools > fishponds, while NH_4^+ followed exactly the opposite pattern. The modestly elevated NH_4^+ levels in the fishponds may in part reflect the inadvertent resuspension of sediments by large fish and/or the kayaks that were used during sampling. The two fishponds, having the

FIGURE 3

DON versus salinity in KAHO fishponds and anchialine pools.



greatest degree of oceanic exchange, were more saline than the other systems. Unnormalized oxidized nutrient concentrations in these two ponds

were lower than those for the inland wells and pools but higher than in the coastal ocean waters (Laws et al., 2004). Levels of DON in the wells

and pools were similar to one another and ~3.5 times greater than those in the fishponds. A plot of DON concentrations versus salinity in the fishponds and anchialine pools is concave upward (Figure 3), which suggests that DON is being utilized biologically in addition to being diluted by seawater.

DOP concentrations were low throughout all water body types; many values were close to or below detection limits. Chl *a* values in the fishponds were five to seven times higher than previously reported concentrations in coastal waters (Laws et al., 2004). Chl *a* levels in the anchialine pools frequently approached detection limits, reflecting the high turnover rates of these small basins.

Having confirmed statistically significant uniformity of water quality parameters within the various water body types, Table 2 summarizes the temporal (including tidal) and spatial variation encountered for all water quality parameters. RSD values for nutrients were generally higher than

TABLE 2

Summary of spatial and temporal RSD values (%).

Parameter	Kalo		Aimakapa		Anchialine Pools		Test Wells	
	Spatial	Temporal	Spatial	Temporal	Spatial	Temporal	Spatial	Temporal
Nitrate	91 ± 39	84 ± 28	117 ± 64	144 ± 28	18 ± 9	26 ± 10	25 ± 10	26 ± 6
Phosphate	72 ± 32	50 ± 16	36 ± 22	60 ± 9	8 ± 4	13 ± 2	8 ± 2	8 ± 3
Silicate	33 ± 19	30 ± 12	5 ± 3	11 ± 1	3 ± 2	6 ± 1	20 ± 2	6 ± 1
Ammonium	41 ± 21	69 ± 17	37 ± 13	92 ± 12	72 ± 47	68 ± 14	78 ± 29	100 ± 18
DON	61 ± 31	55 ± 22	31 ± 17	46 ± 7	28 ± 11	62 ± 6	30 ± 10	62 ± 7
DOP	51 ± 35	75 ± 23	32 ± 26	54 ± 9	45 ± 25	144 ± 35	48 ± 38	167 ± 64
Chl <i>a</i>	66 ± 22	105 ± 36	46 ± 22	64 ± 21	203 ± 46	149 ± 38	no data	
T	9 ± 3	7 ± 2	2 ± 1	8 ± 1	7 ± 12	5 ± 2	2 ± 1	6 ± 3
S	24 ± 5	18 ± 4	3 ± 2	5 ± 1	13 ± 3	11 ± 6	39 ± 11	21 ± 14
D.O.	17 ± 10	22 ± 3	21 ± 14	34 ± 12	14 ± 9	18 ± 9	15 ± 8	13 ± 3
pH	3 ± 1	2 ± 0.6	3 ± 2	4 ± 1.5	2 ± 2	2 ± 2	5 ± 2	4 ± 1.5

Spatial RSD values were calculated for each date and then averaged over all sampling dates. Temporal RSD values were calculated for each site and then averaged over all sites. Due to sampling constraints, hydrological data is available only for the test wells.

those for other parameters, and measures of spatial variation were somewhat lower than those for temporal variation. Overall, spatial and temporal variability in nutrient concentrations were lower for the wells and pools than for the fishponds. This difference reflects primarily the differences in inorganic nutrient concentrations between groundwater and seawater and the proportionate contribution of these two water types at places and times within these aquatic habitats and to a lesser degree variability associated with nutrient uptake by plankton and rooted aquatic plants.

Table 3 gives the median values $\pm$ 95% confidence limits for the nutrient concentrations measured in this study. For a time series containing (in this study) 19 numbers, the 95% confidence limits to the median are the 5th and 15th numbers when the data are ranked from smallest to largest (Tate and Clelland, 1957). In general, the data from the two fishponds showed more temporal noise than the corresponding values from the anchialine pools and wells. Based on a KW test at $\alpha \leq 0.05$, median nitrate, phosphate, and silicate concentration differences of 27%, 11%, and 6%, respectively, were detectable between pairs of anchialine pools. The DON, DOP, and ammonium values were noisier and hence of less use in detecting differences between sampling sites.

Discussion

The combination of groundwater throughput and mixing via ocean tides accounts for much of the variability in nutrient concentrations within the KAHŌ ecosystem, and the data show a high degree of hydrological connectedness among the various aquatic resources. These include

groundwater sources to and through the area, subterranean water exchange spatially within the area, surface and subterranean exchange with surface seawater, and ultimately groundwater inputs to the coastal ocean (Oki, 1999; Oki et al., 1999; Dollar, 2002; Nance, 2002; Brock, 2006; Johnson et al., 2008). Well data depict the water quality in the hydrographic input to this coastal system. The range of temporal variation for the residential wells, which are largely devoid of influences from either tidal mixing or existing developments, sets lower limits on the assessment of temporal changes that may be associated with presumably low levels of anthropogenic influence. The residential wells primarily reflect the hydrologic, meteorological (i.e., rainfall), and geological influences on the groundwater supply. That the nutrient concentrations in the residential wells are similar to those found (Dollar and Atkinson, 1992) in the Waikoloa and Keauhou areas to the north and south of this area imply that similar groundwater hydrological processes are influencing this study site. Comparison of the residential well data with the data from test wells provides another example of this input as it approaches the aquatic habitats seaward. The cause of the roughly threefold higher temporal variability in well and pool nitrate concentrations compared with phosphate (Table 2) is unclear. It is possible that interactions between groundwater and soils in Hawaii and rocks regulate, to some degree, groundwater phosphate concentrations. No comparable geochemical mechanism exists to regulate nitrate concentrations. Except for silicate and ammonium, there were no significant differences in the nutrient concentrations between the two residential wells upgradient of the existing

developments and the test wells down-gradient (seaward) of existing developments. The lower silicate levels and higher salinity (approximately one quarter that of seawater) suggests that mixing/dilution of the freshwater and seawater account for the lower silicate levels in the test wells. A similar explanation together with spatial mixing perhaps accounts for the slightly higher ammonium levels in the test wells relative to the residential wells. The $\text{NO}_3^-/\text{PO}_4^{3-}$ ratios in the residential wells averaged 18 (atom/atom), similar to ratios in deep ocean water (Redfield et al., 1963), in marine phytoplankton, and in other groundwater in Hawaii where agricultural activities are not present in the upstream watershed (Bienfang, 1980; Nance, 2002).

Although one might expect that the much greater tidal flushing of Kaloko Fishpond would cause its inorganic nutrient concentrations to be more variable temporally than those of Aimakapa Fishpond, with the exception of silicate this was not the case, and nitrate concentrations were consistently (across almost all stations) less variable in Kaloko than in Aimakapa. Chl *a* concentrations in both of the fishpond environments were substantially lower than would be expected from complete utilization of the inorganic nutrients supplied by groundwater seepage. For example, assuming Redfield stoichiometry (Redfield, 1958), the 4.5 μM phosphate in the wells (Table 1) should translate to 477 μM phytoplankton carbon, and assuming a C/chl *a* ratio of ~ 50 by mass (Strickland and Parsons, 1972, p. 185), the associated chl *a* concentration would be 114 $\mu\text{g L}^{-1}$. This is roughly an order of magnitude higher than the average chl *a* observed in Aimakapa Pond and Kaloko Fishpond (Table 1). Flushing from groundwater

TABLE 3

Median (M) and lower (L) and upper (H) 95% confidence limits to the median for nutrient concentrations measured in this study.

Station		NO ₃			PO ₄			NH ₄			Si			DON			DOP		
		M	L	H	M	L	H	M	L	H	M	L	H	M	L	H	M	L	H
Kaloko	F17	16.4	5.7	23.6	0.86	0.45	1.45	3.89	2.25	4.91	376	326	477	17	14	32	0.36	0.29	0.47
	G6	3.7	1.1	11.2	0.60	0.44	0.76	3.07	1.5	6.36	256	127	363	16	11	20	0.28	0.23	0.47
	G18	29.5	21	39.7	1.81	1.01	2.06	3.38	2.7	4.76	440	381	488	40	24	51	0.30	0.18	0.62
	M6	22.1	3.3	32.9	1.20	0.73	1.99	3.42	2.1	5.32	358	277	424	19	13	40	0.28	0.1	0.42
	O6	17.4	9.2	29.6	2.00	0.83	2.58	3.32	2.26	4.81	363	257	467	28	13	49	0.31	0.24	0.44
	Q3	43.9	39	56.2	3.19	2.78	3.39	3.25	2.68	5.44	521	483	550	51	43	60	0.14	0.1	0.23
Aimakapa	21	0.5	0.1	1.9	0.89	0.5	1.32	2.84	2.31	7.22	498	482	560	26	20	36	0.84	0.68	1.35
	25	0.8	0.1	2.4	0.94	0.73	1.41	3.36	2.42	6.34	500	463	576	27	19	39	0.88	0.64	1.24
	34	1.2	0.1	2.6	1.16	0.82	1.61	3.15	2.36	5.86	520	488	570	29	23	44	0.94	0.64	1.23
	38	0.7	0.1	2.8	1.04	0.79	1.76	3.24	2.61	6.9	502	461	566	33	21	46	0.99	0.71	1.28
	39	0.6	0.1	2.8	1.11	0.69	1.69	3.17	2.38	6.64	507	477	559	31	22	48	0.87	0.71	1.3
	40	1.1	0.1	3.3	1.08	0.83	2.16	3.56	2.25	8.06	488	452	559	27	22	39	0.98	0.65	1.2
	41	0.5	0.1	5.1	1.16	0.89	2.06	3.62	2.35	4.97	499	477	557	28	23	38	0.92	0.71	1.11
	45	5.2	0.1	19.7	1.78	1.22	3.43	5.29	3.00	8.46	534	496	569	38	22	58	0.59	0.36	0.74
	51	1.1	0.1	15.1	1.18	0.91	3.00	3.58	1.82	4.43	502	479	566	30	21	41	0.70	0.33	0.94
	52	12.2	1.0	21.3	1.82	1.17	2.11	2.77	1.88	4.75	506	495	561	29	10	37	0.58	0.47	0.76
	59	5.3	0.1	31.9	2.52	1.14	3.66	4.03	3.16	7.27	504	481	568	35	26	54	0.76	0.3	1.07
	60	11.1	0.1	28.3	2.64	1.12	3.51	3.35	2.37	5.57	499	484	559	32	24	40	0.70	0.2	0.75

TABLE 3 continued.

Pools	11	78	67	83	3.49	3.3	3.69	3.03	2.54	4.53	548	500	560	86	36	123	0.10	0.10	0.23
	13	89	76	94	3.72	3.58	4.00	2.16	1.02	2.78	550	532	571	88	49	121	0.10	0.10	0.19
	14	101	85	111	3.85	3.72	3.97	1.97	0.82	2.48	567	547	590	103	69	126	0.10	0.10	0.19
	15	93	77	98	4.01	3.87	4.15	2.66	1.89	4.28	581	560	600	79	52	111	0.10	0.10	0.18
	16	89	79	99	4.02	3.84	4.2	1.84	1.53	3.37	577	569	598	83	58	136	0.10	0.10	0.17
	17	93	82	105	4.01	3.82	4.11	2.15	1.55	3.45	584	568	603	80	56	143	0.10	0.10	0.21
	34	102	86	109	3.95	3.76	4.04	2.03	0.86	2.6	568	560	583	85	62	116	0.10	0.10	0.15
	123	89	45	103	3.55	3.1	3.75	7.24	5.78	10.37	572	556	589	110	62	152	0.13	0.10	0.22
	W4258-03	70.58	56.65	75.3	4.37	4.32	4.59	0.2	0.13	1.7	829.9	808.8	854	128.02	56.27	145.17	0.02	0.01	0.29
	W4158-02	81.65	67	90.48	4.11	4.03	4.22	0.13	0.13	0.13	826.4	812.8	841.8	128.6	87.87	170.67	0.01	0.01	0.09
Wells	4061-01	75.7	53.2	86.3	4.12	3.82	4.93	1.68	1.34	2.43	541.8	514	555.2	91.08	69.81	113.1	0.03	0.01	0.15
	4161-01	78.6	62.7	88.9	4.45	4.23	4.58	1.65	0.88	2.38	640.2	590.6	655.8	104.64	47.67	126.45	0.01	0.01	0.01
	4161-02	109.85	96.4	115.3	4.81	4.69	5.16	1.07	0.65	1.66	622	595.2	638.4	112.94	96.7	162.12	0.01	0.01	0.01

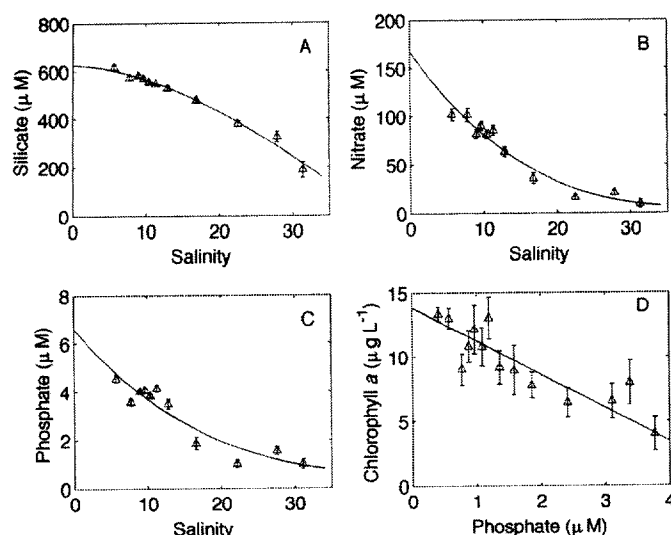
All values are in μM .

throughput and tidal exchange appear to be the most likely mechanisms responsible for keeping the phytoplankton populations in check.

Changes in nutrient concentrations through the system due to hydraulic mixing between high-nutrient, low-salinity groundwater and low-nutrient, high-salinity seawater are illustrated in Figures 4A–4C. Waters traversing this coastal system are influenced primarily by simple mixing and to a lesser degree by biological assimilation (N + P) and possibly chemical leaching (in the case of Si) from the basalt substrate. Given that silicate concentrations in the well waters vastly exceed the capability of biological uptake (Paasche, 1980), one might also expect a straight-line relationship between salinity and silicate throughout the waters of such a system. Such a straight-line relationship between salinity and silicate has been used by Dollar and Atkinson (1992) to describe mixing in the groundwater-influenced coastal system of Hawaii Island. The negative curvature of the silicate data (Figure 4A) may suggest that the pool/pond system may be a source of silicate, presumably the result of leaching from basaltic rocks, but factors such as multiple sources of freshwater that traverse the study area cannot be ruled out. Approximately linear relationships between nutrient concentrations and salinity in aquatic habitats in the Kona area (Brock and Kam, 1997; Dollar and Atkinson, 1992; Dollar, 2002) are taken to reflect the nearly conservative mixing between freshwater and seawater endpoints, i.e., minimal biological uptake during passage through the area. Removal of nutrients by biological or other means leads to positive curvature in the relationship between salinity and nutrient concentrations. Such behavior is evidenced in the relationships

FIGURE 4

Plots of (A) silicate, (B) nitrate, and (C) phosphate versus salinity in the anchialine pools and Kaloko fishpond. The solid curves are nonlinear least squares fits. (D) Chl *a* versus phosphate in Aimakapa Pond. The straight line is a model II geometric mean regression line. In all cases, data on abscissa have been sorted and binned. Error bars are standard deviations of the mean values of ordinate values associated with abscissa values in each bin.



between nitrate and phosphate values for Kaloko Fishpond (Figures 4B and 4C), but the values are at most ~20%–25% below those associated with a simple mixing model (i.e., straight-line relationship between nutrient concentration and salinity).

The positive curvatures of the nitrate + nitrite and phosphate graphs in Figures 4B and 4C are to first approximation directly proportional to the rate of biological uptake, and the implied (nitrate + nitrite)/phosphate removal ratio is 32 on a molar basis. This figure is about 28% higher than the ratio in the freshwater source, ~100% higher than the ratio of 16 typically associated with phytoplankton (Redfield et al., 1963), and similar to the mean ratio of 35 reported for marine benthic plants by Atkinson and Smith (1983). The implication is that the majority of nutrient removal in the Kaloko Fishpond is due to

biota other than phytoplankton, such as rooted aquatic plants and various other benthic organisms, a not surprising conclusion considering the shallowness of the system.

The constancy of salinity in Aimakapa Pond (12.5 ± 0.25 psu) reflects sluggish exchange with the ocean. Variations of phosphate concentrations within the pond were strongly correlated ($r = -0.86$, $p < 0.0001$) with Chl *a* (Figure 4D). However, the absolute value of the slope of the regression line fit to the data implies a P/Chl *a* ratio that is about three to six times larger than the P/Chl *a* ratios of phytoplankton (Parsons et al., 1961). The implication is that $\geq 65\%$ of the phosphate assimilated biologically finds its way into components (such as heterotrophic bacteria, benthic algae, and rooted aquatic plants) of the pond food web other than suspended phytoplankton (Vadstein et al., 1988).

To estimate the flux of nutrients entering the system at the freshwater endpoint requires information on groundwater fluxes. Several previous studies of groundwater transport are germane to the study area, which lies between the Ke-ahole airport and the town of Kailua-Kona. One study estimated groundwater fluxes of $\sim 14 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-1}$ for the Kailua area to the south and $\sim 3.8 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-1}$ for the Keahole area to the north (Nance, 2002). A study just south of *Kaloko-Honokohau* reported fluxes of $\sim 42 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-1}$ along the Honokohau Harbor shoreline (Bienfang, 1980; Gallagher, 1980). A hydrological study based on 1978 groundwater withdrawal conditions estimated a groundwater flux of $7 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ for the park area specifically (Oki, 1991; Oki et al., 1999). Using the freshwater endpoint concentrations (Figure 4) and an estimated freshwater flux of $7 \text{ m}^3 \text{ m}^{-1} \text{ day}^{-1}$ yields daily flux values of 16 kg nitrate + nitrite N km^{-1} , 1.4 kg phosphate P km^{-1} , and 122 kg Si km^{-1} . These translate to annual fluxes of 5.8 tons nitrate + nitrite N km^{-1} , 0.51 tons phosphate P km^{-1} , and 45 tons Si km^{-1} due to groundwater along most of the coastline of the Island of Hawaii. This groundwater nutrient input is so considerable that the Hawaii Department of Health, in its role of enforcing the Clean Water Act, has established special regulatory limits for the Island of Hawaii that account for the elevated coastal ocean nutrient concentrations caused by this natural process (State of Hawaii Department of Health, 2006). The horizontal nutrient transport from the point of intrusion into coastal waters is a function of physics (e.g., wind, tides, and currents) and bathymetry (Cloern, 2001). The negligible signature of high

groundwater nutrient concentrations in either the planktonic or benthic communities appears to be the consequence of the overwhelming oceanic forces of export/transport from the coastal area.

One of the goals of this study was to determine the degree of change in water quality relative to the baseline values reported here that would have to be detected in future studies of KAHO aquatic habitats to state with statistically quantifiable confidence that conditions had changed. Since temporal and spatial variability in water quality was lower in the anchialine pools than in the fishponds, we focused our statistical analysis on water quality in the former. Assuming a subsequent study of similar extent (19 samples collected from each of eight anchialine pools), our type II error analysis indicated that nitrate + nitrite, phosphate, and silicate concentrations would have to increase by 42%, 20%, and 8%, respectively, before the type II error rate would be no more than 5%. Since chl *a* concentrations in the anchialine pools are currently very similar to those in the coastal ocean (Table 1), it is probably reasonable to assume that a 20% increase in chl *a* associated with a similar increase in phosphate concentrations would not seriously disrupt the ecology of the anchialine pools, i.e., the pools do not appear to be near a tipping point *sensu* Scheffer et al. (2009). Thus, the sensitivity of the survey approach utilized in this study appears adequate to provide the sort of warning that is needed to allow time for an informed response to eutrophication problems before disaster is imminent.

The concentration of which one of these nutrients will be most sensitive to anthropogenic effects is unclear, and the ecological importance of higher

concentrations for any of these nutrients is not readily apparent. Any ecosystem response will of course depend on the nature of the anthropogenic activities; in this particular case, this might include changes in groundwater withdrawal rates, changes in nutrient loading, and/or inputs of allochthonous compounds. The fact that salinity-normalized concentrations of nitrate + nitrite and phosphate are higher in the three test wells than in the drinking water wells suggests that even now there is an input of nutrients to the groundwater system upgradient of the park. Nutrient concentrations in the two fishponds appear to be more insensitive indicators of anthropogenic effects due to greater variability in the ponds, leading to lower signal-to-noise ratios.

This study describes a rare example of an aquatic habitat that has both high nutrient levels that are due primarily to natural geological processes and a lack of eutrophication that is due primarily due to flushing rates that exceed rates of plant utilization and growth in this high irradiance setting. Water quality evidenced a high degree of hydrological connectedness among various aquatic habitats within the study area. The high temporal uniformity of nutrient concentrations in the groundwater reflects the predominant strength of hydrologic forces on those concentrations. The similarity of the groundwater nutrient concentrations observed in this study to those observed previously in this area supports the argument that these concentrations are determined primarily by natural processes. This characterization provides the current condition baseline for determining whether future, nearby developments may change freshwater throughput and/or water quality within this coastal habitat. High nutrient

concentrations in the groundwater, the importance of hydraulic throughput, and the high degree of connectedness of the aquatic water habitats caused nutrient levels to be a primary focus in this benchmarking effort against which future conditions could be evaluated quantitatively. Applications in other locales and settings may have concerns for changes due to a variety of different anthropogenic activities, e.g., metals, organic pollutants, etc. Nonetheless, the process exemplified in this work (i.e., design/implementation of a robust sampling effort to embrace a majority of the variability and convey reasonable degrees of freedom for subsequent analyses, and a stepwise statistical analyses to identify various forms of variability and describe the statistical limits of the benchmark condition against which future data can be quantitatively compared) should be applicable to a range of locations and/or parameters of interest.

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