Stream Water Chemical Parameters for Tutuila Island, American Samoa

Eliana Bardi[1], Sharon Fanolua[2], Kristel van Houte-Howes[3], Lisa M. Wade[2], Agnes M. Vargo[2], and Donald L. Vargo[2, 4]

Abstract

Little information exists on the chemical and physical attributes of freshwater resources in American Samoa to aid environmentalists, policymakers, and regulators in making sound decisions concerning their preservation and protection. To help fill this void we measured pH, conductivity, turbidity, temperature, dissolved oxygen, calcium, magnesium, potassium, sodium, reactive phosphorus, ammonium-N, and nitrate-N levels for 44 perennial streams on Tutuila Island at monthly intervals for two years. Based upon phosphorus and nitrogen levels, we partitioned the streams into three levels of human impact. A one-way analysis of variance by level gave significantly different medians for all parameters except pH and turbidity. Only seven streams possibly comply with current water quality standards for phosphorus and nitrogen for fresh surface waters, while none comply with the standard for turbidity. For streams affected only by agrarian and residential activities, monitoring reactive phosphorus and conductivity alone may be sufficient to discern changes in the intensity of human impact.

1 Current address: H.T. Odum Center for Wetlands, University of Florida, Box 116350, Gainesville, FL 32611.

2 American Samoa Community College, Community and Natural Resources, P.O. Box 5319, Pago Pago, AS 96799.

3 Current address: National Institute of Water and Atmospheric Research, Ltd. P.O. Box 11-115, Hamilton, New Zealand.

4 Corresponding author. TEL 684-699-1394; FAX 684-699-5011; donvargo@rocketmail.com

An understanding of biogeochemical processes is essential for effective management and use of fresh waters (Wetzel 2001). While studies have been conducted on freshwater fauna (Burger and Maciolek 1981; Couret and others 1981) and stream-flow characteristics (Wong 1996), little information is available on chemical and physical properties of American Samoa's fresh waters beyond a few dozen desultory measurements of nitrogen, phosphorus, pH, and turbidity performed between 1979 and 1996 (refs. in DiDonato 2005). This paucity of data is particularly troubling because the availability of essential nutrients–nitrogen and phosphorus in particular–shapes the productivity, composition, diversity, dynamics, and interactions of plant, animal, and microbial populations in these ecosystems (Vitousek 2004). While current water quality standards for fresh surface waters in American Samoa state that waters are not to exceed an average turbidity of 5.0 NTU, 150.0   g L^{-1} total phosphorus, 300.0   g L^{-1} total nitrogen, and 5.0 mg L^{-1} total suspended solids, pH is to range between 6.5 and 8.6, and the minimal level for dissolved oxygen is either 6.0 mg L^{-1} or 75% saturation (Environmental Protection Agency 1999), little is known about whether any streams actually meet these standards.

Human beings disturb streams in several ways. They release chemical toxins, excess soil, plant nutrients, and animal wastes into the water. They build impoundments and channelize the stream in order to protect property. They destroy the habitat and introduce invasive species.

The major human disturbances to streams in American Samoa are attributable to residential and agricultural activities. Some village streams have cement embankments and paved compounds on which backyard mechanics inadvertently release small amounts of automotive fluids. Gray water outlets from sinks, showers, and laundries release soaps, detergents, and other household cleansers directly into streams. Where solid waste pickup is unavailable or infrequent, streams are a convenient repository of domestic refuse.

Agriculture has long been suspected to be a substantial contributor to non-point source pollution of surface and ground water. Piggeries often release nutrient-rich, infectious wastes directly into streams. Poor farming practices permit soil and its nutrients to wash into streams, with the soil eventually settling on the fringing coral reef.

A survey conducted in early 2005 by one of us (Fanolua) indicates that American Samoans place a high priority on "clean rivers, streams, and lakes," ranking it after clean drinking water, clean groundwater, and a reliable household water supply on a list of ten water issues (SSPIRWP 2005).

For these reasons we address this dearth of physical and chemical data for stream water quality in order to provide agricultural professionals, policymakers, and regulators with additional science-based information for better stewardship of this vital natural resource.

Over a two-year period we monthly assessed several physical and chemical water quality parameters from all permanent streams on Tutuila Island, American Samoa, that were easily accessible by vehicle. This allowed us to expeditiously access nearly all streams except for a few large streams on the sparsely populated north shore. We collected data on pH, conductivity, turbidity, dissolved oxygen, temperature, reactive phosphorus, ammonium-N, nitrate-N, calcium, magnesium, potassium, and sodium because these were analyzable with our extant soil-testing laboratory resources. Our objective was to obtain a good estimate of medians and ranges of variation for these parameters. Our goal was to use one or more parameters for distinguishing natural variations in water quality from variations caused by humans in order to eventually correlate responses of stream biota to human disturbances.

Most homes on streams are at or near the mouth, with agriculture occurring upstream of villages. Any degradation of water quality, then, occurs near the terminus. Most, if not all of the freshwater invertebrates are thought to be diadromous, that is, their larvae spend part of their life cycles in the open ocean or in estuaries (Couret and others 1981). As they mature they migrate back upstream and so must make two passages through potentially polluted sections.

We used a combination of reactive phosphorus and soluble nitrate-plus-ammonium nitrogen medians to assign streams to one of three putative levels of human impact. These along with conductivity, calcium, potassium, sodium, dissolved oxygen, and temperature gave significantly different medians ($P = 0.05$) across the three impact levels. Turbidity and pH medians, on the other hand, were equal across impact levels. Over half the streams of western Tutuila are categorized as low impact, while over half the streams in central and eastern Tutuila are categorized as high impact. No stream met the water quality standard for turbidity.

Study Area

Tutuila Island, at 14.30 °S and 170.70 °W, is the largest of American Samoa's five high volcanic islands and two atolls, with over 97% of the territory's population of 64 100 (ASGDOC 2004). It is a narrow mountain range that extends 32 km east to west. Over 70% of its soils are Hapludolls formed from olivine basalt and small amounts of andesite and trachyte (Stearns 1944; Nakamura 1984). Its 137 square km are divided into 33 watersheds. It receives nearly 5 000 mm of rain annually, mainly between October and May, and has an average year-round temperature of 26 °C. Of its163 streams, comprising approximately 277 stream kilometers, 141 are considered perennial (Burger and Maciolek 1981). Most streams have short courses and a youthful profile with numerous waterfalls along their steep upper reach. Few are wider than 5 m or deeper than 0.5 m, except pools, during baseflow.

MATERIALS AND METHODS

Field Techniques

Of 112 water courses that are easily accessible by vehicle, we found only 44 with perennial flow (Figure 1). These streams were mainly clustered along 83 km of highway running east-to-west along the south coast but included three streams from the sparsely populated north coast. We sampled 30 streams from bridges at or near the mouth. For the others, where the road did not

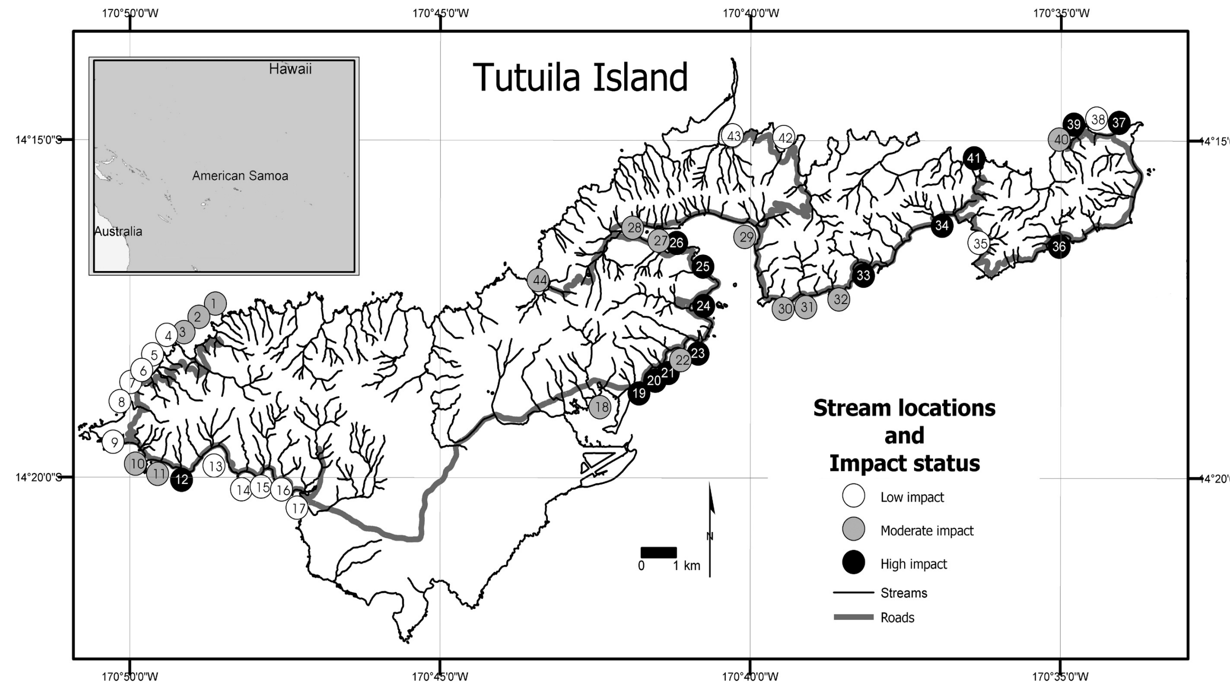

Figure 1 Map of Tutuila Island, American Samoa. Numbered circles identify the location, level of human impact based upon reactive phosphorus and soluble nitrate-plus-ammonium cutoffs, and name of streams in Table 1.

reach the mouth, we sampled at culverts up to 0.5 km from the mouth. We visited these streams between April 2003 and April 2005 during two consecutive rain-free days each month when streams ran clear and the tide was out in order to flush any saltwater intrusion caused by the 1-m tide differential. We used a Horbia U-10 Water Quality Checker for on-site readings of pH, conductivity, turbidity, dissolved oxygen, temperature, and salinity. If a salinity reading was greater than zero, we either sampled the stream later that day or omitted sampling it that month. We collected water, free of air space, in sealable 1-L polyethylene bottles and kept them in ice until we returned to the laboratory, then stored them at 4 ºC.

Laboratory Techniques

We tested for reactive phosphorus, ammonium-N, and nitrate-N within 48 hrs. Filtration was unnecessary, since either the water was clear when collected or suspended solids had settled during refrigeration. We tested for calcium, magnesium, potassium, and sodium within three months after transferring the water to capped, 100-mL polystyrene jars to which a drop of concentrated sulfuric acid was added to prevent precipitation of carbonates during storage at 25 ºC. We analyzed phosphorus by the ascorbic acid method ([Pacey] 1998) using a Turner SP-870 spectrophotometer. We used an Orion model 95-12 ammonia electrode ([Stieg] 1998) and an Orion model 90-02 nitrate ion electrode coupled with an Orion model 93-07 double-junction reference electrode ([Pacey and Stieg] 1998a) to determine ammonium and nitrate levels, respectively, with an Orion model 720A pH/ISE meter. We measured calcium, magnesium, and potassium levels by atomic absorption spectrophotometry and sodium by atomic emission spectrophotometry, following procedures supplied with our Buck Scientific model 200A spectrophotometer. We prepared reagents and made dilutions, when necessary, with distilled water (Waterwise Distiller 7000) passed through activated charcoal. Preliminary comparisons of test results using reagents prepared with distilled water against reagents prepared with Type 1 quality water (Millipore Simplicity deionizing system) were identical. Statistical analyses were performed using SigmaStat.

RESULTS

Phosphorus and, sometimes, nitrogen are generally the limiting elements in freshwater ecosystems. Because both are affected by land use practices, we applied the fresh surface water quality standard limits of 0.150 mg L^{-1} for total phosphorus and 0.300 mg L^{-1} for total nitrogen in order to partition our 44 streams into three categories: streams whose median values for phosphorus and nitrogen were less than or equal to the water quality limits, streams whose median values exceeded one or the other limit, and streams whose median values exceeded both limits. Only seven streams were in first category, that is, in compliance with the current water quality standards if reactive phosphorus is taken as a close approximation of total phosphorus and soluble nitrate-plus-ammonium ions are fair measures of total nitrogen, while 17 streams exceeded both the phosphorus and nitrogen limits.

In order to more evenly distribute the number of streams among the three categories in order to maximize the effici-ency of a subsequent ANOVA, we increased the cutoff for nitrate-plus-ammonium nitrogen by 50% to 0.450 mg L^{-1} (Table 1, Figure 2). We chose this value because roughly half the streams lie on either side of this cutoff, just as roughly half the streams lie on either side of the 0.150 mg L^{-1} cutoff for phosphorus. A one-way analysis of variance by ranks (Kruskal and Wallis 1952), followed by Dunn's (1964) multiple comparison test, gave significant differences among medians for all parameters except turbidity and pH (Table 2).

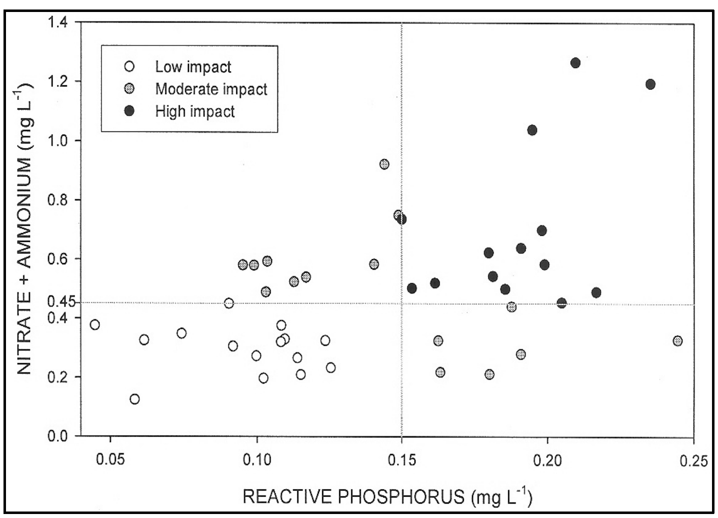

Figure 2. Distribution of 44 streams based on cutoffs of 0.15 mg L^{-1} for reactive phosphorus medians and 0.45 mg L^{-1} for soluble nitrate-plus-ammonium nitrogen medians.

Table 1. Distribution of 44 streams on Tutuila Island[1], American Samoa, into three assumed levels of human impact based on medians for phosphorus and nitrogen.

Impact Level	Map #	Stream No.	Stream Name	Village	Lat S	Long W
Low (n = 15)	4	100301	Maloata	Maloata	14 18 24.46	170 48 44.87
	5	100203	Tuasina E	Fagalii	14 18 32.52	170 49 17.48
	6	100203	Tuasina W	Fagalii	14 18 36.80	170 49 22.56
	7	100202	ASPA pump	Poloa	14 18 38.69	170 49 37.11
	8	100101	Vaitele	Poloa	14 18 59.82	170 49 43.56
	9	103205	Leaute	Failolo	14 19 45.02	170 49 30.40
	13	103202	Saonapule	Seetaga	14 19 32.84	170 48 40.78
	14	103103	Atauloma	Afao	14 19 52.82	170 48 6.92
	15	103101	Asili	Asili	14 19 51.26	170 47 46.58
	16	103005	Vaipuna	Amaluia	14 20 1.16	170 47 31.32
	17	103004	Leafu	Leone	14 19 59.59	170 46 56.78
	35	102103	Alofau	Alofau	14 16 26.92	170 36 4.16
	38	101603	Ogefao	Onenoa	14 14 58.39	170 34 42.98
	42	101006	Tiaiu Falls	Amalau	14 15 18.00	170 39 32.52
	43	101003	Faatafe	Vatia	14 15 7.48	170 40 24.07
Moderate (n = 15)	1	100402	Matavai W	Fagamalo	14 18 1.02	170 48 31.39
	2	100402	Matavai E	Fagamalo	14 18 3.25	170 48 37.53
	3	100401	Tuatafa ridge	Maloata	14 18 8.04	170 48 45.76
	10	103204	Afutele	Agugulu	14 19 51.50	170 49 10.75
	11	103200	Lepisi Falls	Agugulu	14 19 54.40	170 49 3.03
	18	102704	Papa	Nuuuli	14 18 38.45	170 42 35.09
	22	102605	Afu	Faganeanea	14 18 6.04	170 41 19.04
	27	102422	Market	Fagatogo	14 16 38.34	170 41 26.17
	28	102421	Vaipito	Pago Pago	14 16 20.44	170 42 4.94
	29	102404	Lalolamauta	Aua	14 16 10.85	170 39 44.88
	30	102303	Vaitele	Lauliituai	14 17 15.94	170 39 11.65
	31	102301	Visa	Laulii	14 17 10.59	170 38 40.28
	32	102300	Camel Fall	Laulii	14 17 9.90	170 38 30.46
	40	101601	Afimuao	Onenoa	14 15 6.79	170 34 56.81
	44	100805	Leele	Fagasa	14 17 9.08	170 43 14.30
High (n = 14)	12	103203	Vaialoe	Utumea	14 19 41.57	170 48 51.12
	19	102701	Amaile	Nuuuli	14 18 39.59	170 41 50.20
	20	102607	Avau	Avau	14 18 20.93	170 41 34.27
	21	102606	Utulaina	Avau	14 18 18.36	170 41 26.91
	23	102604	Afuelo	Matuu	14 17 55.92	170 40 59.24
	24	102501	Fagaalu	Fagaalu	14 17 27.73	170 41 9.10
	25	102424	Vailoa	Utulei	14 16 56.26	170 41 3.00
	26	102423	Tedi's	Fagatogo	14 16 40.73	170 41 22.31
	33	102203	Alega	Alega	14 16 48.33	170 38 16.30
	34	102108	Auvai	Fagaitua	14 16 8.03	170 36 57.48
	36	102001	Televai	Amouli	14 16 23.22	170 35 0.00
	37	101701	Maupua	Maupua	14 14 59.73	170 34 27.38
	39	101602	Vaisa	Onenoa	14 15 6.10	170 34 51.38
	41	101303	Vaipito	Masausi	14 15 33.44	170 36 22.48

[1] Map # refers to markers in Figure 1. Stream names, where available, are taken from the 1989 USGS topographical map of Tutuila Island or given a descriptive name by us. Coordinates designate sampling sites.

Table 2. Multiple comparisons of physical and chemical parameter medians on pooled data for streams assumed subjected to low, moderate, or high level of human impact based on whether both phosphorus and nitrogen medians were less than or equal to 0.15 and 0.45 mg L^{-1}, respectively (low), either the phosphorus or the nitrogen median exceeded these limits (moderate), or both phosphorus and nitrogen medians exceeded these limits (high)[1].

	---------------- Impact Level --------------------			
Parameter (units)	Low (n)	Moderate (n)	High (n)	Probability
Phosphate-P (mg L^{-1})	0.096^{a} (347)	0.138^{b} (332)	0.148^{c} (277)	< 0.001
$NO_3^- + NH_3$ (mg L^{-1})	0.309^{a} (140)	0.464^{b} (134)	0.685^{c} (106)	< 0.001
Nitrate-N (mg L^{-1})	0.225^{a} (183)	0.324^{b} (134)	0.500^{b} (141)	< 0.001
Ammonia-N (mg L^{-1})	0.083^{a} (140)	0.123^{ab} (134)	0.172^{b} (106)	< 0.001
Conductivity (S m^{-1})	9.8^{a} (348)	12.3^{b} (332)	15.3^{c} (277)	< 0.001
Calcium (mg L^{-1})	1.59^{a} (346)	2.01^{b} (332)	2.56^{c} (277)	< 0.001
Magnesium (mg L^{-1})	2.96^{a} (346)	2.67^{a} (332)	3.13^{b} (277)	< 0.001
Potassium (mg L^{-1})	0.97^{a} (346)	1.57^{b} (332)	2.11^{c} (277)	< 0.001
Sodium (mg L^{-1})	6.51^{a} (346)	8.85^{b} (332)	10.46^{c} (277)	< 0.001
Dissolved O_2 (mg L^{-1})	7.89^{a} (303)	7.47^{b} (291)	7.35^{c} (245)	< 0.001
Temperature (^{o}C)	25.6^{a} (348)	26.2^{b} (332)	27.0^{c} (277)	< 0.001
Turbidity (NTU)	11.0 (103)	12.0 (97)	12.0 (89)	0.418
pH	7.60 (348)	7.58 (332)	7.52 (277)	0.632

[1] Kruskal-Wallis one-way ANOVA on ranks. Items with the same letter(s) superscript indicates no significant difference ($P \geq 0.05$) between medians. Multiple comparisons were made using Dunn's method (Dunn 1964). n = sample size.

In addition to phosphorus and nitrogen concentrations, conductivity and the concentrations of cations that constitute conductivity, except for magnesium, increased from low- to high-impact level. Median stream water temperatures also increased slightly, but significantly, with dissolved oxygen concentrations correspondingly decreasing. Median turbidity values were over twice the water quality standard for this parameter at all three levels of impact, while pH values were all about 7.5.

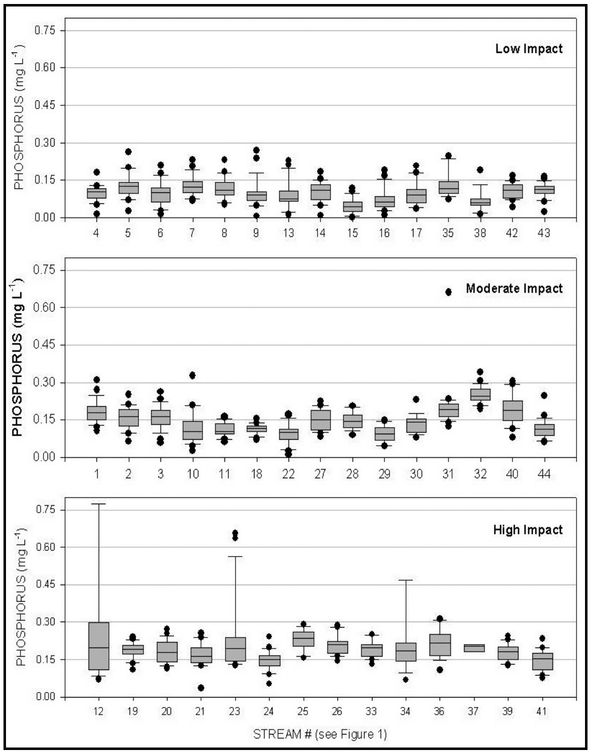

Figure 3. Boxplots of monthly reactive phosphorus concentrations over 24 months. The ends of the boxes define the 25th and 75th percentiles, with a line at the median and error bars defining the 10th and 90th percentiles. Displayed data points lie beyond these extreme percentiles.

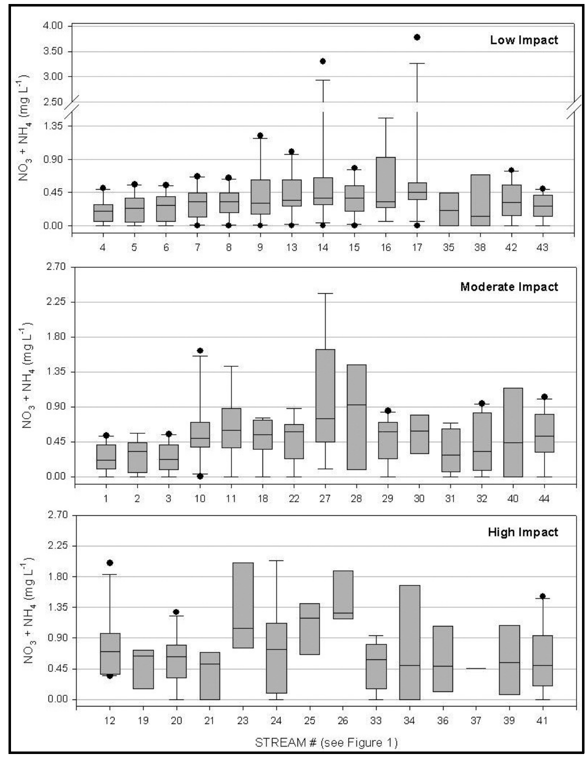

Figure 4. Boxplots of monthly nitrate-N plus ammonium-N concentrations over 24 months. The ends of the boxes define the 25th and 75th percentiles, with a line at the median and error bars defining the 10th and 90th percentiles. Displayed data points lie beyond these extreme percentiles.

Boxplots for reactive phosphorus showed similar ranges in variation for nearly all streams (Figure 3). This pattern was repeated for nearly all of the other parameters except nitrogen (Figure 4). Two low-impact streams, #14 and 17, had remarkably high outliers for soluble nitrate-plus-ammonium nitrogen. The boxplots confirmed that no single reading was adequate for assigning streams to one impact level or another. Even streams in the high impact level would give individual readings within the phosphorus or nitrogen cutoff.

A preponderance of low impact streams lined the island's western coast, while nearly half the streams along the central and eastern coasts were designated as having high human impact. Median values for all parameters of all streams are given in Table 3.

DISCUSSION

We sampled our 44 streams only during periods of quiescence, or normal flow, for safety and to avoid short-lived erratic variability during dynamic flow. We defined our three levels of human impact on pollution gradients for phosphorus and nitrogen alone because these elements are affected by land use practices and are generally limiting for primary production in freshwater ecosystems (Schlensinger 1997). Our impact levels–low, moderate, and high–are used to conveniently label the *relative* intensities of human activity based on our *arbitrary* choice of cutoffs for phosphorus and nitrogen. Representing total phosphorus as orthophosphate and total nitrogen as nitrate, increasing the nitrogen cutoff from 0.300 to 0.450 mg L^{-1} increased the N:P ratio from 3:1 to 4.5:1. This was still far less than the Redfield ratio of 16:1, that is, the ratio of nitrogen to phosphorus in most phytoplankton (Goldman and others, 1979) at which eutrophication might occur at elevated concentrations of either element. These cutoffs allowed for near-equal distribution of the streams among the three impact levels which, in turn, maximized the efficiency of the ANOVA (Snedecor and Cochran 1989).

Phosphorus, in very high amounts, can produce marine algae blooms that lead to eutrophication of near-shore waters and the proliferation of toxic phytoplankton that harm sea animals and humans who eat them. We know of no such incidence ever occurring in American Samoa. High levels can also increase the growth rate of bacteria. The inorganic form is almost exclusively orthophosphate ([Pacey and Stieg] 1998b). Phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample are termed "reactive phos-phorus" ([Pacey and Stieg] 1998b). This form is readily taken up by aquatic plants and microorganisms and is the form we measured.

Inorganic phosphorus comes from the mineral apatite, $Ca_5(PO_4)F$, which is well dispersed through igneous rocks (Troeh and Thompson 1993). The amount of dissolved phosphorus in the soil is extremely small because it is strongly adsorbed to positively charged sites on clays. Natural levels of this element in stream water, therefore, are also correspondingly small. Possible anthropogenic sources in American Samoa include sewage, cleaning compounds, food residues and fertilizers. The median value for reactive phosphorus never exceeded twice the water quality standard for total phosphorus, but individual readings could be four-fold or more higher (Figure 3). Reactive phosphorus is conveniently measured in the laboratory with high accuracy and precision, requiring only a few inexpensive reagents and a modestly priced visible light spectrophotometer.

Nitrate generally occurs in trace quantities in surface water ([Smith and Stieg] 1998). The main sources of excess nitrate are runoff from agricultural lands and oxidized animal wastes (Baird 1999). Intensive cultivation of land, even without the application of fertilizer or manure, facilitates the oxidation of reduced nitrogen to nitrate in decomposed organic matter in the soil (Baird 1999).

Ammonia is also naturally present in surface waters. It is produced largely by deamination of organic nitrogen-containing compounds and by hydrolysis of urea ([Smith and Stieg] 1998). At pH 7.5, the ratio $NH_4^+:NH_3$ is about 60:1. In well-aerated environments, such as shallow, fast-running streams, most of it is converted by nitrifying autotrophs to nitrate, with nitrite as an intermediate (Baird 1999).

Table 3. Median values for stream water quality parameters for 44 streams of Tutuila Island, American Samoa. Stream # refers to markers in Figure 1.

Impact Level	Stream #	P	N	NO3	NH4	Cond	Ca	Mg	K	Na	DO	Temp	Turb	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	S cm^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	°C	NTU	
Low (n = 15)	4	0.102	0.198	0.147	0.071	69	1.28	2.18	0.81	5.19	8.22	25.6	8	7.34
	5	0.125	0.234	0.169	0.075	96	1.58	2.94	1.14	6.09	7.77	25.3	9	7.57
	6	0.100	0.273	0.204	0.083	94	1.32	2.92	1.00	6.57	7.51	25.4	12	7.43
	7	0.124	0.325	0.261	0.095	136	1.92	3.98	1.24	8.32	8.09	25.8	14	7.76
	8	0.110	0.330	0.246	0.118	129	1.59	3.99	1.50	7.40	7.70	25.6	13	7.54
	9	0.092	0.306	0.243	0.102	108	1.72	3.82	1.16	8.08	7.47	25.3	12	7.87
	13	0.074	0.348	0.256	0.091	100	1.66	3.37	0.98	6.89	7.90	25.5	6	7.75
	14	0.108	0.376	0.211	0.118	108	1.74	3.57	1.05	7.07	7.85	25.8	16	7.58
	15	0.045	0.376	0.174	0.052	80	1.49	2.96	0.76	4.92	8.10	25.2	9	7.55
	16	0.062	0.326	0.225	0.101	96	1.94	3.69	0.79	5.45	7.72	25.8	14	7.64
	17	0.090	0.450	0.394	0.145	90	1.59	2.76	0.92	5.58	8.53	25.1	8	7.55
	35	0.115	0.210	0.000	0.000	122	2.32	3.27	0.94	8.69	7.37	26.7	19	7.53
	38	0.058	0.125	0.000	0.000	139	1.28	2.01	0.92	13.50	8.35	26.7	16	8.08
	42	0.108	0.321	0.307	0.093	97	1.14	2.15	0.94	7.40	8.26	25.6	5	7.55
	43	0.114	0.267	0.180	0.078	98	1.28	2.68	0.71	6.51	7.19	25.7	9	7.44
Moderate (n = 15)	1	0.180	0.212	0.173	0.088	89	1.56	2.06	1.30	7.06	7.84	25.6	9	7.58
	2	0.163	0.325	0.232	0.076	90	1.20	2.42	1.04	7.51	7.77	25.6	22	7.57
	3	0.163	0.219	0.160	0.111	103	1.34	2.20	1.47	8.97	6.93	26.0	7	7.41
	10	0.103	0.489	0.355	0.122	145	2.01	4.39	1.27	9.79	7.54	25.7	6	7.85
	11	0.104	0.593	0.397	0.136	173	2.47	4.17	1.51	12.79	8.15	26.2	7	8.44
	18	0.117	0.540	0.340	0.132	113	1.86	2.68	1.56	7.91	7.52	27.0	6	7.07
	22	0.099	0.580	0.474	0.114	129	1.76	3.20	1.25	10.30	7.35	27.6	6	7.50
	27	0.149	0.750	0.880	0.233	147	3.66	2.50	2.54	9.90	6.44	26.6	13	7.28
	28	0.144	0.923	0.183	0.233	196	5.09	3.96	1.89	9.29	7.46	28.8	49	7.44
	29	0.095	0.581	0.409	0.124	102	1.48	2.15	1.32	7.68	6.88	26.2	13	7.49
	30	0.140	0.584	0.544	0.199	124	2.05	1.69	2.09	10.52	7.47	26.7	24	7.38
	31	0.191	0.280	0.236	0.143	123	1.50	2.11	2.00	11.14	6.94	25.4	8	7.65
	32	0.244	0.328	0.269	0.188	167	1.23	2.72	2.15	17.64	7.79	26.5	31	7.91
	40	0.188	0.440	0.391	0.262	196	2.65	4.10	1.68	14.35	6.81	27.5	13	7.76
	44	0.113	0.524	0.500	0.137	129	2.34	2.71	1.43	7.91	8.01	27.3	7	7.97
High (n = 14)	12	0.198	0.700	0.335	0.340	124	1.94	4.06	1.48	8.62	7.12	25.6	11	7.40
	19	0.191	0.640	0.482	0.156	125	2.62	2.82	2.14	9.48	6.55	26.8	15	7.42
	20	0.180	0.624	0.532	0.143	132	2.06	2.65	2.08	10.94	7.70	26.4	19	7.63
	21	0.162	0.520	0.401	0.130	173	3.04	3.21	1.96	14.73	7.08	26.7	6	7.60
	23	0.195	1.040	0.865	0.210	130	2.26	2.84	2.30	10.77	7.08	27.9	13	7.42
	24	0.150	0.737	0.489	0.187	154	3.50	2.93	2.15	9.98	7.62	28.4	76	7.50
	25	0.235	1.195	0.687	0.308	173	2.43	3.02	3.30	14.72	5.39	27.6	30	7.07
	26	0.210	1.266	0.986	0.379	185	3.46	3.92	3.05	12.45	5.67	27.9	9	7.19
	33	0.199	0.584	0.501	0.142	119	1.54	1.94	1.86	10.10	7.87	25.4	7	7.76
	34	0.186	0.500	0.500	0.167	157	2.70	4.05	1.83	11.72	6.84	27.3	14	7.40
	36	0.217	0.490	0.530	0.116	208	3.23	3.68	2.33	15.65	6.44	26.8	17	7.78
	37	0.205	0.454	0.133	0.321	214	1.95	2.89	2.70	16.70	6.49	26.8	5	6.68
	39	0.181	0.544	0.541	0.201	240	2.79	4.51	2.05	16.69	7.85	27.0	9	8.13
	41	0.154	0.503	0.473	0.145	169	2.57	4.13	1.68	12.73	7.84	29.1	15	8.01

Of the choice of methods available for analyzing nitrate-N, we selected the nitrate electrode method in order to avoid a preliminary reduction with cadmium or exposure to hydrazine ([Smith and Stieg] 1998). Similarly, for analyzing ammonium-N we selected the ammonia-selective electrode method in order to avoid a preliminary distillation step required by the titrimetic method or exposure to phenol ([Smith and Stieg] 1998). But we experienced difficulties obtaining acceptable slope values when calibrating the electrodes despite carefully following the manufacturer's instructions. If we could not remedy the problem within the 48-hr holding limit for nitrate analysis ([Keith] 1998), we omitted nitrogen determinations for that month. We also sometimes experienced erratic readings partway through a monthly run. If we could not recalibrate the electrode, subsequent testing was cancelled. Consequently, no more than 14 nitrate and 11 ammonium readings, and in a few cases only 7 nitrate or 4 ammonium readings, were performed on a given stream during 24 months of sampling.

For calculating soluble nitrate-plus-ammonium nitrogen values, we added values of the individual ions only if both were measured. Because we recorded less readings for ammonium-N than for nitrate-N, and for every ammonium-N reading there was a corresponding nitrate-N reading, the number of soluble nitrate-plus-ammonium nitrogen readings equaled the number of ammonium-N readings.

Boxplots of nitrate-plus-ammonium nitrogen (Figure 4) showed a wider range of variation than similar plots for the other parameters. Given the difficulty obtaining readings, as addressed above, this variation may be due as much to imprecision in the test method as to true levels of nitrogen. We were at a loss to explain the outliers recorded for Streams #14 and 17 (Figure 4). Both streams run through villages that have very little agricultural activity, including piggeries, along or upstream of the villages. Near-daily readings were made on Leafu Stream, #17, between 09 June 2001 and 31 December 2003 with a Horbia U-10 probe. Probe readings for the day of sample collection, 17 December 2003, when we recorded the unusually high reading of 3.77 mg L^{-1} for nitrate-N, were unremarkable: pH 8.25, dissolved oxygen 9.07 mg L^{-1} at 25.7 $^{\circ}$C, and conductivity 67 S cm^{-1}. These values were near-normal to 800 readings on this stream, with means $\pm$ standard deviations of 7.61 $\pm$ 0.49 for pH, 8.13 $\pm$ 1.47 mg L^{-1} for dissolved oxygen, and 83 $\pm$ 13 S cm^{-1} for conductivity.

The covariance of soluble nitrate-plus-ammonium nitrogen and reactive phosphorus for streams in the low- and moderate-impact levels were 0.003 and 0.007, respectively, suggesting independent sources for these two elements, while the covariance in high impact level streams, 0.218, suggested that an appreciable amount of these elements may originate from a common source. The most likely candidates were piggery or sewage effluent and fertilizer runoff. But streams with known outfalls of raw sewage from piggeries just upstream of our collection sites were found in all three impact levels.

Since neither ammonium-N nor nitrate-N alone can distinguish among the three levels of impact (Table 2), that the electrode method requires a relatively expensive pH/ISE meter and (in our experience) refractory electrodes, and that alternate methods require either expensive automated instruments or toxic reagents, we were interested in learning if another parameter

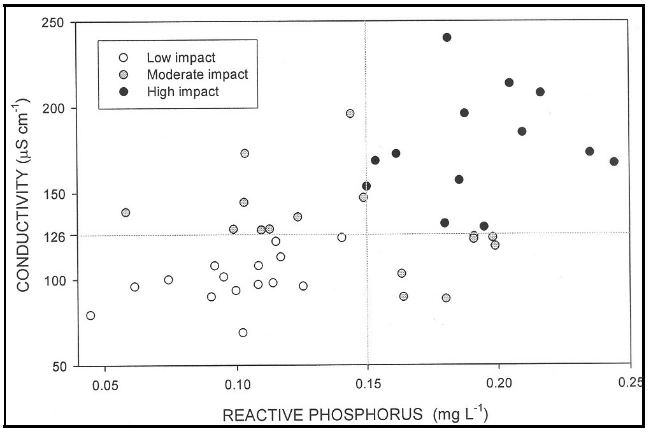

Figure 5. Distribution of 44 streams based on cutoffs of 0.15 mg L^{-1} for reactive phosphorus medians and 126 S cm^{-1} for conductivity medians.

might serve as an acceptable alternative to measuring soluble nitrate-plus-ammonium nitrogen.

Conductivity is easily, quickly, and accurately measured *in situ* with an inexpensive meter by an inexperienced operator. It is a function of the concentrations of several ions. For most natural waters these are the mobile cations calcium, magnesium, potassium, and sodium and the anions bicarbonate, sulfate, and chloride ([Bagdigian] 1998). The contribution to conductivity by various ions is additive, with the relative contribution of each ion being a product of its concentration and equivalent conductance. Because of the relatively low concentrations of these mobile cations, except for sodium, in our streams (see below), we wished to learn if the presence of ammonium and nitrate ions in moderate- and high-impact level streams would make an appreciable contribution to conductivity.

Using median concentrations for calcium, magnesium, potassium, sodium, ammonium, and nitrate ions for high impact streams from Table 2 and assuming a molar ratio of bicarbonate: sulfate:chloride of 4:1:1 for our streams, we calculated ([Bagdigian] 1998) that ammonium and nitrate ions increased conductivity by only 1%. The increasingly higher values for conductivity from low- to high-impact level streams were, therefore, due to other than increases in the concentrations of the nitrogen-based ions, rendering conductivity unsuitable for estimating soluble nitrate and ammonium ion concentrations. But differences in conductivity with impact level might possibly be useful for monitoring impact.

We tested this by ranking streams from lowest to highest in median conductivity and using 126 S cm^{-1} to equally divide the number of streams with medians above and below this cutoff. Using this cutoff and the reactive phosphorus cutoff, we partitioned the 44 streams into three new levels of human impact as we had done with soluble nitrate-plus-ammonium nitrogen (Figure 5). Eleven streams shifted into an adjacent impact level (Table 1, column C), leaving 75% of the streams in their original impact levels.

In an examination of parameter values at various elevations in three pristine streams, we found that conductivity decreased with distance from the mouth (Figure 6), a pattern that was paralleled by the four mobile cations (Figure 7). While the concentrations of phosphorus and the nitrogen-based ions in soil water were relatively constant throughout the watersheds, the mobile cations entered the stream throughout its course at increasingly higher concentrations in the baseflow seepage. Higher concentrations may be due to a greater cation exchange capacity and base saturation in soils at lower elevations and to longer contact time between soil and soil water as infiltrated rain perco-lates down the slope.

Calcium, magnesium, potassium, and sodium are not considered pollutants and were monitored to assess stream water quality for aquaculture purposes. Hardness, which is a function of calcium and magnesium ion concentrations, is important in the culture of several commercial species of fish and shrimp (Buttner 1993). If hardness is below 50 mg L^{-1}, many species do not grow well. A value greater than 100 mg L^{-1} in calcium carbonate is preferred (Cripps and Nakamura 1979; Buttner 1993).

We calculated ([Rexing?] 1998) median stream hardness values ranging from12 to 34 mg equivalent $CaCO_3$ L^{-1}. Aquaculturists raising Red Tilapia, *Tilapia aurea*, or who intend to raise the Giant Malaysian Prawn, *Macrobrachium rosenbergii*, might be advised to increase hardness in stream-fed tanks with the addition of hydrated lime.

The mean concentrations, in mg L^{-1}, of these cations in river waters throughout the world are: 15.0 for calcium, 4.1 for magnesium, 2.3 for potassium, and 6.3 for sodium (Wetzel 2001). The mean concentrations for Tutuila's streams were, respectively: 3.0, 3.0, 1.6, and 8.8 mg L^{-1}. The low concentration of calcium in Tutuila's streams, relative to its concentration in continental waterways, is a consequence of the absence of limestone in the parent rock, which is mostly olivine, $(Mg, Fe)_2SiO_4$, alkali feldspars such as sanidine, $(K, Na)AlSi_3O_8$, and clinopyroxenes such as augite $(Ca, Mg, Fe)_2Si_2O_6$ (Stearns 1944).

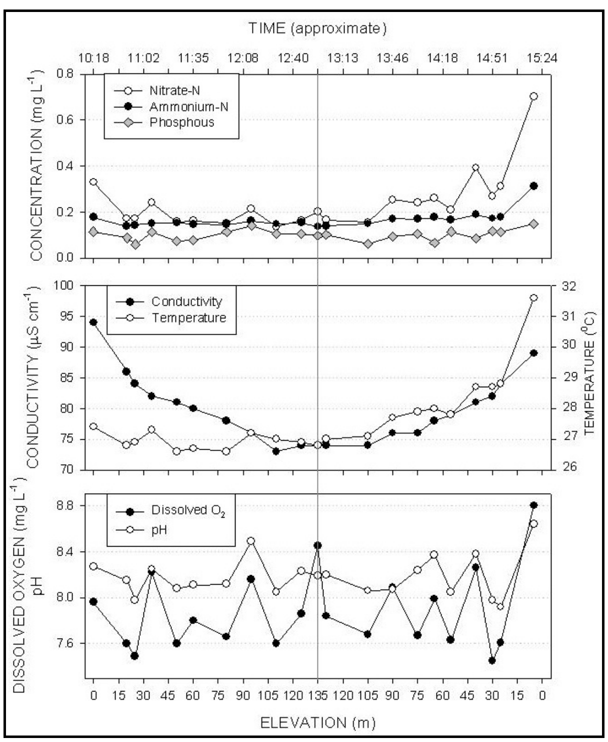

Figure 6. Distribution of 44 streams based on cutoffs of 0.15 mg L^{-1} for reactive phosphorus medians and 126 S cm^{-1} for conductivity medians.

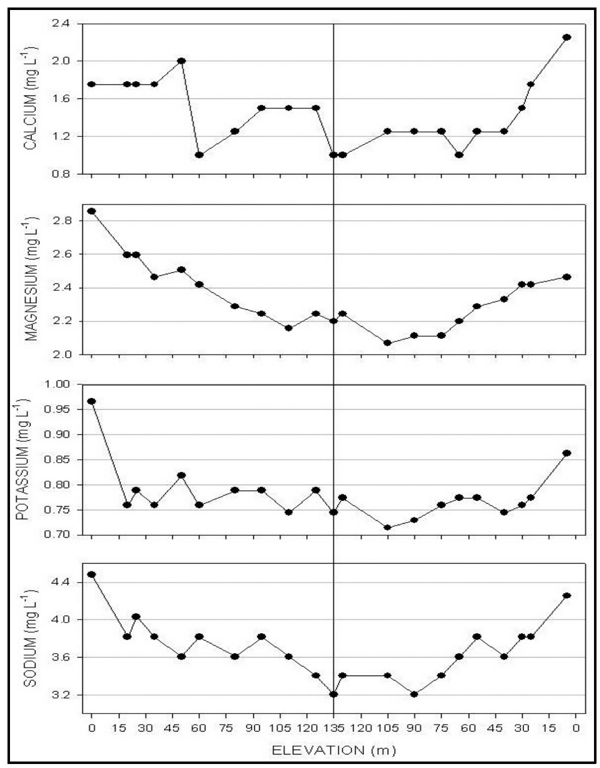

Figure 7.. Changes in water quality parameters with elevation as a surrogate for distance from the stream mouth. Data are for Maloata Stream, #4, on 28 December 2004. All measurements except phosphorus were made *in situ* with a YSI 650 MDS water quality probe. Phosphorus was measured within 24 hrs from 250-mL water samples stored on ice during collection and refrigerated overnight.

The high concentration of sodium relative to worldwide streams as well as to the other cations is unusual. The elevated sodium concentration was not due to incomplete flushing of seawater during sample collection; samples collected at the stream mouths had an average $\pm$ standard deviation sodium concentration of 9.3 $\pm$ 6.7 mg L^{-1}, n = 459, while samples collected far enough from the mouth to be unaffected by tidal inundation had an average sodium concentration of 8.3 $\pm$ 6.1 mg L^{-1}, n = 494. Rather, it may be due to either rapid leaching of sodium from young soils (Troeh and Thompson 1993) or marine aerosol deposition.

Chadwick and others (1999) studied atmospheric deposition of these elements at several sites in Hawaii whose soils ranged in age from 300 years to 4.1 million years. Soils at the youngest sites were the primary source for these cations. At two sites aged 20 000 and 150 000 years, the highly weathered andisols had substantially less exchangeable cations. The number of cation exchange sites continued to diminish with soil age. At the 1.4 million year-old site, an ultisol, most of the chemically reactive non-crystalline minerals had been transformed to less-active clays, while an oxisol at the oldest site had no capacity to supply nutrients.

The volcanoes constituting Tutuila Island range in age from 1 to 1.5 million years (McDougall 1987). Assuming an activation energy of volcanic weathering of 21 kcal mol^{-1} (Brady and others 1999), an average air temperature of 16 ºC for Hawaii (Chadwick and others 1999), and an average air temperature of 26 ºC for American Samoa, the rate of weathering in American Samoa should be about 3.3 times the rate for Hawaii when these figures were applied to the Arrhenius equation. Yet no soil on Tutuila Island resembles a 3.3 to 5.0 million-year-old oxisol. Instead, over 70% are high base-saturated mollisols, with another 16% inceptisols and 3% entisols, or “young” soils (Nakamura 1984). Clearly, soil erosion occurs at a rapid pace, even in undisturbed forests, on this, the most highly eroded of American Samoa’s islands (Stearns 1944). Soils are not left in place long enough to “age” but slough from steep slopes and wash away by frequent and sometimes intense rainfall, exposing rock to further weathering. Farming often occurs upstream of villages, along the slope of narrow valleys, accelerating natural soil loss and runoff. This may account for the increased conductivity and concentrations of these cations, especially sodium, in moderately and highly impacted streams, though at concentrations that pose no threat to either the stream or the marine environments.

The dissolved oxygen concentration was inversely related to stream water temperature and was, on average, at about 95% saturation for a given temperature. Such high saturation rates argue against eutrophication even in streams with the highest concentrations of phosphorus and nitrogen, primarily because these elements generally enter the stream at its terminus. Flowing through villages, where much of the riparian vegetation was removed, exposed streams to more sunlight which, in turn, increased water temperature and thereby decreased its gas-holding capacity. Because water temperature and dissolved oxygen ranged over 5 ºC and 1.2 mg L^{-1}, respectively, at a single site throughout the day, these parameters were of little use for discriminating among impact levels.

The turbidity sensor on the Horiba probe was sometimes either inoperable or gave erratic readings. Because we collected data when streams ran clear, differences in turbidity among the three levels of impact were negligible. Rarely did we record a turbidity reading that did not exceed the 5 NTU limit promulgated in the fresh surface water quality standards. This was in contrast to observations by Couret and others (1981), who reported turbidity readings of 2 to 4 NTU in undisturbed watersheds. Sufficient sunlight penetrates all streams to ensure prolific communities of periphyton to serve as base of the food chain as evident by ubiquitous mats of green filamentous algae.

Differences in median pH values were also not significant across impact levels. The near-neutral pH values of Tutuila's streams was a consequence of the low concentrations of calcium and magnesium. While calcium and magnesium cations may make the dominant contribution to pH through a complex interaction with atmospheric carbon dioxide, increased concentrations merely serve to increase the buffering capacity. The pH of a solution comprising a weak acid, such as carbonic acid, and its salt is independent of dilution and depends only upon the formal ratio of the acid and its salt. As dissolved carbon dioxide is consumed by photosynthesizing plants, pH values tend to rise as bicarbonate anion dissociates into carbon dioxide and hydroxide anion (Baird 1999). Because of their low buffering capacity, the pH of our streams was also affected by the rate of photosynthesis, with higher values as the sun neared its zenith, especially where canopy cover had been removed.

The highest population growth on Tutuila Island is in the Tafuna Plains (between Streams #17 and 18, Figure 1) where there are few streams. Consequently, the local power and water utility had focused its efforts on connecting these residences to a municipal sewer line. A second sewer line serves villages from Fagaalu to the tuna canneries in Atuu (from Stream #24 to 1 km east of Stream #28, Figure1). Residences in all other areas had either an approved septic system or, for a few older structures, a rudimentary cesspool (McPhee, personal communication. See "Acknowledgments"). Piggeries, though, generally flush their wastes directly into streams. The single high impact stream along the western coast (Stream #12), for example, housed several hundred pigs next to the stream and about 300 m from the mouth. Many of the high impact streams may owe their status to such large-scale pig operations. Following the death of a seventh person since 2004 of a suspected case of leptospirosis in May 2005, efforts have begun to enforce an existing law requiring piggeries to be more than 50 feet (17 m) from residences (Esera-Naseri 2005). We plan to join the local Environmental Protection Agency in producing a GIS map locating all piggeries. Once this is completed, we can determine if they may be accountable for the clustering of high-impact level streams in central and eastern Tutuila.

A commonality for streams in the low impact level was an intact riparian buffer. Even where a stream passed through a village, stream banks were planted with lawns and a mix of native and ornamental plants. Piggeries, if present along low-impact streams, housed less than a dozen pigs and were set back from the stream by 50 m or more.

An intact riparian zone alone, however, was not enough to ensure good water quality. Alega Stream, #33, runs through an uninhabited, uncultivated watershed except for three homes and a long-abandoned piggery near its mouth. The single-family landowner is protective of the watershed, since the stream empties into a recreational beach operated by the landowner. Yet our results placed this stream in the high-impact level.

CONCLUSIONS

An understanding of biological, geological, and chemical processes and properties is essential for developing preservation and remediation strategies for watersheds. Our study complements earlier work that addressed the first two processes in American Samoa and confirms, quantitatively, casual observations made in previous studies. Where routine monitoring of nitrogen-based ions is problematic, we recommend monitoring reactive phosphorus levels and conductivity as the easiest and least expensive means for routine testing of stream water, an important consideration for agencies and island nations lacking resources for more thorough testing. An intact riparian buffer is necessary but not sufficient to insure good water quality.

Monitoring of chemical parameters provides only a snapshot of stream conditions during a brief instance, and several readings are needed before drawing conclusions. For these reasons we are using our results toward establishing multimetric indices of biological integrity for our streams. Such a tool should allow for a rapid and accurate assessment of watershed health and a more complete understanding of the processes driving our freshwater ecosystems.

ACKNOWLEDGEMENTS

We thank Nonu Tuisamoa for his excellent technical assistance during the early stages of the study, Eileen Herring for prompt and thorough literature searches, Troy Curry for advice on GIS mapping, Chris McPhee, former wastewater engineer for the local water utility, for information on sewage treatment, and Guy DiDonato for many helpful comments that improved the manuscript. Financial support came from a USDA grant, CRIS Accession Number 0185945, a USDA Region 9 Water Quality Coordination grant managed by the University of Arizona, and an American Samoa Department of Commerce Coral Reef Advisory Group grant, all administered by the American Samoa Community College.

LITERATURE CITED

[ASGDOC] American Samoa Government Department of Commerce. 2004. Combined Statistical Yearbook 2003 & 2004. Pago Pago, AS.

[Bagdigian, R.M.] 1998. Conductivity. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 2000, p. 44-46. American Public Health Association, Washington, D.C.

Baird C. 1999. Environmental chemistry, 2nd ed. W.H. Freeman and Company, New York.

Brady P.V., R.I. Dorn, A.J. Brazel, J. Clark, R.B. Moore, and T. Glidewell. 1999. Direct measurement of the combined effects of lichen, rainfall, and temperature on silicate weathering. Geochimica et Cosmochimica Acta (63) 3293-3300 - Werner Stumm Special Volume.

Burger I.L. and J.A. Maciolek. 1981. Map inventory of nonmarine aquatic resources of American Samoa. US Fish and Wildlife Service, Seattle, WA.

Buttner J.K. 1993. An introduction to water chemistry in freshwater aquaculture. Northeastern Regional Aquaculture Center Fact Sheet No. 170-1993. Dartmouth, MA.

Chadwick O.A., L.A. Derry, P.M. Vitousek, B.J. Huebert, and L.O. Hedin. 1999. Changing sources for nutrients during four million years of ecosystem development. Nature. 397:491-497.

Couret C.L., D.M. Devaney, J.I. Ford, R. Narahara, G. Roehm, and G.W. Smith.1981. American Samoa stream inventory. US Army Corps of Engineers, Honolulu, HI.

Cripps M.C. and R.M. Nakamura.1979. Inhibition of growth of *Macrobrachium rosenbergii* by calcium carbonate water hardness. Proceedings of the World Mariculture Society. 10:575-580.

DiDonato, G.T. 2005. Nitrogen and phosphorus concentrations in tropical Pacific insular streams: historical data from Tutuila, American Samoa. Micronesica 37:235-248.

Dunn O.J. 1964. Multiple comparisons using rank sums. Technometrics. 6:241-252.

Environmental Protection Agency. 1999. American Samoa Water Quality Standards. Fresh surface water. Available from: www.epa.gov/ost/standards/wqslibrary/ territories/american_samoa_9_wqs.pdf.

Esera-Naseri, T. September 30, 2005. ASEPA and DOH are enforcing piggery laws, issuing citations. Samoa News: p.6.

Goldman, J.C., J.J. McCarthy, and D.G. Peavey. 1979. Growth rate influence on the chemical composition of phytoplankton in oceanic waters. Nature 279: 210-215.

[Keith, L.H.] 1998. Sample storage and preservation. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 1000, p. 33-35. American Public Health Association, Washington, D.C.

Kruskal,W.H. and W.A.Wallis. 1952. Use of ranks in one-criterion variance analysis. J. Amer. Statist. Assoc. 47:583-621. Addendum. *Ibid*. 1953. 48:907-911.

Nakamura, S. 1984. Soil survey of American Samoa. USDA Soil Conservation Service. US Government Printing Office: 1984 0-412-446 QL 3.

[Pacey, G.E.] 1998. Ascorbic acid method. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 4000, p.146-147. American Public Health Association, Washington, D.C.

[Pacey, G.E. and S. Stieg] 1998a. Nitrate electrode method. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 4000, p.116. American Public Health Association, Washington, D.C.

[Pacey, G.E. and S. Stieg] 1998b. Phosphorus. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 4000, p.139-142. American Public Health Association, Washington, D.C.

[Rexing, D.J.?] 1998. Hardness by calculation. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 2000, p. 37. American Public Health Association, Washington, D.C.

Schlesinger W.H. 1997. Biogeochemistry: An analysis of global change. Academic Press, San Diego.

[Smith, R-K. and S. Stieg] 1998. Nitrogen. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20th ed. Part 4000, p. 99-100. American Public Health Association, Washington, D.C.

Snedecor, G.W. and W.G. Cochran. 1989. Statistical methods. 8th ed. Iowa State University Press, Ames.

[SSPIRWP] Southwest States & Pacific Islands Regional Water Program. 2005. Water issues are a high priority in the Pacific. HPIWQ001. Available from: http://ag.arizona.edu/region9wq/resourcespublications.htm.

Stearns, H.T. 1944. Geology of the Samoan islands. Bulletin of the Geological Society of America. 55: 1279-1332.

[Stieg, S.] 1998. Ammonia-selective electrode method. *In* L.S. Clesceri, A.E. Greenberg, and A.D. Eaton (ed.) Standard methods for the examination of water and wastewater. 20^{th} ed. Part 4000, p.106-107. American Public Health Association, Washington, D.C.

Troeh, F.R. and L.M. Thompson. 1993. Soils and soil fertility. 5^{th} ed. Oxford University Press, New York, NY.

Vitousek, P.M. 2004. Nutrient cycling and limitation: Hawai'i as a model system. Princeton University Press, Princeton, NJ.

Wetzel R.G. 2001. Limnology: Lake and river ecosystems. 3rd ed. Academic Press, San Diego, CA.

Wong M.F. 1996. Analysis of streamflow characteristics for streams on the island of Tutuila, American Samoa. USGS Water-Resources Investigations Report 95-4185. Honolulu, HI.