

Stream Nutrient Concentrations on the Windward Coast of Hawai'i Island and Their Relationship to Watershed Characteristics¹

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Abstract: Dissolved inorganic and organic nutrients and physiochemical parameters were measured in 24 Hawai'i Island streams. Particulate nutrients and instantaneous nutrient and sediment fluxes were measured in half of these streams. Stream waters were dilute and slightly alkaline and had low concentrations of ammonium, orthophosphate, dissolved organic phosphorus, and total suspended solids. Particulate matter comprised 45%, 73%, and 28% of nitrogen, phosphorus, and carbon pools, respectively. Dissolved nitrogen was comprised primarily of organic nitrogen (54%) and nitrate (34%). In some streams, nitrate and total nitrogen concentrations were slightly elevated relative to Hawai'i Department of Health (HDOH) water quality standards. Instantaneous nitrate yields for the streams plus 26 HDOH stations were calculated, and the average from the combined data set was 7.1 (SD 11.1) moles N day⁻¹ km⁻². Nitrate concentrations and yields were 2.1 and 3.5 times higher, respectively, in Kohala watersheds than in Mauna Kea watersheds. Regression analysis was used to evaluate whether water quality parameters are predicted by watershed area, mean annual rainfall, population density, or percentage of agricultural land. Many water quality parameters were not predicted by these variables. In Mauna Kea streams, concentrations of dissolved organic nitrogen and dissolved organic carbon increased with increasing watershed area, nitrate concentrations increased with increasing population density, and both specific conductivity and nitrate yield increased with increasing percentage of agricultural lands. In Kohala streams, nitrate concentrations and yields were not predicted by watershed characteristics. Overall, watershed characteristics, as quantified in this study, were not strong predictors of water quality.

ANTHROPOGENIC ACTIVITIES worldwide are greatly increasing the amounts of nutrients and sediments entering streams and rivers and being exported downstream to coastal waters (Howarth et al. 2000, Syvitski et al. 2005). High nitrogen and phosphorus fluxes (mass per unit time exported by a watershed) are as-

sociated with the occurrence of nuisance and toxic algal blooms, fish and shellfish kills, hypoxic and anoxic bottom waters, degradation of habitat, and loss of recreational opportunities and aesthetic value (Jickells 1998, Dodds 2006). High sediment fluxes have some of the same impacts as high nutrient fluxes, including increasing nutrient concentrations, decreasing dissolved oxygen concentrations, degrading habitat, and depreciating aesthetic value (reviewed in Dodds [2002]). However, unlike nutrients, excessive sediments can decrease primary production and smother benthic communities.

In the United States, management under the Clean Water Act has substantially reduced nutrients originating from point sources. Attention is now being directed at reducing nutrient and sediment pollution derived from nonpoint sources such as runoff from urban

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areas or cultivated fields. Nonpoint pollutants can be quantified in terms of concentration or in terms of fluxes. Understanding sources of nutrients and sediment is the first step in remediation of polluted water bodies. Studies are expensive, however, and most of what we know about sources and impacts of elevated nutrient and sediment fluxes from lotic systems is based on research in temperate areas. Tropical lotic systems have generally received less attention except for systems like the Amazon and Orinoco that have been extensively studied (reviewed in Cushing et al. [1995]). A tool developed under the U.S. Clean Water Act and a starting point for managing nonpoint pollutants is the Total Maximum Daily Load (TMDL). TMDLs are a calculation of the maximum amount of a pollutant (nutrients, sediments, toxics) that can enter a particular water body without exceeding water quality standards set under the Clean Water Act. TMDLs are based on measurements of fluxes, the discrepancy between observed and desired concentrations, and quantitative estimates of pollutant sources. Once pollutant sources are identified and flux (loading) goals for anthropogenic sources are established, remediation programs can be implemented. Nonpoint pollutants are typically reduced through voluntary implementation of Best Management Practices (BMPs). Recommendations for BMPs appropriate to Hawai'i have been developed (Hawai'i Office of Planning and Hawai'i Department of Health 2000, Hawai'i Commission on Water Resource Management 2008). Examples of BMPs include use of permeable paving, planting riparian buffer strips, minimizing logging roads, improving livestock rotation, reducing pig and goat populations, reducing fertilizer use by better matching applications to crop needs, building constructed wetlands, integrating detention basins into golf courses, and passing stricter grubbing and grading ordinances.

In Hawai'i, the Department of Health (HDOH) administers the U.S. Clean Water Act and is charged, among other things, with monitoring water quality in streams and coastal waters and developing TMDLs. According to the latest assessment report, the state had 93 streams and 209 coastal water bodies on its §303(d) list of impaired water

bodies (State of Hawai'i 2006). As of early 2010, however, only eight TMDLs representing 14 streams have been completed. The TMDL reports (HDOH 2010) are a valuable source of flux data and information on nutrient sources. Nevertheless, resources clearly fall short of what would be required to comprehensively characterize stream water quality and its response to anthropogenic pressures, management activities, invasive species, and climate change.

There are, however, several non-HDOH sources of water quality data for Hawaiian streams. Hoover (2002) reviewed much of the data collected or published before 2002. In 1998–2001, the U.S. Geological Survey (USGS) conducted comprehensive sampling on O'ahu Island as part of its National Water Quality Assessment Program (Oki and Brasher 2003, Anthony et al. 2004). Other researchers have measured nutrients and/or sediment as part of investigations into anthropogenic effects on stream ecology (Larned and Santos 2000, Laws and Roth 2004, Kinzie et al. 2006, Larned et al. 2008, Wiegner et al. 2009), terrestrial effects on coastal waters (Soicher and Peterson 1997, Ringuet and Mackenzie 2005, Cox et al. 2006, De Carlo et al. 2007), and general hydrology (Laws and Ferentinos 2003, De Carlo et al. 2004). Recent measurements of nutrient concentrations and fluxes in O'ahu urban stormwater (Presley and Jamison 2009) provide information relevant to assessing urban impacts on streams. An alternative or adjunct to examining water chemistry is to conduct biological and physical assessments of stream condition. A statewide assessment was conducted in 1990 (U.S. National Park Service Hawai'i Cooperative Park Service Unit 1990), and detailed ones have been conducted for three streams on Hawai'i Island (Kido 1998, 2008). Those studies have shown that land use and stream hydrologic conditions can affect nutrient and sediment concentrations and fluxes. Generalizing these results is difficult, however, because of Hawai'i's diverse climate, geologic age, and land use, not to mention evolving anthropogenic pressures and natural hydrologic fluctuations.

Next to O'ahu, the island of Hawai'i has the second largest population in the state

(Juvik and Juvik 1998) and is projected to experience the most rapid growth and development in the state in the next 20 yr (Hawai'i Department of Business, Economic Development, and Tourism 2007). There are 129 named perennial streams on the island and nearly all of them are on the windward eastern slopes (hereinafter East Hawai'i). Streams are concentrated on Mauna Kea and Kohala volcanoes because Kilauea and Mauna Loa volcanoes are largely too permeable and youthful to support perennial streams, and even ephemeral streams are rare. Monitoring conducted under the auspices of the U.S. Clean Water Act has raised concerns about nutrients and turbidity in several East Hawai'i streams (State of Hawai'i 2006). As a result, a TMDL for streams entering Hilo Bay is currently under development (Presley et al. 2008). Reported routine stream monitoring in East Hawai'i virtually ceased after 2002 because funding levels were insufficient to support both stream and coastal monitoring. Coastal waters continue to be monitored primarily for recreational health safety. A community group attempted to fill in the data gap for streams by monitoring several streams and springs near Hilo (Young and Godzsak 2008), but their funding was short-lived. Also, there were two recent ecology studies in East Hawai'i that measured organic nutrient fluxes in two streams for several months to 2 yr (Larned et al. 2008, Wiegner et al. 2009). Those studies notwithstanding, the existing data are insufficient to precisely characterize the concentrations and fluxes of nutrients and sediment in East Hawai'i streams. This, plus the lack of data on nutrient sources and estimates of BMP-related flux reductions, has compromised the ability of the Hilo Bay Watershed Advisory Group to obtain U.S. Clean Water Act funding for BMP demonstration projects.

Scarcity of recent data makes it difficult to identify and attribute changes in stream water quality associated with watershed land use change. The most notable recent change occurred in the 1990s when former sugarcane lands became fallow or were converted to diversified agriculture. Water quality data are particularly sparse in the case of organic nutrient concentrations and nutrient and sedi-

ment fluxes, both of which are important in ecosystem dynamics and watershed management. Statistical and conceptual models are tools that may allow us to make the necessary estimates; application of such models to Hawaiian watersheds is under development (Polyakov et al. 2007, Gaut 2009, Okano 2009).

The goals of the study reported here were to (1) develop a preliminary water quality data base for East Hawai'i and (2) examine the relationship between watershed characteristics and stream water quality. To accomplish these goals, Geographical Information Systems (GIS) were used to delineate watershed boundaries and derive their natural (area and precipitation) and anthropogenic (land use and population) characteristics. Stream water samples were collected from delineated watersheds during base-flow and high-flow conditions and assayed for nutrients and sediment. The relationships among water quality parameters and watershed characteristics were then evaluated using various statistical approaches. Data from this project provide preliminary baseline information on nutrient concentrations, nutrient yields, and possible anthropogenic influences for watersheds in East Hawai'i. These data can be used to develop monitoring and restoration plans for this region.

Acronyms: DIN, dissolved inorganic nitrogen; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; DOP, dissolved organic phosphorus; PC, particulate carbon; PCA, principal component analysis; PN, particulate nitrogen; PP, particulate phosphorus; TC, total carbon; TDN, total dissolved nitrogen; TDP, total dissolved phosphorus; TN, total nitrogen; TOC, total organic carbon; TP, total phosphorus; TSS, total suspended solids.

MATERIALS AND METHODS

Experimental Design

Forty-one grab samples were obtained from 24 streams on the eastern (windward) slope of the island of Hawai'i. Most of these streams are located along the eastern flank of Mauna Kea (Figures 1 and 2) and flow through deep,

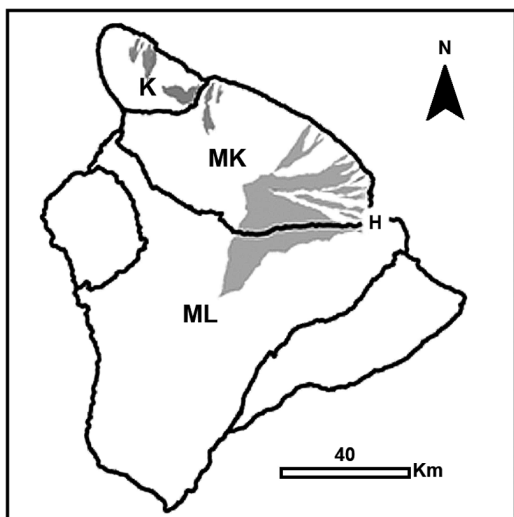


FIGURE 1. Location of study watersheds (gray shading) and volcanoes (outlined) on Hawai'i Island. In order of increasing age, the volcanoes in the study area are Mauna Loa (ML), Mauna Kea (MK), and Kohala (K). The location of Hilo is marked "H."

steep-sided gulches affording difficult accessibility. Because roads are sparse, sampling was conducted at the few locations where road crossings provided access to streams. All samples were assayed for dissolved inorganic and organic nutrients (except DOP), suspended sediment, and physiochemical parameters. Stream discharge was measured when feasible. A special effort was made to sample streams after rainfall-runoff events, and these samples were additionally assayed for particulate nutrients and DOP. However, many of these "storm" samples have low TSS and appear to be closer to base-flow conditions than to true storm conditions. This may have occurred because storm hydrographs for most of the watersheds are on the order of hours to 1 day. For this reason, samples may have been collected on the receding limb of the hydrograph when conditions were returning to base-flow levels. Repeat samples were obtained from nine streams, generally at intervals of weeks to months. All samples were collected during February, March, April, and July of 2005.

We also used data collected by the HDOH at 26 sites on 17 Mauna Kea and Kohala streams (Figures 1 and 2). The HDOH data, which consist of simultaneous measurements of stream discharge and $\text{NO}_3^- + \text{NO}_2^-$ concentration, were obtained from <http://www.epa.gov/storet>.

We used GIS techniques to determine characteristics (size, land use designation, population, and precipitation) of each stream's watershed. Stepwise multiple linear regressions were used to determine if watershed characteristics were predictive of concentrations of nutrients and fluxes of nitrate. Principal component analysis was used to synthesize our complex data sets to identify streams with anomalous water chemistry and identify groups of streams with similar concentrations of nutrients.

Watershed Characterization

The contributing drainage area (watershed) upstream of sampling sites (including HDOH sites) was delineated on the basis of topography using a 30 m Digital Elevation Model (DEM) from the USGS and GIS routines (Table 1). The location of HDOH stations was obtained from <http://hawaii.gov/dbedt/gis>. Our technique delineated watersheds entirely on the basis of topographic slope and did not take continuity of stream channels into account. Results were compared with stream maps developed by the USGS and the Hawai'i Department of Natural Resources Division of Aquatic Resources (DAR) stream data set (available from <http://hawaii.gov/dbedt/gis>) to identify locations where mapped streams implausibly crossed topographic divides. In such cases, adjustments were made if, in the judgment of the analyst, the DEM failed to correctly locate topographic divides. In two cases, areas above reservoirs were excluded.

Stream data from the Hawai'i Stream Assessment (U.S. National Park Service Hawai'i Cooperative Park Service Unit 1990) and DAR were used to identify unusual stream features such as dams, concrete channels, ephemeral flows, and diversions. We did not attempt to quantify diversions occurring at

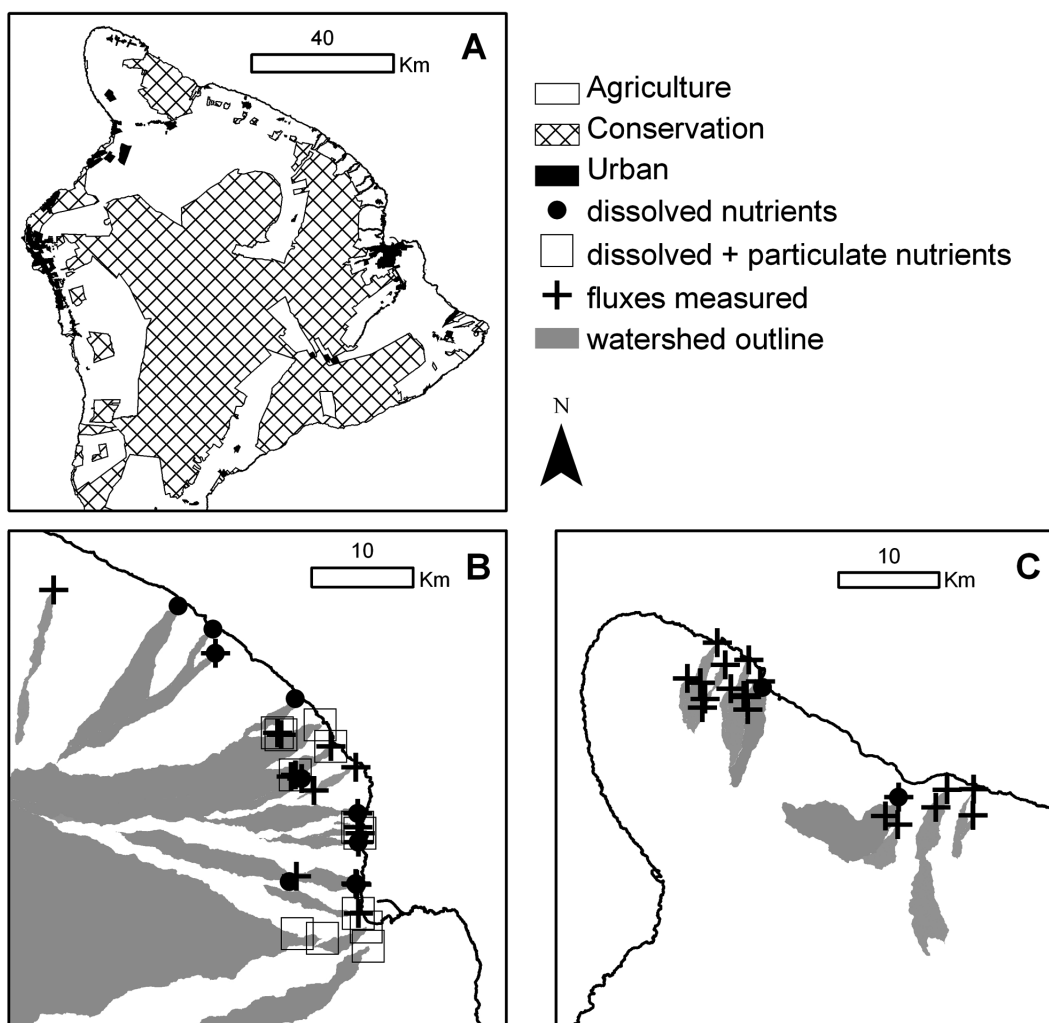


FIGURE 2. Location of sampling sites on Hawai'i Island: *A*, land use designation; *B*, type of data collected (southern portion of the study area); *C*, type of data collected (northern portion of the study area). "Dissolved nutrients" refers to inorganic and organic N and P species, plus physiochemical parameters. HDOH sites have a "+" without a colored dot or square.

the time of stream sampling. Any unusual conditions or known diversions are noted in Table 2.

Watershed maps were overlain onto a map of land use allocation (hereinafter "zoning") to determine the percentage of the watershed in each zoning category (conservation, agricultural, and urban). We used land use maps (County of Hawai'i 2005) that were previously digitized by the GIS Office of the

Hawai'i Department of Planning. The population of each watershed was calculated from 2000 census data (obtained from <http://hawaii.gov/dbedt/gis>), assuming that population density is spatially uniform across each census block. Average annual precipitation was obtained by rasterizing contour data from Giambelluca et al. (1986) and then performing a GIS overlay to obtain mean values for the watershed. All GIS analyses were per-

TABLE 1
Hawai'i Island Watersheds Used in This Study

Stream Sites (Volcano)	Area (km ²)	Zoning: Cons-Ag-Urb (%)	Population	Mean Annual Precipitation (mm)	<i>n</i>			
					Basic	Particulate	Nitrate flux	Other fluxes
Dominantly conservation (mostly forested)								
'Akaka Falls trib. (MK)	0.45	94-6-0	0	5,876	3	2	1	1
Pololū U (K)	0.78	78-22-0	1	2,789	0	0	2	0
Mā'ili (MK)	0.81	97-3-0	1	6,341	1	0	0	0
Hālawa U (K)	0.84	77-23-0	0	2,494	0	0	2	0
Niuli'i U (K)	1.7	72-28-0	2	2,560	0	0	2	0
Ainako (ML)	3.1	84-2-14	275	4,834	3	3	0	0
Kama'e'e (MK)	3.3	66-34-0	0	5,013	3	2	1	1
Pahe'ehe'e (MK)	5.3	79-21-0	2	5,872	1	0	1	1
Kaiwilahilahi (MK)	17	74-26-0	4	3,193	1	0	1	1
Kawainui (MK)	21	73-28-0	19	5,675	1	0	1	1
Hakalau (MK)	23	67-33-0	6	4,875	3	2	0	0
Honoli'i U (MK)	30	97-0-3	44	4,884	0	0	2	0
Honoli'i L (MK)	34	86-14-0	138	4,917	1	0	2	0
Wailoa-Waipi'o U (K)	42	96-4-0	14	3,298	1	0	2	0
Kolekole U (MK)	45	74-26-0	16	3,599	0	0	4	0
Kolekole L (MK)	52	71-29-0	24	3,900	3	3	5	1
Wailoa-Waipi'o L (K)	64	73-27-0	452	3,008	0	0	1	0
Umauma, S. Fork (MK)	74	68-32-0	1	2,568	2	1	1	1
Waiākea (ML)	82	70-27-3	529	3,881	2	2	0	0
Wailuku (ML + MK)	574	79-21-0	240	2,260	1	1	0	0
Dominantly agricultural								
Halelua U (K)	0.23	7-93-0	0	2,402	0	0	1	0
Kapehu U (MK)	0.39	2-98-0	4	5,443	0	0	2	0
Alakahi (MK)	0.55	1-99-0	7	4,016	1	1	1	1
Kalaoa (MK)	1.9	0-100-0	38	4,407	4	3	1	1
Hapahapai U (K)	2.3	0-100-0	0	2,056	0	0	2	0
Kaiwiki (MK)	3.3	0-99-0	20	4,388	1	0	1	1
Hālawa L (K)	3.4	28-72-0	44	2,075	0	0	1	0
Kapehu L (MK)	3.5	0-100-0	6	4,235	0	0	2	0
Wainaiā U (K)	3.5	12-88-0	0	2,266	0	0	3	0
Kapulena L (MK)	4.5	20-80-0	6	2,250	0	0	1	0
Ōpe'a (MK)	5.2	26-74-0	0	4,408	1	0	0	0
Waikama U (K)	5.9	32-68-0	5	2,774	0	0	4	0
Ka'ie'ie (MK)	6.2	19-79-2	192	6,317	1	0	1	1
Lā'ākea L (K)	6.9	31-69-0	368	2,494	0	0	1	0
Waikama L (K)	7.0	27-73-0	8	2,635	0	0	4	0
Pūkihae (MK)	7.8	25-75-0	58	5,270	3	3	1	1
Wainaiā L (K)	10.0	4-90-5	424	1,960	0	0	1	0
Waipunalau U (MK)	12	32-68-0	8	1,358	0	0	1	0
Waipunahoe U (MK)	25	0-100-0	50	1,436	0	0	1	0
Waipunahoe L (MK)	31	4-96-0	54	1,568	0	0	1	0
Mixed land use								
Kawaikālia U (MK)	0.91	51-49-0	0	2,196	0	0	1	0
'A'amakāō U (K)	2.9	38-62-0	3	2,420	0	0	2	0
Manowai'ōpae (MK)	4.3	38-62-1	191	4,195	1	0	0	0
Niuli'i L (K)	7.7	36-61-3	104	2,199	0	0	2	0
Pololū (K)	15	58-42-0	9	1,975	1	0	0	0
Ka'awali'i (MK)	37	54-46-0	25	3,086	1	0	0	0
Dominantly urban								
'Alenaio (ML)	5.3	0-30-70	4,159	4,099	1	1	0	0

Note: Volcanoes are coded as ML (Mauna Loa), MK (Mauna Kea), and K (Kohala). Sites sampled by the HDOH are denoted by "U" (upper) or "L" (lower). Zoning refers to the percentage of the watershed that is designated for conservation (Cons.), agricultural (Ag.), or urban (Urb.) uses. Population (number of persons) is from the 2000 census. "Basic" measurements consist of dissolved nutrients and physiochemical parameters, "Particulate" measurements consist of particulate nutrients and DOP, and "Other fluxes" include a wide variety of dissolved and particulate nutrients.

TABLE 2
Watersheds with Unusual Characteristics

Site	Comment
Wailoa-Waipū'o	Unlike the other watersheds in this study, the lower and middle reaches contain a meandering channel flowing through a well-developed, relatively flat alluvial valley. Streamflow is reduced by diversions in the headwaters. Both sampling sites are in the lower valley.
Pololū	The Pololū watershed is a smaller, less-developed version of Wailoa-Waipū'o. The site in the headwaters (Pololū U) is perennial. The stream was not flowing at the lower site (Pololū) at the time of sampling; the water sample was therefore collected from a pond behind the beach.
'Alenaio	Ephemeral stream. Sample site is in the channelized reach in the town of Hilo.
Waiākea	Ephemeral stream. Sample site is in the channelized reach in the town of Hilo.
Wailuku	The Wailuku River watershed is the largest in the state. The upper portion drains the upper slopes of Mauna Kea as well as (possibly noncontributing) barren lava flows on Mauna Loa. The sample site is above the town of Hilo.

formed using ESRI software (ArcGIS 9.0 and 9.2, ArcView 3.2).

Description of Watersheds

With basin-average rainfall exceeding 1,300 mm per year, all the watersheds examined in this study may be characterized as humid (Table 1). Variations in rainfall reflect elevation and orientation to the trade winds. Between sea level and the inversion level (approximately 2,000 m elevation), rainfall increases with elevation, but declines markedly above the inversion level. Rainfall along a given elevation contour is heaviest about 10 km north of Hilo and decreases northward from there until reaching Kohala Mountain. On Kohala, there

is a rainfall maximum between Waipū'o and Pololū valleys. At the locations sampled, all streams were perennial except for two that drain the young soils of Mauna Loa and the lower Pololū site, which is discussed in Table 2. Many streams are ephemeral in their headwaters. Only one watershed is urbanized, and the others are either lightly populated or unpopulated. Of the nonurbanized streams, half are dominated by agricultural land use designation, and the other half are dominated by conservation designation. Much of the land designated for agriculture is not currently being cultivated, however. In large part, this reflects the demise of sugarcane. Some agricultural lands are fallow and others are being used for grazing or diversified crops. Small areas have been converted to forest plantations. In a few areas, new low-density housing was built during the 2000s. Most of the land designated as conservation is forested, except at the highest elevations, where scrub or grasslands prevail.

Sample Collection

Samples were collected with an acid-cleaned depth-integrated sampler (Rickly Hydrologic). When conditions were safe for wading, multiple subsamples were obtained from across the cross section of the stream and pooled in a plastic bucket that was prerinced with stream water. For dissolved nutrients, subsamples taken from the bucket were filtered on-site using precombusted (500°C for 6 hr) GF/F (Whatman) filters. Filtered samples and unfiltered samples were placed on ice for transport to the laboratory and stored frozen until analysis. During higher-discharge events, unfiltered subsamples were also taken for TP. The pH (Orion 266 S) and specific conductivity (Hach Sension 156) of the sample in the bucket were measured at streamside.

Analytical Analyses

Stream water samples were analyzed for concentrations of NH_4^+ (USGS method 2525-89; detection limit [d.l.] $1 \mu\text{mol liter}^{-1}$) (hereinafter referred to as ammonium), $\text{NO}_3^- + \text{NO}_2^-$

(U.S. Environmental Protection Agency [USEPA] method 353.2; d.l. $0.1 \mu\text{mol liter}^{-1}$) (hereinafter referred to as nitrate), PO_4^{3-} (USEPA method 365.1; d.l. $0.1 \mu\text{mol liter}^{-1}$) (hereinafter referred to as orthophosphate and equivalent to soluble reactive phosphorus), TDP (USGS I-4650-03; d.l. $0.1 \mu\text{mol liter}^{-1}$), and TP (unfiltered sample; USGS I-4650-03; d.l. $0.1 \mu\text{mol liter}^{-1}$) and were measured using a Technicon Autoanalyzer II. TDN was analyzed by high-temperature combustion, followed by chemiluminescent detection of nitric oxide (Shimadzu TOC-V, TNM-1; method ASTM D5176; d.l. $1 \mu\text{mol liter}^{-1}$). Percentage recoveries for all analyte check standards were between $93\% \pm 5\%$ (average \pm SD) and $115\% \pm 25\%$. DON was calculated from the difference between TDN and DIN ($\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$). DOP was calculated from the difference between the TDP and PO_4^{3-} concentrations. PP was calculated as the difference among TP, DOP, and PO_4^{3-} . DOC was measured by high-temperature combustion (Shimadzu TOC-V, TNM-1; method USEPA 415.1; d.l. $10 \mu\text{mol liter}^{-1}$) following the recommendations of Sharp et al. (2002). TSS were measured by filtering a known volume of water onto a preweighed, precombusted GF/F filter (Whatman), which was then dried to a constant mass (70°C) and reweighed (APHA et al. 1995). The dried TSS filter was then subsequently analyzed for PC and PN on a CHN analyzer (Costech Analytical Technologies). TN was calculated from the sum of TDN and PN. TOC was calculated as the sum of DOC and PC. All samples were analyzed at the University of Hawai'i at Hilo Analytical Laboratory.

Discharge, Flux, and Yield Calculations

When conditions were safe for wading, stream discharge was measured with a pygmy current meter (AA Price) and a top-setting wading rod. A cross section oriented perpendicular to the flow was divided into approximately 10 subsections; water velocity and depth were measured at the center of each subsection. Discharge through each subsection was computed as the product of water velocity, the width of the subsection, and average water

depth. Average water depth within the subsection was calculated using the assumption that water depth varied linearly between measurement points. Unit discharge, which has the same units as rainfall rate, was calculated as stream discharge (volume time^{-1}) divided by watershed area. Instantaneous nutrient and sediment fluxes (amount time^{-1}) were calculated as the product of stream discharge and nutrient (or sediment) concentration. Yields were calculated as fluxes divided by the drainage area of the watershed.

Statistical Analyses

Stepwise multiple linear regressions (Sigma-Stat 3.5) were used to evaluate whether watershed characteristics predicted water quality conditions at the watershed outlet (sample site) (Draper and Smith 1981). Three data sets were analyzed using regression analysis, as follows: (1) The main water quality data set comprised water quality data from 24 streams (dependent variables) and the watershed characteristics of those streams (independent variables). The water quality variables included physiochemical parameters, dissolved inorganic nutrients, DON, and DOC. (2) The particulate data set comprised particulate nutrient and DOP data from 11 streams (dependent variables) and the watershed characteristics of those streams (independent variables). DOP was included in this analysis because it was only assayed during high-flow conditions when particulates were quantified too. (3) The flux data set comprised nitrate concentrations, nitrate fluxes, nitrate yields, and stream discharge (dependent variables) at 37 sites on 30 streams. Watershed characteristics were the independent variables.

At some sites, data were collected on multiple days; repeat measurements at a given site were averaged together before analysis. Concentrations less than detection were averaged using one-half the detection limit. If all measurements at a given site were below detection, the numerical value was set to one-half the detection limit. (These averaging procedures were used for all the statistical analyses and for reporting data in the tables.) Regression analysis requires that variables be nor-

mally distributed and orthogonal (not redundant or correlated). TN, TDN, TP, and TC were therefore not included in the analysis because they are equal to the sum of their constituent parameters. Also, watershed area was not used as an independent variable when predicting yield, which is equal to flux divided by watershed area. All water quality variables and watershed characteristics were examined for normality and transformed, if indicated, by taking the square root or natural logarithm. Parameters were then Z transformed to zero mean and unit variance so that all regression coefficients were at the same scale. Selection of the normality transformation and execution of the two transforms was conducted separately for each data set subjected to regression analysis. Watershed characteristics can be both intrinsic and extrinsic, and there is considerable correlation among all possible watershed characteristic variables. The number of variables was therefore reduced to a few that best represented the data set with the least amount of cross-correlations. These were watershed area, percentage zoned in agriculture, rainfall, and population density.

Water quality differences between the three volcanoes were evaluated using untransformed (not normalized) data and the Mann-Whitney *U* Test (SigmaStat 3.5). Mauna Loa streams were not included in the comparison because of a very small sample size ($n = 4$). Principal components analysis (PCA) (Jolliffe 2002) was used to synthesize our complex data so that we could detect sites with anomalous water chemistry or identify groups of watersheds with similar concentrations of nutrients. PCA was chosen for this task because it: (1) has been widely used to look for patterns in complex environmental data sets (Petersen et al. 2001, Bengraine and Marhaba 2003, Primpas et al. 2010), (2) provides information on internal structure of the data, and (3) makes no assumptions regarding probability distribution. We did not use a nonlinear ordination method because a methods comparison study showed that a nonlinear model produced only a slight improvement in the variance explained (Lischeid and Bittersohl 2008).

PCA uses eigenvector decomposition to remap a large number of potentially correlated variables into less-correlated summary variables, the most important of which are the first (PC1) and second (PC2) factors. Each factor is a weighted average of the original variables, and the weights reveal the relative contribution of each of the original variables. Commonly PC1 and PC2 reflect two distinct groups of influential variables (see Primpas et al. [2010] for an example). Calculations (Matlab software version 7.0) were performed on the data set consisting of physiochemical parameters and dissolved nutrients ($n = 24$). The redundant variable TDN, which is the sum of DON, nitrate, and ammonium, was not included.

RESULTS

Characterization of Water Quality

Stream waters had low specific conductivities ($66.1 \mu\text{S cm}^{-1} \pm 33.2$), were slightly alkaline (7.5 ± 0.4), and had low TSS concentrations ($2.5 \pm 2.9 \text{ mg liter}^{-1}$) (mean \pm SD) (Table 3). Concentrations of orthophosphate, DOP, and ammonium were quite low; many samples had concentrations $<0.1 \mu\text{mol liter}^{-1}$, $<0.1 \mu\text{mol liter}^{-1}$, and $<1 \mu\text{mol liter}^{-1}$, respectively (Table 4). Moderate concentrations of nitrate ($2.81 \pm 4.20 \mu\text{mol liter}^{-1}$), DON ($3.22 \pm 3.22 \mu\text{mol liter}^{-1}$), and DOC ($136.3 \pm 105.5 \mu\text{mol liter}^{-1}$) were observed. Averaged (\pm SD) across the streams and conditions in the study, the TN pool was dominated by PN ($45\% \pm 9.0\%$) ($n = 11$) (Table 5 and Figure 3). The TDN pool was dominated by DON ($54\% \pm 30.0\%$) and nitrate ($34\% \pm 32.0\%$) ($n = 24$). Like TN, TP was dominated by particulate forms, with PP comprising $73\% \pm 26\%$ of the phosphorus pool. In contrast, the majority of organic carbon in the streams was DOC ($72\% \pm 10\%$), with PC contributing $28\% (\pm 10\%)$.

Geographic Variability

Interwatershed comparisons were investigated using principal component variables PC1 and PC2, both of which succinctly summarize the dissolved nutrient and physiochemical data.

TABLE 3
Mean (\pm SD) Physiochemical Parameters in Selected Streams on Hawai'i Island

Stream	pH	Specific Conductivity (μ S cm ⁻¹)	TSS (mg liter ⁻¹)
Dominantly conservation (all Mauna Kea)			
'Akaka Falls trib.	7.34 \pm 0.25	79.2 \pm 5.9	0.90 \pm 0.58
Mā'ili	7.10	29.3	1.35
Ainako	7.08 \pm 0.26	36.6 \pm 7.5	4.97 \pm 2.65
Kama'e'e	7.37 \pm 0.47	43.1 \pm 21.6	2.94 \pm 1.97
Pahe'ehe'e	7.79	84.1	0.24
Kaiwilahilahi	7.65	88.9	0.07
Kawainui	7.89	58.9	0.50
Hakalau	7.03 \pm 0.35	27.3 \pm 10.0	8.84 \pm 8.07
Honoli'i L.	7.28	43.2	1.60
Ka'awali'i (half Ag)	7.75	83.8	0.04
Kolekole L.	7.06 \pm 0.14	25.5 \pm 11.9	3.29 \pm 0.98
Umauma, SF	6.73 \pm 0.70	25.2 \pm 15.9	1.00 \pm 0.48
Dominantly agricultural (all Mauna Kea)			
Alakahi	7.67	93.2	1.23
Kalaoa	7.33 \pm 0.44	80.4 \pm 8.7	1.27 \pm 1.17
Kaiwiki	7.97	111.6	0.10
Manowai'ōpae	8.01	120.1	0.67
Ōpe'a	7.85	122.1	0.69
Ka'ie'ie	7.79	86.5	0.13
Pūkihae	7.45 \pm 0.37	67.0 \pm 22.3	4.56 \pm 4.71
Unusual streams ^a			
'Alenaio (U, ML, E)	7.24	33.4	4.40
Pololū (K, P)	7.79	31.2	6.76
Waiākea (ML, E)	7.08 \pm 0.05	42.1 \pm 13.4	10.83 \pm 2.73
Wailoa-Waipi'o U (K)	8.25	123.9	0.83
Wailuku (L, ML + MK)	7.03	50.8	2.36
Average across all streams (\pm SD)	7.5 \pm 0.4	66.1 \pm 33.2	2.5 \pm 2.9

Note: Watersheds are listed from small to large within a group. Sampling was conducted during February, March, April, and July of 2005.

^a K, Kohala; MK, Mauna Kea; ML, Mauna Loa; L, large; U, urban; P, pond sample; E, ephemeral.

PC1 and PC2 explained 54% and 18%, respectively, of the variability in the data set. PC2 is (mostly) a weighted average of inorganic nutrient and sediment concentrations; samples with elevated concentrations of those parameters have large positive values of PC2. PC1 is (mostly) a weighted average of dissolved organic nutrients, pH, and specific conductivity; samples with elevated concentrations of dissolved organic nutrients but low pH and low specific conductivity have large positive values of PC1. A plot of PC1 versus PC2 (Figure 4) reveals two sites with anomalous water chemistry: Pololū, which has very high levels of organic nutrients, and Wailoa-Waipi'o, which has low levels of organic nutrients. The unusual water quality in Pololū is

not surprising because the stream was not flowing freely at the time of sampling, and the sample was taken from a pond behind the beach berm. Compared with the other watersheds in Figure 4, Wailoa-Waipi'o is unusual by virtue of its size (fourth largest), soils (the only watershed besides Pololū on Kohala Volcano), physiography (broad floodplain and dissected uplands), and land use (active agriculture immediately upstream of the sampling site). There are several interesting geographical associations revealed in Figure 4. All four streams on Mauna Loa have similar water quality in spite of disparities in size and the fact that two are perennial and two are ephemeral. If Pololū is excluded, PC1 tends to decrease toward the north, although not

TABLE 4
Mean (±SD) Dissolved Nutrient Concentrations in Selected Streams on Hawai'i Island

Stream	NO ₃ ⁻ + NO ₂ ⁻	NH ₄ ⁺	DON	TDN	PO ₄ ³⁻	DOP	DOC
μmol liter ⁻¹							
Dominantly conservation (All Mauna Kea except Ainako)							
'Akaka Falls trib.	0.41 ± 0.47	all <1.0	2.85 ± 1.66	3.76 ± 1.31	all <0.1	0.03 ± 0.04	69.35 ± 22.36
Mā'ili	1.03	<1.0	1.16	2.69	<0.1	—	43.15
Ainako	2.52 ± 1.75	0.98 ± 0.84	6.39 ± 8.45	9.98 ± 7.24	all <0.1	0.0 ± 0.0	148.41 ± 54.38
Kama'e'e	0.09 ± 0.08	all <1.0	2.99 ± 0.67	3.59 ± 0.65	all <0.1	0.0 ± 0.0	158.87 ± 56.04
Pahe'ehe'e	<0.1	<1.0	1.10	1.65	<0.1	—	63.87
Kaiwilahilahi	0.89	<1.0	2.51	3.90	<0.1	—	73.58
Kawainui	<0.1	<1.0	3.21	3.76	<0.1	—	118.60
Hakalau	0.22 ± 0.20	all <1.0	6.17 ± 3.09	6.92 ± 3.14	all <0.1	0.0 ± 0.0	291.97 ± 58.46
Honoli'i L	0.31	<1.0	3.90	4.71	<0.1	—	216.20
Ka'awali'i (half Ag)	3.36	<1.0	1.09	4.95	<0.1	—	42.10
Kolekole L	0.34 ± 0.18	all <1.0	5.15 ± 0.06	5.49 ± 0.13	all <0.1	0.0 ± 0.0	300.90 ± 86.38
Umauma South Fork	0.09 ± 0.13	all <1.0	4.94 ± 1.50	5.56 ± 1.41	all <0.1	0.0	293.50 ± 109.60
Dominantly agricultural (all Mauna Kea)							
Alakahi	1.23	<1.0	2.22	3.95	<0.1	0.0	71.3
Kalaoa	4.43 ± 4.18	all <1.0	0.90 ± 1.30	5.81 ± 3.52	all <0.1	0.02 ± 0.03	58.57 ± 13.16
Kaiwiki	9.96	<1.0	0.47	10.93	<0.1	—	48.88
Manowai'ōpae	5.63	<1.0	0.23	6.36	0.37	—	26.37
Ōpe'a	4.06	<1.0	1.32	5.88	0.12	—	18.65
Ka'ie'ie	0.35	<1.0	2.37	3.22	<0.1	—	62.62
Pūkīhae	1.24 ± 1.02	all <1.0	2.29 ± 0.70	4.03 ± 1.30	all <0.1	0.0 ± 0.0	88.83 ± 17.63
Unusual streams ^d							
'Alenaio (U, ML, E)	2.71	<1.0	5.19	8.40	<0.1	0.0	196.10
Pololū (K, P)	0.27	1.11	15.75	17.13	0.11	—	401.90
Waiākea (ML, E)	7.36 ± 6.53	all <1.0	2.77 ± 2.18	10.62 ± 4.34	all <0.1	0.0	172.25 ± 13.36
Wailoa-Waipi'o (U, K)	18.35	<1.0	0.0	16.47	0.95	—	69.01
Wailuku (L, ML + MK)	2.38	1.30	2.78	6.46	<0.1	0.0	235.20
Average across all streams	2.81 ± 4.20	—	3.22 ± 3.22	6.51 ± 3.98	—	0.04 ± 0.10	136.3 ± 105.5

Note: — indicates no measurement. Watersheds are listed from small to large within a group. Sampling was conducted during February, March, April, and July of 2005.

^d U, urban; K, Kohala; MK, Mauna Kea; ML, Mauna Loa; L, large; P, pond sample; E, ephemeral.

consistently. Three large watersheds ~15 km north of Hilo have similar water quality, as do the three smallest Mauna Kea watersheds.

In summary, although there is considerable scatter, there are observable geographic trends in summary variables. These trends are associated with the particular volcanoes, latitude/proximity, and watershed size. It is possible that these patterns are an artifact re-

sulting from the tendency to sample adjacent streams on the same day. A PCA plot organized by sampling day (not shown) did not support this hypothesis, however.

Flux and Yield Data

Measured nutrient and sediment fluxes are reported as yields (fluxes per unit area of water-

TABLE 5
Mean (\pm SD) Particulate and Total Nutrient Concentrations in Selected Streams on Hawai'i Island

Stream	TN ($\mu\text{mol liter}^{-1}$)	TP ($\mu\text{mol liter}^{-1}$)	PN ($\mu\text{mol liter}^{-1}$)	PP ($\mu\text{mol liter}^{-1}$)	PC ($\mu\text{mol liter}^{-1}$)	TOC ($\mu\text{mol liter}^{-1}$)
Dominantly conservation (forested) (all Mauna Kea)						
'Akaka Falls trib.	5.30 \pm 1.74	0.07 \pm 0.03	1.43 \pm 0.09	0.00 \pm 0.00	14.17 \pm 2.65	70.6 \pm 4.9
Ainako	17.32 \pm 10.90	0.19 \pm 0.12	7.43 \pm 4.02	0.14 \pm 0.12	111.09 \pm 61.14	259.5 \pm 115.0
Kama'e'e	8.99 \pm 0.77	0.17 \pm 0.17	5.13 \pm 1.41	0.12 \pm 0.17	71.89 \pm 19.85	259.3 \pm 57.0
Hakalau	23.46 \pm 11.90	0.48 \pm 0.41	15.96 \pm 16.10	0.48 \pm 0.41	94.76 \pm 35.18	417.4 \pm 69.6
Kolekole L	11.74 \pm 2.19	0.21 \pm 0.21	6.25 \pm 2.21	0.16 \pm 0.21	75.49 \pm 14.16	376.4 \pm 99.5
Umauma, SF	8.33	<0.1	3.77	0.00	46.20	417.2
Dominantly agricultural (all Mauna Kea)						
Alakahi	—	0.21	—	0.16	—	—
Kalaoa	9.07 \pm 5.25	0.18 \pm 0.18	2.80 \pm 1.20	0.11 \pm 0.16	30.12 \pm 11.65	89.0 \pm 23.3
Pūkihae	8.33 \pm 4.13	0.23 \pm 0.16	4.30 \pm 2.91	0.18 \pm 0.16	61.75 \pm 51.85	150.6 \pm 68.2
Unusual streams ^a						
'Alenaio (U, ML, E)	14.94	0.44	6.54	0.39	87.13	283.2
Waiākea (C, ML, E)	18.56 \pm 5.09	0.87	7.94 \pm 0.75	0.82	103.7 \pm 6.5	276.0 \pm 6.9
Wailuku (L, C, ML + MK)	10.41	<0.1	3.95	0.00	56.3	291.5
Average across all streams	12.40 \pm 5.49	0.26 \pm 0.23	5.95 \pm 3.86	0.21 \pm 0.24	68.42 \pm 30.44	262.8 \pm 113.5

Note: Streams are listed from small to large within a group. — indicates no measurement. Sampling was conducted during February, March, April, and July of 2005.

^a U, dominantly urban; C, dominantly conservation; ML, Mauna Loa; MK, Mauna Kea; L, large; E, ephemeral.

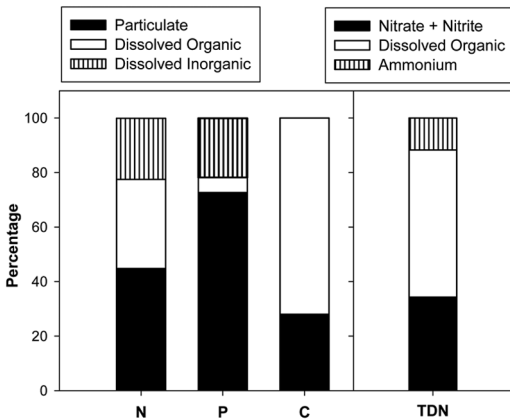


FIGURE 3. Relative proportions of dissolved, particulate, organic, and inorganic nutrients in selected streams on Hawai'i Island. Values are averages across 24 (TDN), 11 (N, C), or nine (P, two additional streams had no detectable P) streams.

shed) to facilitate interwatershed comparisons (Tables 6 and 7). DON, DOC, and TSS yields varied as much as two to three orders of magnitude among different streams. Particulate and total fluxes were measured at only a few sites, so there is little information on how they varied among streams. Nitrate yields, which were measured at 37 sites, averaged 7.1 (\pm 11.1) moles N day⁻¹ km⁻² and varied two and a half orders of magnitude among different streams. Nitrate concentrations, nitrate yields, and unit discharges were 2.1, 3.5, and 2.3 times higher, respectively, for Kohala watersheds than for Mauna Kea watersheds (Table 8). The median values of these nitrate variables were greater for Kohala streams than for the Mauna Kea streams ($P = .02$ [concentration], $P = <.001$ [yield], and $P = .02$ [unit discharge]). Also, the median nitrate concentration in Mauna

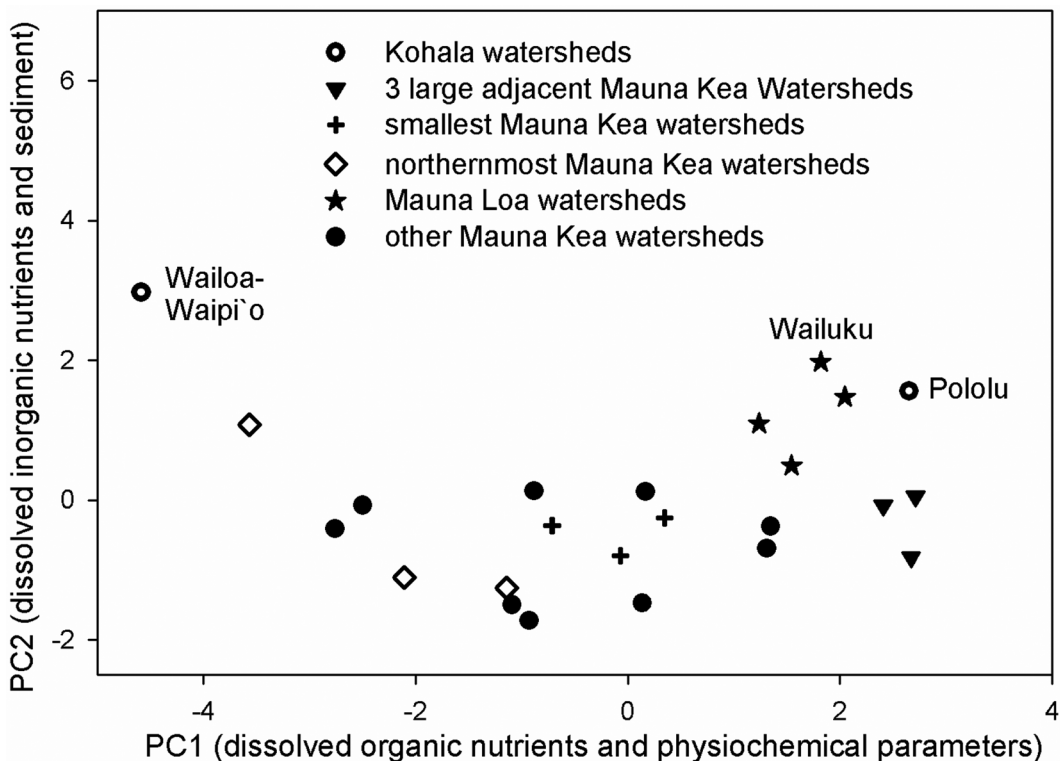


FIGURE 4. Principal components derived from measurements of dissolved nutrients and physiochemical parameters in selected Hawai'i Island streams. Watersheds that plot close together on the graph have similar water quality.

Loa streams was greater than the median in Mauna Kea streams ($P = .04$). There was no significant difference between Mauna Loa and Kohala median nitrate concentrations.

Do Watershed Characteristics Predict Water Quality?

A stepwise multiple linear regression model was used to evaluate whether population density, agricultural land use designation, average annual basin-average rainfall, or watershed area predicted observed stream water quality (Table 9). Because the Mauna Loa and Kohala streams differ in many respects from the Mauna Kea streams, some regressions were conducted using only the relatively homogeneous Mauna Kea streams. For Mauna Kea

streams, pH and concentrations of TSS, ammonium, orthophosphate, DOP, PP, PN, and PC were not predicted by watershed characteristics. For those watersheds, specific conductivity tended to increase with increasing percentage of agriculture ($r^2 = 0.33$), and nitrate concentrations tended to increase with increasing population density ($r^2 = 0.37$). Both DOC and DON increased with increasing watershed area ($r^2 = 0.29$ and 0.24 , respectively). When watersheds from all three volcanoes were analyzed together, similar results were obtained for specific conductivity and DOC, but DON did not vary with area, and ammonium tended to become more dilute with increasing rainfall.

Because Kohala streams have higher nitrate concentrations and yields than Mauna Kea streams (Table 8), flux and yield analyses were conducted separately for each volcano.

TABLE 6
Instantaneous Nutrient and Sediment Yields in Selected Streams on Hawai'i Island

Stream	Unit Discharge (mm day ⁻¹)	(moles day ⁻¹ km ⁻²)							TSS (kg km ⁻² day ⁻¹)	
		DON	PN	PP	DOC	PC	TN	TP		
Dominantly conservation (forested) (All Mauna Kea)										
'Akaka Falls trib.	12.9	38.5	—	0.90	1,223.	—	—	—	<1.29	20.
Kama'e'e	2.6	6.4	—	—	263.	—	—	—	—	1.8
Pāhe'ehe'e	0.71	0.80	—	—	46.	—	—	—	—	0.17
Kauihilahi	0.03	0.10	—	—	2.	—	—	—	—	0.002
Kawainui	0.63	2.0	—	—	75.	—	—	—	—	0.31
Kolekole L	4.5	20.6	22	0.54	978.	300.	47	—	0.54	12.
Umauma, S. Fork	0.12	0.70	—	—	26.	—	—	—	—	0.08
Dominantly agriculture (all Mauna Kea)										
Alakahi	2.2	4.9	—	0.46	157.	—	—	—	0.46	2.7
Kalaoa	4.7	13.9	—	—	269.	—	—	—	—	0.42
Kauiwiki	4.0	1.9	—	—	196.	—	—	—	—	0.40
Ka'ie'ie	1.7	4.1	—	—	108.	—	—	—	—	0.22
Pūkihae	4.4	6.6	7.8	0.00	362.	93.	23	—	<0.44	3.4
Kohala (dominantly conservation)										
Wailoa-Waip'o U	1.1	0.0	—	—	74.	—	—	—	—	0.89
Average across streams ± SD	3.0 ± 3.4	7.7 ± 11.0	14.8 ± 10.0	0.48 ± 0.37	291 ± 378	196 ± 146	35. ± 17.	—	—	3.3 ± 6.0
Average as kg yr ⁻¹ km ⁻²		47.1 as N	75.7 as N	5.4 as P	1,270 as C	860 as C	180 as N			1,170

Note: See Table 7 for nitrate values. Watersheds are listed from small to large within a group. — indicates no measurement. All measured concentrations for ammonium and orthophosphate were below detection. Sampling was conducted during February and March 2005.

TABLE 7
Instantaneous Yields of $\text{NO}_3^- + \text{NO}_2^-$ in Selected Streams on Hawai'i Island

Site	$\text{NO}_3^- + \text{NO}_2^-$ Concentration ($\mu\text{mol liter}^{-1}$)	Unit Discharge (mm day^{-1})	$\text{NO}_3^- + \text{NO}_2^-$ Yield ($\text{moles day}^{-1} \text{ km}^{-2}$)
Mauna Kea watersheds (dominantly agriculture)			
Kapehu U	1.95 ± 2.42	3.0 ± 0.4	6.4 ± 8.1
Alakahi	1.23	2.2	2.7
Kalaoa	1.09	4.7	5.1
Kaiwiki	9.96	4.0	40
Kapehu L	3.35 ± 4.15	2.6 ± 0.5	9.8 ± 12.6
Kapulena L	0.29	0.25	0.072
Ka'ie'ie	0.35	1.7	0.60
Pūkīhae	1.42	4.4	6.2
Waipunalau U	2.35	0.03	0.070
Waipunahoe U	0.43	0.05	0.023
Waipunahoe L	0.41	0.27	0.11
Mauna Kea watersheds (dominantly conservation)			
'Akaka Falls trib.	<0.1	13	<1.3
Kawaikālia U	0.26	4.0	1.0
Kama'e'e	<0.1	2.6	<0.26
Pahe'ehe'e	<0.1	0.71	<0.071
Kaiwilahilahi	0.89	0.03	0.023
Kawainui	<0.1	0.63	<0.062
Honoli'i U	0.93 ± 0.89	0.95 ± 0.20	0.79 ± 0.66
Honoli'i L ^a	1.59 ± 1.68	1.5 ± 0.3	2.1 ± 2.0
Kolekole U	1.67 ± 2.65	1.5 ± 2.1	1.3 ± 1.4
Kolekole L ^a	0.76 ± 0.70	2.4 ± 2.1	1.5 ± 1.5
Umauma, S. Fork	<0.1	0.12	<0.012
Kohala watersheds (dominantly agriculture)			
Halelua U	0.33	14	4.5
Hapahapai U	1.50 ± 1.22	1.2 ± 0.2	1.7 ± 1.3
'A'amakāō U	6.04 ± 6.97	1.9 ± 0.0	11 ± 13
Hālawa L	3.02	0.63	1.9
Wainaia U	6.05 ± 4.61	1.7 ± 1.2	13 ± 16
Waikama U	2.65 ± 3.55	1.6 ± 1.5	3.3 ± 3.5
Lālākea L	1.01	6.3	6.4
Waikama L	2.97 ± 3.96	3.3 ± 2.5	6.8 ± 6.6
Niuli'i L	5.86 ± 5.93	3.4 ± 2.2	13 ± 7
Wainaia L	9.88	5.2	51
Kohala watersheds (dominantly conservation)			
Pololū U	1.89 ± 1.58	3.5 ± 0.5	7.1 ± 6.6
Hālawa U	2.17 ± 1.97	2.3 ± 1.1	6.0 ± 6.9
Niuli'i U	4.08 ± 3.40	7.0 ± 4.4	$21. \pm 6$
Wailoa-Waipi'o U ^a	9.90 ± 11.96	10 ± 13	$24. \pm 6$
Wailoa-Waipi'o L	0.82	18	15

Note: Sites with multiple measurements are reported as means \pm SD. Measurements at HDOH sites (denoted "U" or "L") were taken between January 2001 and August 2002. The remaining sites (this study) were sampled in February through March 2005. Watersheds are listed from small to large within a group.

^a Measurements taken by both HDOH (2001–2002) and this study (2005).

For Kohala watersheds, nitrate fluxes increased with increasing contributing area, which explained 83% of the variance in the fluxes (Table 9). Flux is the product of discharge and concentration, so it is instruc-

tive to examine discharge and concentration separately. In Kohala discharge, but not concentration, increased with increasing area ($r^2 = 0.78$). Neither nitrate concentration nor nitrate yields were predicted by Kohala

TABLE 8
Summary of Nitrate Yields in Selected Hawai'i Island Streams

Parameter	Kohala Streams	Mauna Kea Streams	Mauna Loa Streams
NO ₃ ⁻ + NO ₂ ⁻ concentration (μmol liter ⁻¹)	3.65 ± 3.09	1.72 ± 2.24	3.74 ± 2.42
NO ₃ ⁻ + NO ₂ ⁻ yield (moles day ⁻¹ km ⁻²)	12.40 ± 12.55	3.57 ± 8.56	—
(kg yr ⁻¹ km ⁻² as N)	64.2 ± 63.5	18.3 ± 43.8	—
Unit discharge (mm day ⁻¹)	5.34 ± 5.08	2.30 ± 2.83	—
Watershed area km ²	10.6 ± 17.9 (<i>n</i> = 15)	17.2 ± 20.0 (<i>n</i> = 22)	166 ± 274
	10.9 ± 17.4 (<i>n</i> = 16)	17.0 ± 18.8 (<i>n</i> = 27)	
<i>n</i>	16 (concentration)	27 (concentration)	4 (concentration)
	15 (yield, discharge)	22 (yield, discharge)	

Note: All yield and discharge values are from instantaneous measurements and are calculated as averages (±SD) across streams. Concentration averages include all available measurements, including days when discharge (and thus yield) was not measured.

TABLE 9
Predictions of Water Quality in Selected Hawai'i Island Streams Using a Stepwise Multiple Linear Regression Model

Predicted Variable	Predictive Variable(s)	Regression Coefficient (Standard Error)	<i>r</i> ²	<i>P</i>	<i>n</i>
All watersheds					
Specific conductivity ^a	% agriculture ^a	0.41 (0.20)	0.16	0.05	24
[DOC] ^b	Watershed area ^b	0.51 (0.18)	0.26	0.01	24
[NH ₄ ⁺] ^b	Rain	-0.43 (0.19)	0.19	0.04	24
[NO ₃ ⁻ + NO ₂ ⁻] ^a	Population density ^b	0.32 (0.14)	0.10	0.03	47
Not predicted at 95% level: pH, [TSS], [DON], [PO ₄ ³⁻], [DOP], [PP], [PN], [PC]					
Mauna Kea watersheds sampled for diverse water quality parameters					
Specific conductivity	% agriculture ^a	0.58 (0.20)	0.33	0.01	18
[DON] ^a	Watershed area ^b	0.49 (0.21)	0.24	0.04	18
[DOC] ^b	Watershed area ^b	0.54 (0.21)	0.29	0.02	18
Not predicted at 95% level: pH, [TSS], [NH ₄ ⁺], [PO ₄ ³⁻], [DOP], [PP], [PN], [PC] (see below for nitrate)					
Mauna Kea watersheds with nitrate flux					
Nitrate conc. ^b	Population density ^b	0.61 (0.18)	0.37	<0.01	22
Discharge ^b	Watershed area ^b	0.61 (0.16)	0.54	<0.01	22
	Rain ^b	0.64 (0.16)		<0.01	
Nitrate flux ^b	Population density ^b	0.47 (0.20)	0.22	0.03	22
Nitrate yield ^b	% agriculture	0.51 (0.16)	0.47	<0.01	22
	Rain ^b	0.54 (0.16)		<0.01	22
Kohala watersheds with nitrate flux data					
Nitrate flux ^b	Watershed area ^b	0.91 (0.11)	0.83	<0.001	15
Discharge ^b	Watershed area ^b	0.88 (0.13)	0.78	<0.001	15
Not predicted at 95% level: nitrate concentration and nitrate yield					

Note: Variables have been rescaled to zero mean and unit variance so that all regression coefficients are at the same scale.

^a Square root transformation.

^b Natural logarithm transformation.

watershed characteristics. For the Mauna Kea watersheds, nitrate fluxes increased with increasing population density, but only 22% of the variability was explained by that parameter. Nitrate concentrations increased with increasing population density ($r^2 = 0.37$); dis-

charge increased with increasing area and rainfall ($r^2 = 0.54$). Nitrate yields for the Mauna Kea watersheds increased with increasing percentage agriculture and with increasing rainfall; together these two variables explain 47% of the variation in the yields.

Additional regressions were run to evaluate the possibility that Mauna Kea's lower nitrate concentrations are due to lower anthropogenic pressures. When data from all three volcanoes were analyzed together, nitrate concentrations increased with increasing population density, but the r^2 was very low (0.10). When a volcano index was added as an independent variable (with a value of 0 for Mauna Kea and a value of 1 for Mauna Loa and Kohala), r^2 increased to 0.24, with population density (coefficient 0.27 ± 0.13 , $P = .05$) accounting for 7% of the variability in concentrations and volcano (coefficient 0.379 ± 0.26 , $P < .01$) accounting for 17% of the variability. These results suggest that although population trends are partly responsible for Mauna Kea's relatively low nitrate concentrations, other factors, probably soils, are more important.

In summary, the regression analyses indicated that more intense anthropogenic pressures were associated with higher concentrations of some nitrogen species and also with higher specific conductivity (reflecting higher total dissolved ions). Also, concentrations of organic nutrients tended to increase with increasing watershed area. For Mauna Kea watersheds, nitrate yields and fluxes tended to increase with increasing anthropogenic influence, but a similar relationship was not apparent in Kohala watersheds. Indeed, most water quality parameters were not predicted by watershed characteristics. Moreover, even the statistically significant relationships were weak; on average only one-third of the variability in predicted variables was explained by watershed characteristics. As is discussed in the next section, limitations of the watershed characteristics data, particularly for land use, could be partly responsible for the low r^2 values.

DISCUSSION

Although the data from this study provide important preliminary baseline information, the spatial and especially temporal density of samples was too sparse to provide a truly comprehensive and statistically robust picture. Moreover, noise was introduced into the data by the fact that not all the samples were cross-

TABLE 10

Water Quality Standards for Streams Applicable during the Wet Season from 1 November to 30 April (Hawai'i Administrative Rules, Chapter 11-54, 2004)

Parameter	Geometric Mean Shall Not Exceed	No More Than 10% Values Shall Exceed
TN	17.8 $\mu\text{mol liter}^{-1}$	37.1 $\mu\text{mol liter}^{-1}$
$\text{NO}_3^- + \text{NO}_2^-$	5.0 $\mu\text{mol liter}^{-1}$	12.8 $\mu\text{mol liter}^{-1}$
TP	1.6 $\mu\text{mol liter}^{-1}$	3.2 $\mu\text{mol liter}^{-1}$
TSS	20 mg liter^{-1}	50 mg liter^{-1}
pH	Shall not deviate more than 0.5 units from ambient conditions. Shall not be lower than 4.5 nor higher than 8.0	

sectionally integrated (composites of subsamples taken at different distances across the stream), and at least one stream was affected by diversions. These caveats notwithstanding, it is still informative to evaluate how observed nutrient concentrations and yields compare with water quality standards and with values elsewhere.

It is surprising that two of 24 streams sampled in this study were more alkaline ($\text{pH} > 8$) than is allowable under Hawai'i's regulatory water quality standards (Table 10). To determine if a stream station's nutrient and sediment concentrations meet Hawai'i's regulatory standards, the geometric mean of at least six repeat measurements is compared with the "regulatory benchmark" (the value in the second column of Table 10). Our data set does not have enough repeat measurements to evaluate regulatory compliance, but it is still possible to compare measurements with the regulatory benchmarks. In all 12 streams in which TP was measured, concentrations were below the regulatory benchmark. Seven of the 34 streams had nitrate concentrations that were high enough (geometric mean $> 5 \mu\text{mol liter}^{-1}$ at one or more stations) to raise the question of whether or not nitrate standards were met. Further, two of 11 streams sampled for TN had concentrations that were sufficiently high (geometric mean $> 17.8 \mu\text{mol liter}^{-1}$) to raise the question of whether or not TN standards were met. For all 24 streams sampled, TSS concentrations were below the

regulatory benchmark. This is notable because TSS is generally considered to be closely associated with turbidity, and high turbidity is the most common reason that Hawaiian streams exceed regulatory standards (State of Hawai'i 2006). Our results are similar to those obtained by Young and Godzszak (2008), who for 6 months conducted monthly monitoring of streams and springs in the Hilo area and found that ammonium, TP, TSS, and turbidity were within regulatory limits but that nitrate and TN were above regulatory limits in three springs.

The average nitrate concentration measured in this study ($2.8 \mu\text{mol liter}^{-1}$ including HDOH sites) is at least an order of magnitude greater than that found in unpolluted tropical rivers (global range of 0.07 to $0.21 \mu\text{mol N liter}^{-1}$) (Meybeck 1982). On the other hand, the East Hawai'i values are two orders of magnitude lower than what is found in heavily polluted regions such as Brittany, France, where 80% of rivers exceed the drinking water standard of $800 \mu\text{mol liter}^{-1}$ (Molenat and Gascuel-Oudoux 2002), the lower Mississippi River, where average nitrate concentrations were about $100 \mu\text{mol liter}^{-1}$ in the 1990s (Goolsby et al. 2000), or certain reaches of Waimānalo stream on O'ahu, where base-flow concentrations of $\sim 500 \mu\text{mol liter}^{-1}$ may reflect contamination from agricultural manures (Laws and Ferentinos 2003).

Comprehensive measurements on O'ahu Island streams were made in 1999–2001 as part of the USGS National Water Quality Assessment Program (Anthony et al. 2004). Nitrate, orthophosphate, and TP concentrations from our study are lower than those found in O'ahu urban streams and are roughly an order of magnitude lower than those found in O'ahu mixed-use streams. This is consistent with the lower intensity of land use in the lightly populated watersheds of East Hawai'i. The USGS study also found very high concentrations of pesticides in streambed sediment of some O'ahu streams with urbanized or mixed (but not forested) land uses (Anthony et al. 2004). In that study, streambed sediment exhibited elevated concentrations of heavy metals and arsenic in urban and agricultural watersheds, respectively. Field data and land

use history suggest that it is likely that a number of East Hawai'i streams also suffer from arsenic contamination of streambed sediment (Tait 2008).

The TP yields observed in our study are similar to what is expected from natural sources of P (Withers and Jarvie 2008) and are mostly below the median value for undeveloped watersheds in the United States (Clark et al. 2000, Mueller and Spahr 2006). The low concentration of dissolved P species in East Hawai'i streams is not surprising because iron-rich tropical soils are usually impoverished in available P, with both geochemical sorption and microbial demand competing for soil P (Olander and Vitousek 2005).

TN yields, which were measured at only two locations, are similar to or slightly higher than estimates of background for undeveloped U.S. watersheds (Clark et al. 2000, Mueller and Spahr 2006, Howarth 2008). Median nitrate yield in our study, which was measured at 37 locations, is less than the median value for undeveloped U.S. watersheds (Clark et al. 2000, Mueller and Spahr 2006). All these results are consistent with the low level of development in East Hawai'i.

It is generally accepted that a substantial part of the annual nutrient and sediment flux can be transported during high-flow (storm) events that augment fluxes carried during base-flow periods. This phenomenon has been observed in the Wailuku River (Wiegner et al. 2009), and studies elsewhere in Hawai'i have demonstrated the importance of storm flows in the nutrient dynamics of coastal waters (Soicher and Peterson 1997, Hoover 2002, Ringuet and Mackenzie 2005, Cox et al. 2006, De Carlo et al. 2007). Observations of storm-flow fluxes are particularly important for identifying sources of nonpoint pollutants and quantifying their inputs, but unfortunately such measurements require autosamplers, which are expensive. One of the most valuable flux data sets in East Hawai'i is that of Presley et al. (2008), who for 2 yr measured storm-flow fluxes in an ephemeral Mauna Loa stream. If our instantaneous base-flow measurements are representative of typical base-flow conditions, then our perennial Mauna

Kea streams exported an order of magnitude more nitrate (per year per unit area) in their base flows than the ephemeral Mauna Loa stream exported as storm flow (per year per unit area).

As measured in this study, Kohala watersheds had significantly greater stream nitrate concentrations and nitrate yields than Mauna Kea watersheds. Over time, atmospheric nitrogen is added to soils by fixation or wet/dry deposition, which is why older Hawaiian soils (Kohala) tend to have more nitrogen than younger Hawaiian soils (Mauna Kea) (Vitousek et al. 2003, Vitousek 2004, Porder et al. 2005). By this logic one would expect Mauna Loa streams to have lower nitrate concentrations than Mauna Kea streams. Although our data show the opposite trend, it is difficult to draw robust conclusions from the small number of Mauna Loa samples. Another puzzle is that Mauna Kea watersheds showed an anthropogenic signal in nitrate concentrations, fluxes, and yields, whereas Kohala watersheds did not. This discrepancy is difficult to explain, but it is possible that Kohala and Mauna Kea soils differ in terms of soil microbial activity or rates of nitrogen cycling.

There are several important limitations of the data used for the regression analysis, and for this reason the regression results should be considered preliminary. Temporally sparse and asynchronous measurements introduced noise into the water quality and flux data. We did not account for the possibility that land closer to the stream may have greater influence than land farther from the stream (Omernik et al. 1981), nor were allowances made for noncontributing areas. There are watershed characteristics that we also did not account for: for example, the presence of nitrogen-fixing plants that would be expected to increase nitrogen concentrations in soils and streams (Compton et al. 2003, Hughes and Denslow 2005). Perhaps most important, much of the land designated for agriculture is not currently being farmed, and we do not have detailed data on the type of agriculture being practiced in those areas that are being farmed. We consider the development of updated and more detailed maps of agricultural activity to be a priority for future research.

The C-CAP and GAP data sets (available at <http://hawaii.gov/dbedt/gis>) are valuable starting points, but currently they do not distinguish between different types of agricultural activity.

These limitations notwithstanding, it is our opinion that our results pose the hypothesis that anthropogenic activities in Mauna Kea watersheds have resulted in slight increases in nitrate concentrations and yields. Because there are no point sources in the watersheds in our study, attention will be directed at nonpoint sources. The regression results suggest that agricultural activity in Mauna Kea watersheds may contribute to higher concentrations of dissolved ions and larger nitrate yields. This is consistent with agricultural applications of fertilizer. Mauna Kea watersheds also exhibit a positive correlation between human population density and nitrate fluxes. This could reflect fertilizer in residential yards, planting of ornamental nitrogen-fixing plants, or the tendency of rural residents to keep a few head of livestock or cultivate small areas. Sewage is another source of nitrate, and many homes in East Hawai'i dispose of their domestic wastes using cesspools or septic tanks (Hawai'i County General Plan 2005). We should note, however, that none of the samples from this study exhibited nutrient concentrations high enough to be indicative of contamination by manures, fertilizer, or sewage. In addition, there is no evidence that anthropogenic activities were affecting organic nutrients at the time of the study. The tendency for organic nutrients to become more concentrated with increasing watershed area is consistent with results of a prior study that examined biological in-stream processing in an East Hawai'i stream (Larned et al. 2008).

There are a number of factors that could alter future nutrient or sediment concentrations in East Hawai'i streams. If demographic trends hold, East Hawai'i will experience modest levels of residential development in future decades, although the region as a whole is likely to remain sparsely populated. There are many areas in East Hawai'i where cesspools and septic tanks will continue to be used for new residential construction. Also, consid-

ering the large amount of underutilized agricultural land, a revitalization of agriculture could occur in response to changing economics, an emphasis on statewide food security, or development of a biofuel industry. Shifts in vegetation communities (for example, spread of the invasive nitrogen-fixing Albizia [*Falcataria moluccana*] tree) could increase nitrogen levels in streams. A detailed understanding of ecosystem functioning will require distinguishing between different forms of nutrients, differences between storm-flow and base-flow contributions, and more comprehensive measurements of terrestrial fluxes to coastal water bodies. Further investigation into anthropogenic influences on nutrient loads will require more detailed land use data and more frequent hydrologic and water quality observations. In some cases, very high time resolution data (subhour) will be needed to capture dynamics of flashy runoff events (Tomlinson and De Carlo 2003). In our opinion, nitrate is the most important parameter to investigate in East Hawaiian streams, and it would be worthwhile to examine TN and turbidity as well.

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