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Nutrient Chemistry of the Coastal Waters of Guam

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Abstract—Concentrations of nitrate + nitrite (NO_x), reactive phosphate (RP), silica, iron, and chloride in Guam's aquifer, rivers, and coastal waters have been surveyed at various sites between February 1988 and September 1990. Nearshore waters to leeward (west coast) are enriched several fold over those to windward, and are more rapidly depleted and attain lower concentrations with distance from shore. Also, waters within 0.1 km of shore are enriched in NO_x and Si^- over those 0.5 to 8 km offshore, especially to leeward. River plumes, essentially all of which occur within a 10 km region, rarely discharge past the reef crest, except during rain that lasts several days. Sills at river mouths shoreward of reef moats entrain terrigenous material in the oligohaline zone that is recycled through estuarine plankton. Total annual runoff from the southern rivers that drain the lateritic southern province is approximately equal to aquifer leakage from the equally-sized northern carbonate plateau. Because the two terrains have distinct geochemical properties, both the type and amount of nutrients delivered to the coastal zones of each province are quite different. Further, individual aquifer subbasins have distinct Si^-/Cl^- fields. As a result, significant differences in biological community structure and production may occur between windward and leeward sides as well as between lateritic and carbonate provinces, but dramatic physical differences between the two coasts makes testing of hypotheses extremely difficult.

Introduction

The "island mass effect" has been described as an enrichment in plankton due to nutrient enrichment of waters near islands (Doty & Oguri 1956, Dandonneau & Charpy 1985). This effect occurs regardless of whether the island is a high volcanic one with rivers or an atoll without them (Sander 1981). At Guam, two types of runoff occur, but other than studies of single sites (e.g. Lassuy 1979, Matson 1991), neither the chemistry of the coastal waters nor fluxes from the two provinces has been reported. Southern rivers drain lateritic/argillaceous terrain, while in the north there are no rivers on the carbonate plateau. Instead, the massive, karstic, carbonate plateau is underlain by an aquifer that is divided into several subbasins that leak, into the coastal zone, large amounts of brackish waters

from the mixing or transition zone that are rich in Si^- and NO_x and often in Fe and P. While the general effects of rivers are well-known and obvious, the impact of groundwaters has not been generally appreciated (but see Johannes 1980, D'Elia et al. 1981, Lewis 1987, Matson 1987, 1989a, 1991). This report provides the first general survey of the nutrient chemistry of Guam's coastal waters, compares nutrient fluxes from the two distinct terrains, and offers a discussion of the possible reasons for observed differences between windward and leeward waters.

Materials and Methods

THE STUDY SITES

Surface waters were taken from rivers, aquifer beach seeps, wells, moats, lagoons, and on leeward and windward transects hundreds to thousands of meters from shore (Fig. 1). The Ylig and Pago (two of the largest rivers) were sampled during storms that produced visible turbidity within the estuaries and during dry season stratification. Extrapolations of total river runoff were made from discharge data from the Ugum River, which has the only continuously-operating gauging station on Guam. A summary of the sites and locations is given in Table 1.

SAMPLING AND ANALYSIS

All samples were obtained in LPE bottles that had been acid-cleaned and subsequently rinsed at least four times on site with ambient waters. Bottles for offshore samples were also soaked for 10 to 30 min on-site prior to rinsing. Bottles were placed in the shade at ambient temperatures and returned to the Marine Laboratory usually within 4 hours. Nutrients were analyzed either immediately or within 24 h on refrigerated samples. Samples, except for some river waters, were not filtered because of normally insignificant particle density and the potential electrostatic problems associated with ions in waters made particle-free by filtration (A. Knapp, Bermuda Biol. St. Res., pers. comm.).

All data are reported in μmol l^{-1} (μM) unfiltered water (except where noted), except salinity (‰), which was calculated from Cl^- assuming 550 mM $Cl^- = 35.0$ ‰ (Stumm & Morgan 1981). Subsamples for analysis of nitrite plus nitrate (i.e. NO_x) were shaken for >2 hr in 20 ml scintillation vials with spongy Cd (Jones 1984), and, except for a few aquifer seep waters, nitrites were never greater than 0.005 μM. Ammonium was measured with an Orion probe, but concentrations were usually less than the 2–5 μM detection limit except in sewage effluents, which were as high as 2 mM. Silica and reactive P (RP) were measured with molybdate according to Parsons et al. (1984), and iron was measured with Ferrozine (Murray & Gill 1978). Doubly-deionized reverse-osmosis water, deionized dehumidifier condensation water, or windward offshore seawater was used as a reagent blank where appropriate. Sensitivity was increased in low nutrient waters by using 5 or 10 cm quartz spectrophotometer cells. A summary of detection limits and relative precision (i.e. precision [± 1 S.D.] of replicates at concentrations 5 times the detection limit) is given in Table 2.

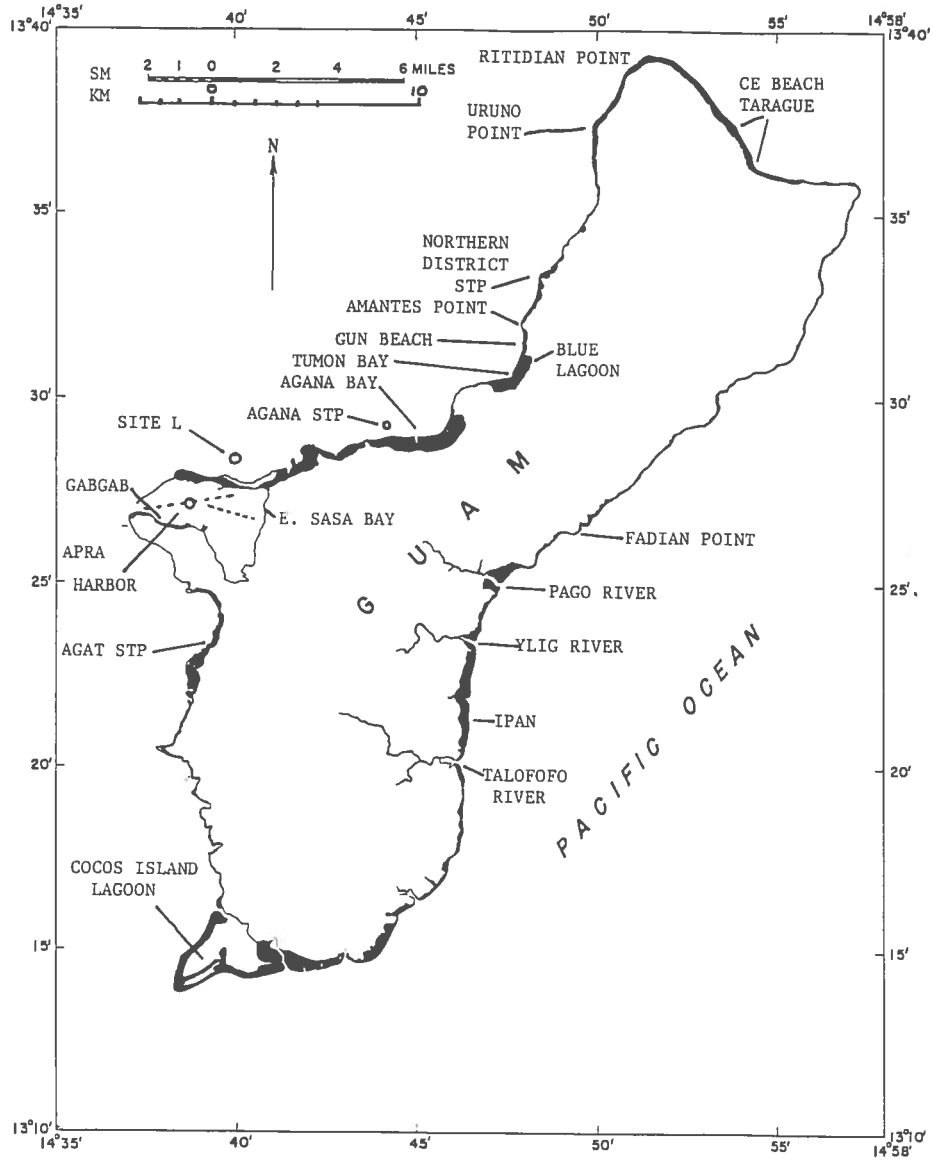


Figure 1. Map of Guam showing the study sites.

DISCHARGE, EVAPOTRANSPIRATION, AND LEAKAGE CALCULATIONS

Discharge data for the Ugum River watershed (5.4% of southern Guam's area) were obtained from the U. S. Geological Survey (USGS), and extrapolated to the entire area of southern Guam. River discharge to the southern coastline (per m of perimeter per day) was calculated by dividing the average daily discharge figure for each month by the 80,000 m perimeter (based on USGS topographic

Table 1. Sampling locations and dates.

Site	Samples	Date
Rivers:		
Ylig	Salinity, nutrients	25 October 1988
Ylig	Salinity	4 September 1990
Pago	O_2, salinity	10 February 1990
Pago	Salinity	4 September 1990
Talofofo	Salinity	4 September 1990
Aquifer waters:		
Tumon Bay	Salinity, nutrients	May 1988–Sept 1989
CE Beach	Salinity, nutrients	June 1988–May 1989
Fadian	Salinity, nutrients	June 1988–May 1989
Apra Harbor	Salinity, nutrients	August 1990
Northeast coast	Salinity, nutrients	July, August 1990
Northwest coast	Salinity, nutrients	Feb 1988–Sept 1988
Sewage effluents	Salinity, nutrients	1989 (quarterly)
Ipan reef flat	Salinity, nutrients, productivity	Spring 1989
Cocos Lagoon	Salinity, nutrients, productivity	Spring 1989

Table 2. Chemical methods, detection limits, and precision.

	Method	Detection Limit (μM)	Relative Precision
NO_x	Cd reduction (Jones 1984)	0.010	±0.005
Si^-	Mo (Parsons et al. 1984)	0.50	±0.1
RP	Mo (Parsons et al. 1984)	0.005	±0.001
Fe	Ferrozine (Murray & Gill 1978)	0.02	±0.01
NH_4^+	Orion probe	2	±1
Cl^-	$AgNO_3$ (Automated Chloridometer)	1,000	±9

map of Guam [1:50,000, 1978 ed.], not including the perimeter of Apra Harbor) for an estimate of $m^3\ m^{-1}$ of shoreline d^{-1}.

For estimates of evapotranspiration, it was assumed (Barrett et al. 1982, unpublished report to Guam E.P.A.) that (1) insignificant amounts of water are stored in the southern province, and (2) the difference between rainfall and runoff from the southern rivers could therefore be assumed to be equal to evapotranspiration (43% of rainfall). For the period 1984 to 1989, I calculated average evapotranspiration to be 49% of rainfall, based on rainfall records obtained from Naval Oceanography Command Center (NOCC), located at Naval Air Station, Guam, and runoff data for the Ugum River (tens of km south of the rain gauge). Seasonally, this figure ranges between 20 and 60% of rainfall.

For an estimate of leakage from the northern aquifer, it was assumed that waters leak into the coastal zone from the aquifer system around the entire periphery of northern Guam (ca. 256 km^2). Monthly pumping of drinking water

(ca. 25 mgd [or 94750 m^3 d^{-1}], Public Utilities Agency of Guam estimate) and evapotranspiration (49%, above) were subtracted from the 45 year average monthly rainfall record obtained from NOCC. Average monthly leakage was divided by the perimeter of the northern platform (57,000 m) and expressed as m^3 m^{-1} of shoreline d^{-1}. Thus, aquifer leakage is here considered to equal net annual recharge.

Results and Discussion

RIVER AND AQUIFER DISCHARGE

River discharge extrapolated to all of southern Guam is shown in Figure 2. Between October 1984 and March 1989, discharge ranged up to 158 million m^3 per month; up to 65 m^3 is delivered to each m of the coast per day. Although the northern and southern provinces of Guam are of similar area, the perimeters are different due to the many river mouths and embayments in the south. Nonetheless, average monthly freshwater discharge from the rivers and leakage from the aquifer are similar (Fig. 3). These calculations do not, however, indicate what happens to these waters (or their contents) after arrival at the shoreline. Many different geo- and bio-chemical reactions may take place, especially in river estuaries (as opposed to aquifer estuaries) as a function of discharge rate, tidal stage, and morphometry of the receiving zone basin (discussed below).

River discharge responds quickly to rainfall because of the small size of Guam's watersheds and the relatively impervious nature of the lateritic soils (Fig. 4). Frequently, large storms at night produce runoff events that are flushed into the estuaries by sunrise: they are not detected until several months later when gauging station data are inspected. When significant rain falls after dry periods,

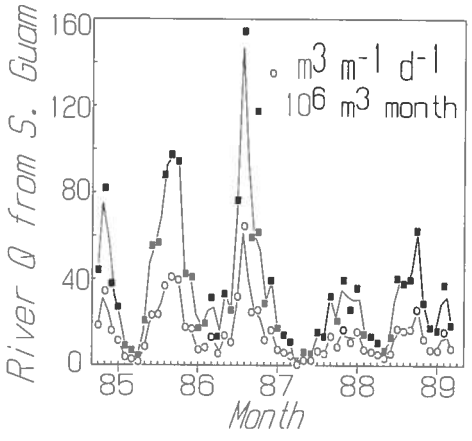


Figure 2. Extrapolated river discharge (Q) from all southern Guam's rivers. Data are presented in units of total m^3 $month^{-1}$ and in m^3 m^{-1} of southern shoreline (ca. 80,000 m) d^{-1}.

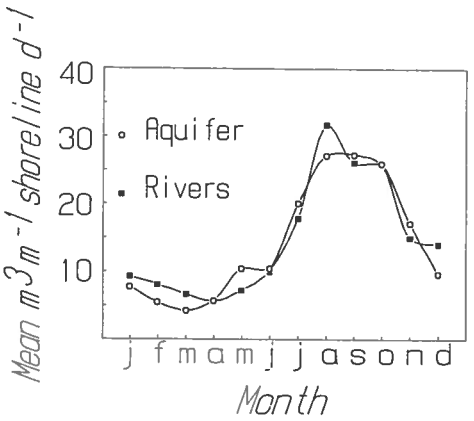


Figure 3. Average monthly discharge (1985 to 1988) from all rivers and the aquifer m^{-1} of shoreline d^{-1}. The northern shoreline perimeter is ca. 57,000 m.

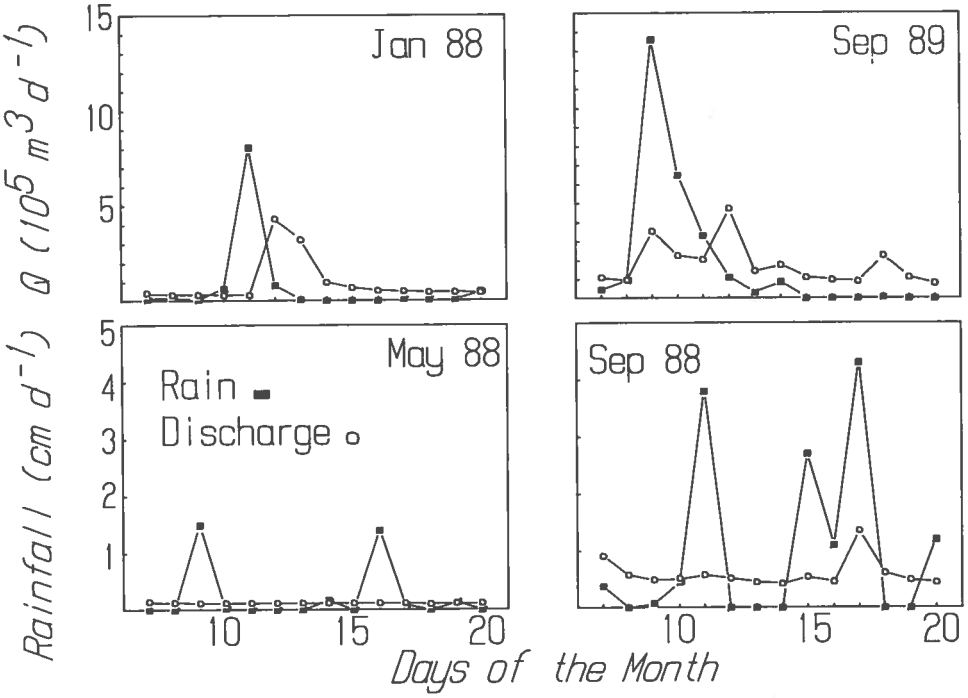


Figure 4. Ugum River hydrographs and Naval Air Station rainfall data for several rainfall events in the wet (June to December) and dry (January to May) seasons. The data for January 1988 are from Typhoon Roy.

such as during Typhoon Roy in January 1988 and a record rain on 2–3 September 1990 (discussed below), rivers generally respond within 5 to 8 hours and quickly return to baseflow. After saturating rain events, especially those that occur during the wet season, interflow and groundwater continue to infiltrate the stream beds and extend both the time and rate of return to baseflow (e.g. September 1989). When soils are wet but below their maximum water holding capacity, some rainfall events may produce little if any runoff (e.g. May and September 1988). This can be called stored water but because the soils dry out very quickly and are quite thin, it is assumed that evapotranspiration is much more important than this so-called stored water.

Estimates of discharge of aquifer water to the coastal zone are tenuous at best, but have been corroborated with several independent measurements (using weirs) of discrete flow at beach seeps (Emory 1962, Zolan 1982, Matson 1989a), subsurface coastal sediment salt gradients, and pieziometers in Tumon Bay sediments (Matson, 1990). These data support earlier theoretical considerations (Mink 1976, Contractor et al. 1981), especially hydrological constraints and data that validate "steady-state" models of aquifer volume, input, and output (Contractor & Srivastava 1989).

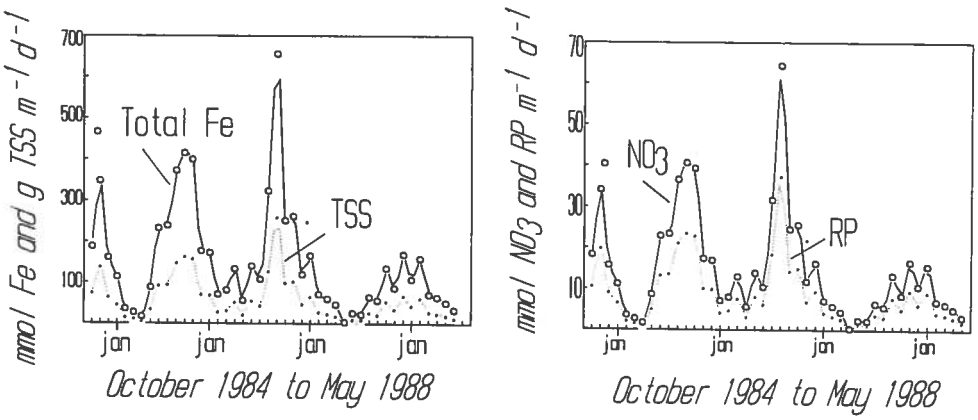
Leakage is not uniform throughout the northern perimeter and discrete areas of high leakage rates occur through fissures and cracks throughout the northern

platform (Emory 1962). However, regardless of whether leakage occurs from discrete seeps or from the entire mixing zone at the periphery of the aquifer, the same amount of water leaks out because leakage is controlled by water recharge, head which is sequentially controlled by rainfall, and evapotranspiration. Variations in and characteristics of aquifer discharge are discussed in a separate section below. Examples are given for discrete beach seeps at which flow can be measured.

EXPORT OF RIVER-BORNE MATERIAL TO THE COAST

The estimated average daily export of Fe, total suspended solids (TSS), NO_3^- and RP to a hypothetical meter of shoreline per day (as above) is given in Figs. 5 and 6. The nutrient data were obtained from annual averages in Zolan & Ellis-Neill (1986). Flux of TSS ranges up to 250 g m^{-1} of shoreline day^{-1}, while Fe was as high as 650 mmol m^{-1} day^{-1}. Nitrate and RP export were as high as 65 and 38 mmol m^{-1} day^{-1}.

The effect that these exports have on the coastal reef system of southern Guam is not well known. Calculated river inputs to the system have been made (Matson 1989b), and are based on a hypothetical reef that is 500 m from shore in 1 m of water. These calculations show that annual input from rivers approximately equals the contents within the top few cm of sediment, but neither deep core nor sedimentation data have been obtained. Further, no comparisons have yet been made of productivity levels or of coral feeding mode between southern (river influenced) and northern (aquifer influenced) reef communities. Thus it is difficult to assess the potential impact of this flux on the coral reef community. Stable isotope analysis (Fry & Sherr 1983), incorporation of fulvic acids into corals (Boto & Isdale 1985, Klein et al. 1990), and other techniques could be used to identify any differences between nutrient and energy flows in these two types of systems.

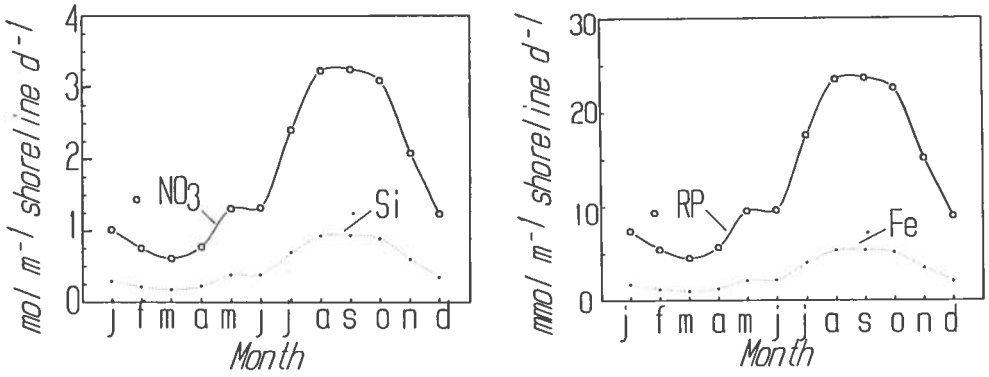


Figures 5 and 6. Figure 5 (left). Average daily discharge of iron and total suspended solids (TSS) m^{-1} of shoreline d^{-1} from all of Guam's rivers. Iron data from Matson (1989 and unpublished) and Zolan & Ellis-Neill (1982). TSS data from Zolan & Ellis-Neill (1982). Figure 6. As in Figure 5, for nitrate and reactive P.

GENERAL CHEMISTRY AND HYDROLOGY OF THE AQUIFER

Aquifer hydrology and nutrient chemistry are discussed elsewhere (Matson in prep.), but the salient features will be extracted here for a general comparison with river export data. Calculated average daily nitrate flux ranges up to 3.2 mol m^{-1} of shoreline d^{-1} (Fig. 7), which is up to 100 times greater than from rivers to the southern coastal zone. This is due to the extensive enrichment of the aquifer waters with nitrate (average of 114 μM, and up to 450 μM). Nitrate is produced in the thin soils via oxidation of organic N and NH_4^+ (Matson 1987). In contrast, reactive P export from the northern province is approximately equivalent to that to the southern coast (Fig. 8). This is because only small amounts of RP can be dissolved into fresh aquifer water that is in contact with apatite in the carbonate plateau at sealevel and to the general lack of P in lateritic soils of the south. Silica export in aquifer waters ranges from 0.25 to 1 mol m^{-1} d^{-1}, which is about 0.3% of that from the Si^--rich southern soils (Matson 1989b). The enormous difference in iron and silica exports between the two provinces is obviously due to the large supply of Si^- in the volcanic soils of the south. In contrast, the soil layer of the northern plateau is only ca. 10 to 80 cm thick so that less silica and iron are available for dissolution and transport into the aquifer.

While differences between northern and southern exports are rather easily described, differences among rivers or among the several subbasins of the aquifer are less obvious. Zolan & Ellis-Neill (1986) provide a detailed study of metal and nutrient concentrations in several of the larger rivers. Here I show that, while nitrate concentrations of aquifer waters change rapidly in response to rainfall events (Matson 1989a), the silica and chloride concentrations in beach seep and coastal well waters are both less variable and are typical of distinct subbasins. In Fig. 9, silica *vs.* salinity data are plotted from four different subbasins, each of which has a distinctive Cl^-/Si^- field. At Tarague (CE Beach), on Guam's north coast, beach seep salinity is routinely ca. 1 ‰, with Si^- between 10 and 20 μM.



Figures 7 and 8. Figure 7 (left). Average daily leakage of nitrate and silica m^{-1} shoreline d^{-1} from the northern aquifer. Aquifer leakage calculations are described in the text, and nutrient data are averages of those at the beach seeps at Tumon Bay (Blue Lagoon) and CE Beach (Tarague) and from the freshwater well at Fadian. Figure 8. As in Figure 7, for reactive P and iron.

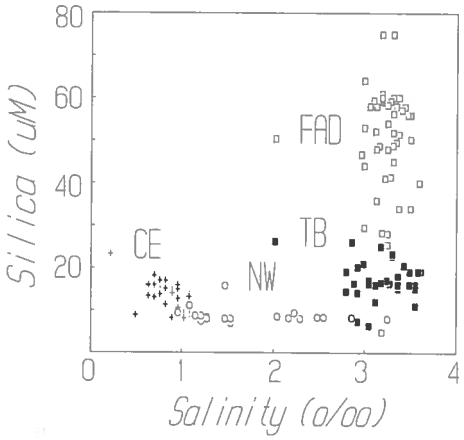


Figure 9. Silica concentration *vs.* salinity of the beach seeps (CE Beach, Tumon Bay, and Northwest coast) and wells (Fadian).

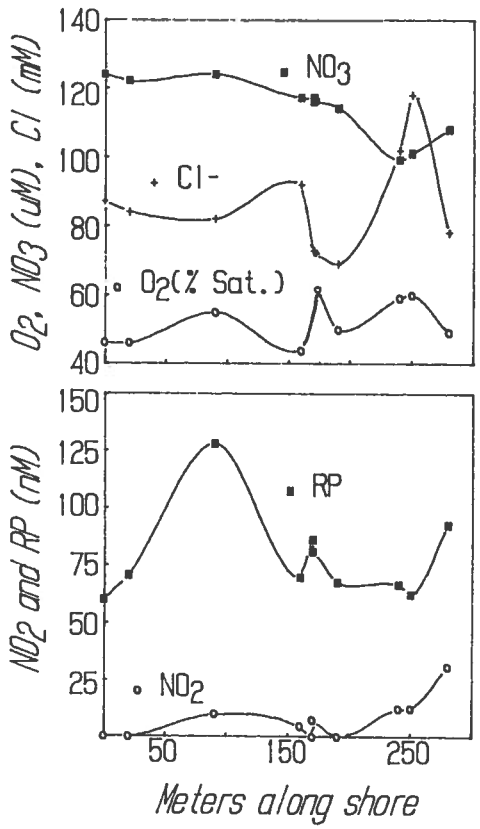


Figure 10. Variability in the chemistry of beach seep waters along shore in northeastern Tumon Bay. Meter zero is at the northern end of the Reef Hotel property.

On the northwest coast (NW), both the salinity range and content are greater (up to 3.3 ‰), but Si^- is routinely lower, around 10 μM. In Tumon Bay (TB), beach seep waters were studied in more detail (discussed below, Matson 1991), have a more variable Cl^- content, and the range in Si^- content is greater than at both the NW and CE sites. At the Fadian aquaculture facility, the freshwater well has a Cl^- content which is curiously similar to that at TB (which presumably drains directly off the top of the sealevel mixing zone), but the Si^- data average 2 to 3 times higher. These higher Si^- concentrations at Fadian are presumably caused by the flow of percolating rainwater over volcanic basement rock prior to reaching the well. This so-called well is actually in a cave a few meters above sealevel.

Chemical characteristics of individual, routinely-observed, discrete, aquifer beach seeps that are only a few tens of meters apart also vary remarkably. For example, data in Fig. 10 were all taken within an hour along a 300 m long transect northeast from the Reef Hotel to the Okura Hotel on Tumon Bay. In general, the differences among them can be attributed to leakage from discrete fissures and cracks in the underlying limestone from isolated, constant sources.

The chemistry of these individual seeps is described in Table 3. Of special interest was the depletion in O_2 content (saturation $\approx$ 245 μM) and the relatively high levels of nitrite, the production of which consumes 2 mol oxygen per mol NH_4^+. A linear regression of oxygen depletion from saturation on nitrite content was calculated, but the slope of the line was not significantly different from zero. However, a scatter plot (not shown) revealed an intriguing trend that might suggest a significantly positive relationship if more data were available. Such a relationship may indicate that both oxygen-depleted waters and soluble nitrite are exported into the aquifer simultaneously in percolating waters from surface soils. The lack of subsequent nitrite oxidation to nitrate in the aquifer may indicate that water residence time is too short for this reaction to proceed to completion. Further, it might provide direct evidence for rapid (i.e. hours to days) flow of surface soil water through the aquifer to the coastal zone. Alternately, it might provide evidence for incomplete oxidation of ammonium (to equally soluble nitrite) in relatively oxygen-poor soil water.

Similar changes can also occur within a tidal cycle (Fig. 11). Nitrate and chloride data were collected approximately every 0.5 hr for half tidal cycles in April 1987 and June 1989 from the largest beach seep in Tumon Bay (ca. 100 m southwest of the Okura Hotel). Samples were collected beginning at low tide until the seep was submerged by flood tide waters. Within each tidal cycle, Cl^- and

Table 3. Chemistry of individual aquifer beach seeps between the Reef and Okura Hotels, Tumon Bay

Station Number[a]	mM Cl^-	μM NO_3	μM NO_2	μM RP	μM O_2	pH
BL-1a	69	122	0.018	0.55		7.05
BL-1b	69	115	0.071	0.68		7.38
BL-2	69	117	0.018	0.63	139	7.32
BL-3	69	118	0.15	0.85	141	7.40
BL-4	70	115	0.071	0.61	138	7.30
BL-5	69	113	0.005	0.69	131	7.38
BL-6	70	115	0.045	0.71	131	7.47
BL-7	72	117	0.005	0.77	128	7.34
BL-8	71	115	0.15	1.1	130	7.38
BL-9	72	116	0.005	0.82	126	7.40
BL-10	73	117	0.005	0.86	125	7.40
BL-A	87	124	0.005	0.60	114	7.38
BL-B	84	122	0.005	0.71	114	7.30
BL-C	82	124	0.097	1.3	136	7.43
BL-D	92	117	0.045	0.70	109	7.40
BL-E	72	116	0.071	0.81	155	7.50
BL-F	70	114	0.005	0.68	123	7.39
OK-A	102	99	0.12	0.67	145	7.38
OK-B	118	101	0.12	0.62	147	7.36
OK-C	78	108	0.31	0.93	123	7.42

[a] Low tide beach transect from Reef Hotel to Okura Hotel.

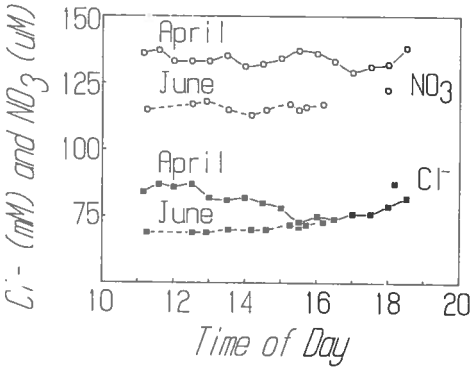


Figure 11. Temporal variation in the chemistry of the Blue Lagoon beach seep in Tumon Bay in April 1987 and June 1989.

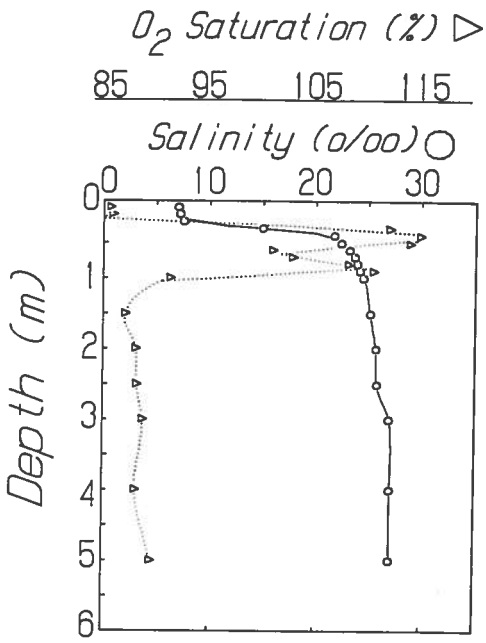


Figure 12. Salinity and oxygen *vs.* depth in the Pago River estuary at the Rte. 4 bridge, February 1990.

NO_x change as a result of mixing of aquifer and seawater within the nearshore mixing zone of the aquifer that occurs several meters back under the beach. The difference in the average nitrate concentrations in these two tidal cycles is attributed to (1) tidally-forced changes in the position of the mixing zone and (2) the previous rainfall history and subsequent changes in the rates of soil nitrification (Matson 1989a, in prep.).

CHARACTERISTICS OF THE RIVER MOUTHS AND ESTUARIES

Guam's rivers are strongly stratified regardless of season due to the essentially ubiquitous occurrence of cross-mouth bars at the river mouths, usually within a hundred meters of the Rte. 4 bridges. These bars are largely constructed of marine sediment when river discharge is low (dry season) and river sediment when discharge is high. Evidence of this has been obtained from sediment cores obtained throughout the Ylig and oligohaline zone of the Pago. These cores (not shown) reveal obvious "laminations" of alternating layers of carbonate and terrestrial mud. This situation has been described for major continental estuaries (Meade 1972), and is more easily seen in these tropical settings because of the presence of carbonate.

The bars or sills, resembling those of fjords, increase the residence time of water upriver of them to as long as months if significant runoff does not occur. Bottom water salt wedge intrusion is limited to that which can spill over the sills upriver on the flood tide. For example, hydrocast data taken in February 1990 (the dry season) from the Pago River at the Rte. 4 bridge show strong vertical

stratification and the absence of full strength seawater to the bottom (Fig. 12). Several hundred meters downriver of this 5 m deep site, the mouth of the river is <1 m deep, seaward of which full strength seawater occurs at high tide.

In fact, even near-record rainfall, such as that which occurred on 2–3 September 1990 (almost 11 inches in 24 hr) does not erode the pycnocline at the river mouths by more than about 0.5 m. Below 1 m, salinity in the Pago River 2 days after this record September 1990 storm was essentially the same as in February, 8 months earlier and well into the dry season (Fig. 13). Strong pycnoclines were observed on the same day after this September storm under the Rte. 4 bridges over the Ylig and Talofofo Rivers (Fig. 14).

Storms of this magnitude can discharge 0.2 to 0.8 m deep plumes of sediment-laden water several km seaward of the reef front. Two particular examples may suffice. First, a transect of the surface 0.2 m of the Ylig River on 25 October 1988 after several days of rain shows a linear increase in salinity (percent seawater) and decrease in river-borne nutrients with distance to a point 2 km seaward of the reef front in essentially oceanic waters (Fig. 15). That the data are essentially superimposable when plotted against salinity (‰) (Fig. 16), shows that, during large storms, salinity increases with distance (not with receiving water volume) and that little vertical mixing occurs either upriver or in the estuary as the surface water plume spreads out and is diluted in the wide bay. Thus, during large storms, the residence time for surface river water nearshore is short.

Second, during exceptionally calm weather in August of 1990, samples were obtained on a northeast cruise to windward for offshore seawater upwind of

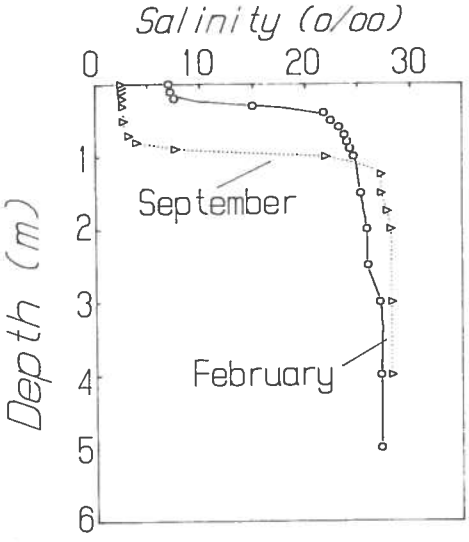


Figure 13. Salinity *vs.* depth in the Pago River estuary at the Rte. 4 bridge during the dry season (February 1990) and 2 days after a large storm (11 inches of rain in 24 hours) in September, 1990).

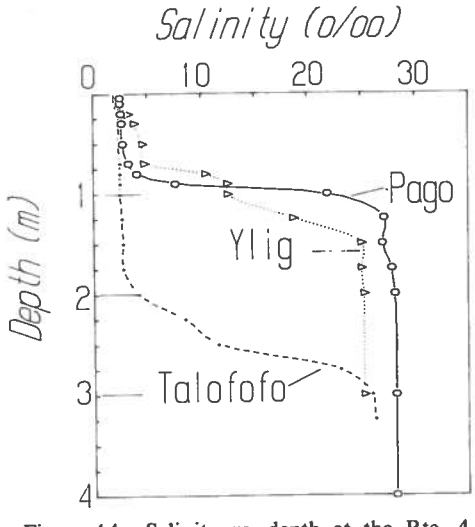


Figure 14. Salinity *vs.* depth at the Rte. 4 bridge on the Pago, Ylig, and Talofofo River estuaries 2 days after 11 inches of rain in 24 hours in September 1990.

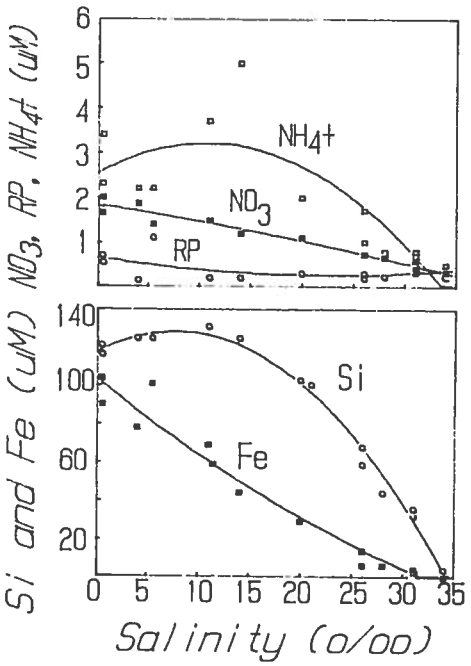


Figure 15. Nutrient concentrations in the surface waters (0.2 m) of the Ylig River estuary *vs.* distance from the Rte. 4 bridge after a large storm on 25 October 1988.

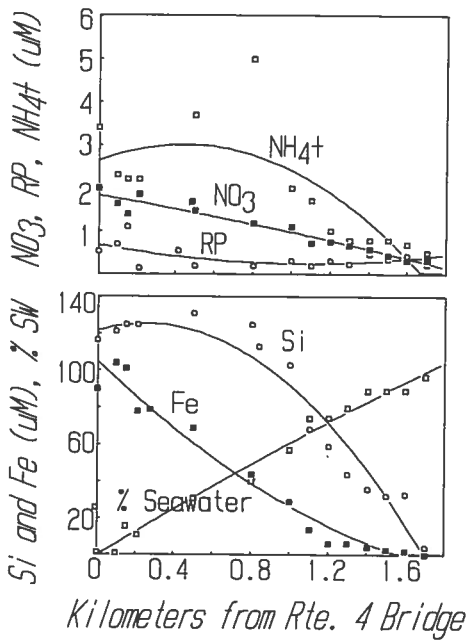


Figure 16. As in Figure 15, *vs.* salinity.

Guam. Approximately 5 km from the mouth of the Ylig, a large (several km^2), isolated, dispersed, and floating mat of swordgrass and bamboo was encountered. It resembled a "slick" of organic-rich water in its iridescence and was bordered by several hundred bamboo trunks. Five surface water samples were taken within this area and are compared with 8 taken seaward and outside of the area within the next hour (Table 4). The error of individual analyses of Cl^- is ± 5.5 mM at 550 mM Cl^-, so that the differences between means are actually not significant. Only NO_x and Si^- were significantly different, while RP values were highly variable and statistically the same (this sort of RP variability in offshore waters is discussed below). It is postulated that, during the previous night, sufficient rainfall and runoff occurred during low tide so as to cause a "blowout" of a bamboo dam that had developed over perhaps several months upriver in the Ylig. This dam and its associated debris floated out of the river directly into the sea in the absence of sufficient wind to keep this flotsam onshore. During the normal tradewind weather, these "blowouts" are normally returned to and stranded on the beaches of the entire southeastern coast, and rarely get past the reef front. Thus it appears that coastal waters of the southern province are most affected by river runoff only during major events, and rarely by steady flux of gradually mixed estuary water.

All three major rivers discussed above have deep narrow channels that open into wide shallow bays (reef moats) that reduce river water velocity, and increase

Table 4. Chemistry of the seawater within the bamboo flotsam and adjacent offshore waters, August 1990.

	mM Cl^-	μM NO_x	μM RP	μM Si
Bamboo (N=5)				
$\bar{X}$	553	0.146	0.254	4.18
±1 SD	2.9	0.014	0.066	0.48
Offshore (N=8)				
$\bar{X}$	560	0.113	0.210	2.96
±1 SD	1.6	0.027	0.069	0.21
P value (ANOVA[a])	0.0004	0.0263	0.283	0.0000

[a] Comparison of equality of the means, variances unequal in Welch and Brown-Forsythe tests.

spreading, chemical flocculation, and deposition nearshore. This is especially true for Fe, Si^- and P (Eckert & Sholkovitz 1976, Liss 1976, Morris et al. 1978). As a result of this morphologically controlled flow during non-storm runoff periods, these rivers generally have very low exchange ratios, long turnover times, and develop a rich plankton, much of which may be recycled, consumed, and deposited within the estuaries. This scenario provides, to the estuaries, terrestrial material that has been recycled through plankton in the lower estuary and reef flat that does not resemble the original material that eroded from land. Direct evidence of this has been obtained with stable isotope data from waters and sediments of the Ylig (Matson 1990), Chesapeake waters (Sigelo et al. 1982), and Pamlico Sound, the largest barrier beach sound in North America (Matson & Brinson 1990). Such isotope data support the conclusion that homogenous, linear, downriver distributions of the distinctively terrestrial isotopes of C and N occur due to long turnover times and recycling through plankton and benthos. This conclusion can be inferred for P, Fe, and Si^- as well.

NUTRIENT CHEMISTRY OF APRA HARBOR

On the leeward (west) side of Guam, the effects of river discharge on coastal nutrient chemistry can also be demonstrated with transect data from East Sasa Bay to the mouth of Apra Harbor (Fig. 17). These data were obtained a week prior to the record 11 inches of rain that fell on 2–3 September 1990, but after exceptional wave and groundswell turbulence within the harbor due to passing of another storm. This produced strong vertical mixing within the harbor waters down to 20 m with weak evidence of residual stratification at 30 m (Fig. 18). The accumulations of sediment-derived nitrite and nitrate in the bottom waters (Fig. 19) indicate that vertical mixing was insufficient to destroy gradients that are maintained by nutrient regeneration in and flux from the sediments. The curve for Fe may be interpreted to represent particulate fractions that accumulated at the bottom of the mixing zone above the layers that were still stratified and which had high levels of NO_x.

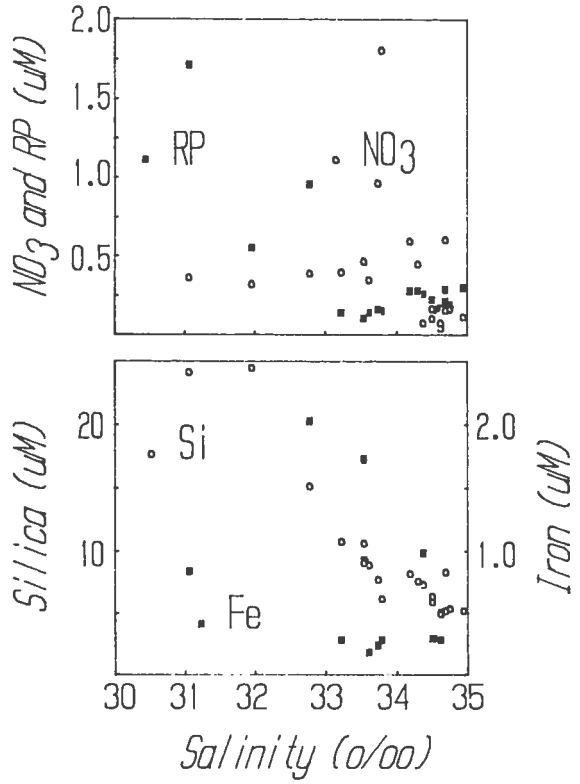


Figure 17. Nutrient concentrations *vs.* salinity over a transect from the commercial port to the mouth of the Apra Harbor, August, 1990.

SEAWATER CHEMISTRY TO WINDWARD

Offshore waters to the northeast of Guam were sampled on three occasions in July and August of 1990 on two parallel 60° magnetic transects parallel to and at distances of 4 and 8 km from shore (Fig. 20). Salinity was almost always between 34 and 36 ‰, except nearshore where aquifer water decreased salinities to as low as 33.4 ‰ (described below). Reactive P showed no systematic relationship with salinity (at this or any other site), but offshore Si^- increased (almost doubled) between 34.5 and 36.0 ‰. This Si^- increase plus the simultaneous decrease in NO_x implies that N from the aquifer stimulated Si^- uptake by nearshore epiphytic diatoms, or that net Si^- dissolution occurred at the higher salinities. The lower NO_x values are considered normal for offshore waters, while the higher values are considered to be due to enrichment with groundwaters that persists after Cl^- dilution is undetectable.

SEAWATER CHEMISTRY OF THE NORTHWEST COAST

Data from sites between Gun Beach (just north of Gognga Cove in Tumon Bay) and Uruno Point are given in Fig. 21. In comparison with the northeast coast data (Fig. 20), nitrate concentrations are substantially higher and silica

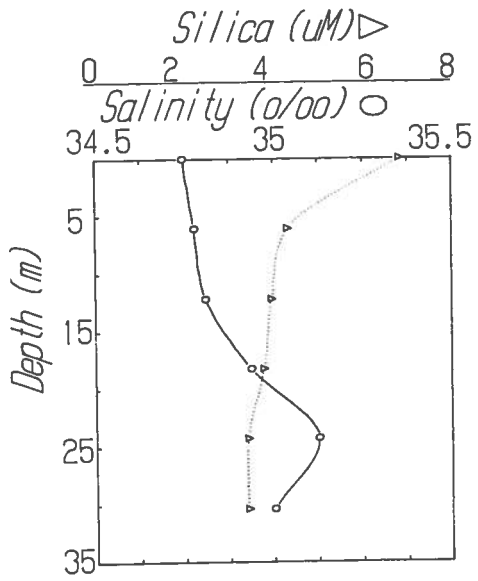


Figure 18. Silica and salinity *vs.* depth in central Apra Harbor at a site due north of Gabgab Beach.

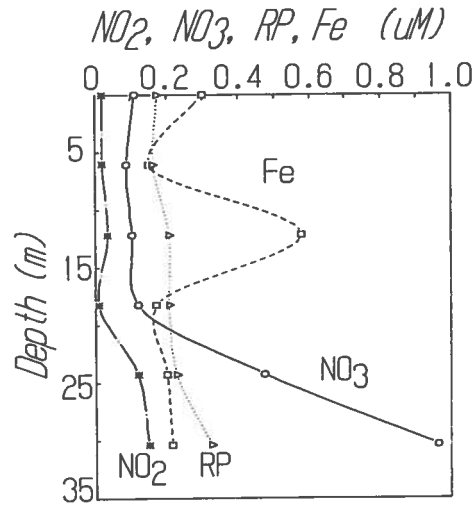


Figure 19. As in Figure 18, for nitrite, nitrate, reactive P, and iron.

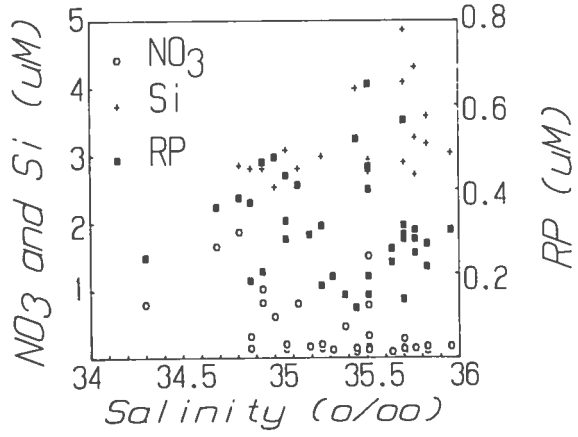


Figure 20. Nutrient concentrations *vs.* salinity of surface waters (0.2 m) off the northeast coast of Guam, July 1990. Only waters with salinity >34 ‰ are shown.

concentrations are slightly lower. Specifically, on the windward (northeast) coast, nitrate contents were rarely higher than 1 μM, although they range to 5 μM above salinities of 34 ‰ on the leeward (northwest) coast. Leeward coast Si^- levels rarely exceed 3 μM, while to windward, they range up to 4 or 5 μM.

This relative enrichment in leeward N and depletion in Si^- possibly results from aquifer leakage that is both richer in N and poorer in Si^- and which spreads

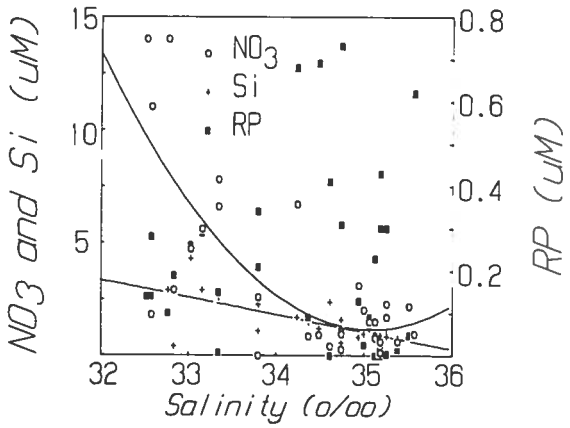


Figure 21. Nutrient concentrations *vs.* salinity of nearshore (<100m of shore) surface waters (0.2 m) off the northwest coast of Guam between Gun Beach and Artero's Beach, 1987 to 1990. Only waters with salinity >32 ‰ are shown.

out to leeward and is entrained nearshore. Because of the extensive excursions of volcanic basement above sealevel on the windward coast, aquifer water chemistry should be different from that on the leeward coast, where volcanic basements are well below sealevel. On the windward coast percolating groundwater may gain Si^- and lose nitrate as it flows over impervious, Si^--rich, volcanic basement prior to reaching sealevel. Alternately, diatom biomass and Si^- uptake on the leeward coast (in a regime of excess N) may be greater due to the occurrence of more calm conditions and more extensive shallow water reefs. The high variability among the phosphate data in waters of both coasts presumably represents P that is resuspended and dissolved from carbonate sediments in turbulent nearshore waters.

CHEMISTRY OF TUMON BAY WATERS

Figure 22 contains a representative suite of Tumon Bay data, not including a large number of samples of "red-tide" waters that are discussed in a companion paper (Matson 1991). Phosphate data show no obvious patterns that could be associated with runoff from construction sites, aquifers, or storm drainage. In contrast, relatively Si^--rich material must be supplied to northeastern Tumon Bay in order to increase concentrations to as high as 17 μM at 33 ‰. This is the same Si^- content as the beach seep water (Fig. 9) so that dilution with relatively Si^--poor seawater has not lowered the Si^- content. However, the range in Si^- contents is great (from 1 to 17 μM), so that either intermittent enrichment due to runoff events or uptake in blooms is implied. Nitrate contents cluster around 1 to 5 μM at salinities >32 ‰, but can range up to 19 μM when salinity is as low as 28 ‰. Thus it appears that Tumon Bay water chemistry is largely controlled by aquifer and other subsurface discharge and not by surface runoff.

Actually Tumon Bay is a type of estuary that is unique to tropical carbonate land masses. Its brackish waters are due almost exclusively to groundwater that

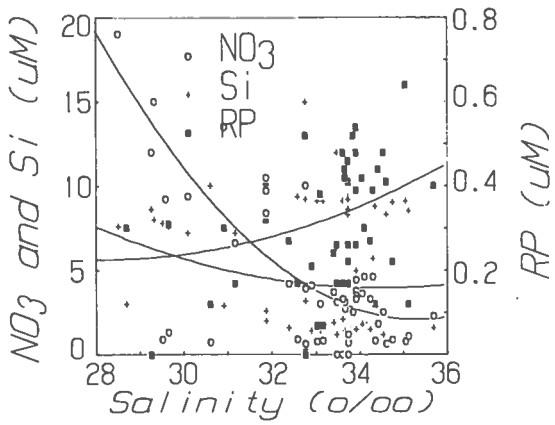


Figure 22. Nutrient concentrations *vs.* salinity in Tumon Bay, 1986 to 1990, for salinities >28 ‰.

Table 5. Nitrate concentrations (mean ±1 SD) in Guam's coastal waters with salinities >30 ‰ (>470 mM Cl^-).

Site	μM	±1 SD	N
Windward			
Ipan reef flat	0.52	(0.43)	25
transect 0.5 km offshore	0.24	(0.27)	33
transect 4–8 km offshore	0.12	(0.046)	33
Cocos Island lagoon	0.086	(0.087)	17
Leeward			
Tumon Bay	2.1	(0.8)	69
transect 0.1 km offshore	1.9	(2.6)	24
Site L (1–2 km N of Apra)	0.29	(?)	18
transect 5 km offshore	0.014	(0.017)	11

contains virtually no sediment, and very little Fe, reduced N, organic matter, or P in comparison with estuaries that receive surface water runoff. At times, the northeastern corner of the bay has salinities as low as 22 ‰ with nitrate concentrations as high as 40 μM. This typically occurs during calm weather when winds that cascade over the northeast cliff line are not sufficiently strong to drive vertical mixing. Aquifer beach seep water plumes can be transported several hundreds of meters to the barrier reef, essentially intact and strongly stratified. Salinities as low as 20 ‰ have been observed in low tide waters on the reef crest at Tumon Bay among coral heads (A.S. Quenga, thesis in preparation).

COMPARATIVE OFFSHORE/ONSHORE NUTRIENT CHEMISTRY

Nitrate content of waters with salinities greater than 30.0 ‰ are summarized in Table 5. The highest concentrations occur nearshore on the leeward coast (Tumon Bay and the leeward transect 0.1 km from shore), and are caused by

leakage of aquifer waters. Interestingly, the lowest concentrations also occur to leeward (offshore). The ocean waters that flood Cocos Lagoon (off the south shore) within a *Halodule* (seagrass) bed also contain the lowest levels. Site L (a few km north of Apra Harbor, Lassuy 1979) and the waters in the windward transect 0.5 km offshore have equal nitrate contents. On the windward side, nitrates are lower than on the leeward side due to occurrence of volcanic basalts above sealevel on the northeastern shore. These basalts reduce the area of the carbonate aquifer so as to lower its impact on the nitrate content of the adjacent coastal waters in comparison with the leeward northwest coast where volcanic basalts occur below sea level.

The Ipan reef flat (eastern windward shore) and Cocos Lagoon data were taken during diel studies in the Spring of 1989 on single days. Thus, they can be used to demonstrate nitrate variability at single sites due to both biological activity and tidal changes. Nitrogen levels in reef and seagrass communities such as these are probably most significantly affected by ocean water flux, N fixation (especially at Ipan, Matson unpub. data), and nitrification (Wafar et al. 1990). In contrast, the Cocos site is within an atoll lagoon in waters above an extensive seagrass bed. It is likely that net nitrification occurs at this site.

Taken together, windward nitrates are generally lower than those to leeward, but the leeward data have a greater variability (i.e. a range of group means from 0.014 to 2.1 μM). On the windward side, the nearshore average (0.24 μM) is only twice as high as the offshore average (0.12), while to leeward, nearshore averages are much greater than those offshore. Also, offshore leeward data are much lower than those offshore to windward. Even if the Tumon data were eliminated from these comparisons (due to bias from direct and substantial nitrate enrichment by beach seeps), nearshore leeward nitrates are almost 4 times higher than those from nearshore windward (Ipan). Thus, the nearshore-offshore surface water concentration gradient is much greater on the leeward side of Guam.

In Table 6, I summarize nutrient data from all ocean waters (except for Apra Harbor and Fadian), with salinities greater than 34.4 ‰, which is the approximate lower limit for ocean waters near Guam (Tchernia 1980). Ocean waters above and immediately below the thermocline are generally 34.5 ‰, while nearshore within the thermocline, salinity peaks at about 35.1 ‰ (Lassuy 1979). This lower value for nearshore thermocline waters may be caused by lateral exchange of high-salinity aquifer water that occurs below the aquifer's pycnocline at depths of 75–110 m below MSL (Contractor & Srivastava 1989). However, the precision of Cl^- analysis limits the salinity resolution to ± 0.32 ‰ (i.e. 0.9% of the Cl^- content).

In any case, an obvious land effect occurs. To windward, high Si^- and low NO_x nearshore are primarily due to the differences in geological structure between the windward and leeward coasts of the northern carbonate plateau (discussed above). Also, based on observations of biological community sizes (discussed below), total biological activity above the thermocline may be greater and occur in a larger area to leeward and result in more nitrate and silica removal with distance from shore. Accordingly, reactive P levels are higher to windward, pos-

Table 6. Average (± SD) nutrient concentrations (μM) in Guam's coastal waters with salinity > 34.36 ‰ (540 mM Cl^-, except for Apra Harbor and Fadian data).

	NO_x	RP	Si^-	Salinity	N
Northeast offshore (transects July & August)					
$\bar{X}$	0.121	0.270	2.60	35.5	33
±1 SD	0.047	0.094	0.81	0.30	
All Northeast (including nearshore)					
$\bar{X}$	0.268	0.294	2.97	35.4	64
±1 SD	0.366	0.112	0.80	0.33	
Northwest (without STP data)					
$\bar{X}$	1.92	0.198	1.22	35.0	24
±1 SD	2.63	0.217	1.51	0.31	
Northern District STP (quarterly suite near sewage effluent)					
$\bar{X}$	0.872	0.196	No data	35.4	27
±1 SD	1.34	0.227		0.45	
Tumon Bay (central northeastern corner)					
$\bar{X}$	1.81	0.349	5.55	34.7	10
±1 SD	1.20	0.157	3.41	0.43	
East Agana (quarterly suite near sewage effluent)					
$\bar{X}$	1.52	0.190	No data	35.0	40
±1 SD	2.87	0.180		0.99	
Apra Harbor (transects seaward)					
$\bar{X}$	0.381	0.350	8.15	34.1	25
±1 SD	0.379	0.327	5.34	0.97	
Agat (quarterly suite near sewage effluent)					
$\bar{X}$	1.22	0.279	No data	34.6	36
±1 SD	2.29	0.379		1.00	
Ipan reef flat (diel study on windward reef flat)					
$\bar{X}$	0.52	0.11	No data	No data	25
±1 SD	0.43	0.036			
Cocos Island Lagoon (diel study in *Halodule* bed)					
$\bar{X}$	0.086	0.096	No data	No data	17
±1 SD	0.087	0.116			
Fadian Seawater Well (ca. 25 m below MSL, weekly for a year)					
$\bar{X}$	8.54	0.473	7.16	33.8	50
±1 SD	2.13	0.165	1.77	0.80	

sibly due to lower removal rates because of both the occurrence of less nitrate in ocean waters (already removed from upwind waters prior to arrival at Guam?), higher rates of oceanic water flux, and less aquifer water on this upwind side.

Nutrient levels near the three sewage effluents (Table 6) are not very different from other leeward surface waters. Although ammonium and RP levels in the

effluents are often as high as 2 and 0.1 mM, respectively, rapid dilution to ambient levels and full-strength seawater salinity occurs within tens of meters of the discharge sites. However, the specific ion probe used to measure ammonium has a detection limit of ca. 2 μM, which is up to 20 times greater than ambient levels in full-strength seawater.

Waters with relatively long residence times in lagoons and moats can have either high or low nutrient levels depending upon content of source waters and tidal flushing. For example, Cocos Island lagoon waters are derived from nutrient-depleted upwind ocean waters. Within the lagoon, further removal can occur on patch reefs and in seagrass communities, but net flux of NH_4^+, RP, and Si^- from sediments can occur. In Tumon Bay, complete tidal flushing occurs on the order of weeks to months, especially in the northeastern corner that is enriched with aquifer seepage. In Apra Harbor, depths of up to 60 m, ocean water input on the bottom through a 35 m deep mouth, as well as stratification increases the flushing time to ca. months to years. On the Ipan reef flat, high NO_x and low RP occur due to high rates of N input from a small groundwater recharge plateau and high rates of N fixation on the reef (Matson unpub. data). The higher N levels from terrestrial and in situ processes (in comparison with the source water from windward) allows greater P removal.

HYDROLOGY AND COASTAL NUTRIENT CHEMISTRY

I suggest that hydrological differences between both the northern and southern provinces and the upwind and downwind waters cause the large differences in nutrient content. Further, because of these differences, (1) biological nutrient removal and total production are greater to leeward, (2) these removed nutrients are transported downwind as particulate biomass away from Guam, and (3) equivalent particle transport from southeastern Guam occurs around the southern tip due to outwelling from rivers. I present several hydrological arguments, including surface mixing with nutrient-rich thermocline waters and outwelling of nutrient-rich subaquifer seawater in support of this hypothesis.

First, Guam (13° 15′ to 39′ N) is within a region that extends from about 6° N to 15° N which has one of the shallowest permanent thermoclines of the Pacific (Tchernia 1980, Amesbury & Babin 1990). North of Apra Harbor, the thermocline begins at about 100 m where nitrate and phosphate concentrations increase at least 5 fold within the next 100 m, and attain deep ocean concentrations of ca. 33 and 2.5 μM, respectively, at about 500 m (Lassuy 1979). In some cases, however, no discernable thermocline exists in these nearshore leeward waters of Guam. For example, some of Lassuy's (1979) hydrocast data show a continuous decrease in temperature from the surface to 300 or 400 m (Stas. 7, 9, and 10). Also, unpublished bathythermograph data obtained by R. H. Randall in 1973 show similar continuous increases in temperature from the surface to 1000 feet (ca. 305 m). These eroded pycnoclines indicate that mixing of surface water with thermocline water has occurred. Second, the 600 foot (180 m) bottom contour (within the variably distinct thermocline) is generally within 2 km of both the leeward and windward coasts, although there are some areas on the

leeward coast where this depth occurs within 1 km of shore. Thus, vertical mixing of nutrient-rich thermocline waters can potentially have an equal impact on nutrient levels on nearshore waters of both coasts. Mixing of surface waters with nutrient-rich thermocline waters occurs predominantly between late May and late October (Amesbury & Babin 1990). This is when the thermocline is eroded because of low wind speed. As a result, nutrient data from windward in August (which, because of normally rough water, is the only time we could sample) are not (1) representative of average conditions, or (2) validly compared with leeward water samples collected in spring.

Nonetheless, in a general sense, less nutrient enrichment with thermocline waters can be expected to occur on the windward side. This is because prevailing winds from the ENE drive surface waters obliquely downwind along the east (windward) coast. In the northern hemisphere, downwelling occurs when the coast is to the right of the wind, such as to windward of Guam. To leeward, the coast is to the left of the wind, which causes upwelling. Surface water therefore "piles up" on the windward coast which forces thermocline water downward and also drives surface water to the southwest along shore. Thus, windward waters are less affected by nutrient-rich thermocline waters, but, during southward transport along shore, are enriched with waters at the mouths of the Pago, Ylig, Talofofo, Pauliluc, and Inarajan river estuaries.

Conversely, leeward surface waters must be driven downwind and away from the island because of the obliquely offshore (downwind) predominant wind vector. Thus, surface waters to leeward are simultaneously enriched by upwelling of thermocline waters nearshore and by leakage of waters into the intertidal from the more extensive leeward aquifer. In contrast to the scenario described above for windward shoreline water transport, current meter studies have shown that leeward nearshore waters within the top 90 m recirculate unpredictably and do not appear to be routinely affected by tides or predictable currents (Huddell et al. 1974). This would be expected if strong nearshore upwelling occurs.

Leeward surface waters that are driven offshore by prevailing winds soon encounter currents and visible fronts within a few km of shore. The fronts are caused by wind-driven net surface water transport (but not for bottom waters, Huddell et al. 1974) through Rota channel north of Guam and may create a vertical barrier to mixing and increase the nearshore water residence time. Relative to windward waters that are equidistant from shore, these leeward waters may be "sequestered" behind the fronts long enough to deplete them of nutrients. Also, further south along the leeward coast, net surface water movement occurs parallel to shore between Amantes Point and Apra Harbor (Huddell et al. 1974). In this area, nutrient-enriched surface waters are transported away from the northern aquifer towards the Glass Breakwater through an area that receives very little discharge from either aquifers or rivers (i.e., between Agana Bay and the entrace to Apra Harbor). Thus, southward transport may not enrich leeward waters as it does for windward waters that entrain river discharge.

Direct, quantitative measurements of nutrient upwelling in oligotrophic waters are necessary to substantiate the hypotheses described above. However, they are extremely difficult to make because nutrients are removed from solution almost as fast as they appear (Garside 1985). Therefore, several indirect estimates have been made, but the data obtained are often substantially different from each other. For example, vertical NO_x flux to the surface waters of the oligotrophic tropical and subtropical Atlantic has been reported to range from 0.14 (Lewis et al. 1986) to 1.6 (Jenkins 1988) mmol m^{-2} d^{-1}. At Guam, this would enrich the 100 m deep waters above the thermocline by ca. 1.4 to 16 μM d-1, which is substantial and comparable to enrichment via aquifer waters. Individually, the studies are sound, but of necessity depend on at least one assumption: either an unmeasured eddy diffusivity factor in the former or, for the latter, a NO_x value that is predicted from a deep-water relationship with seasonal δ^3He anomalies. At Guam, the higher salinity thermocline waters could provide a useful conservative tracer of upwelling, but more accurate and precise data than those obtained in this study are required. Seasonal temperature and salinity profiles are needed from both upwind and downwind sides of Guam.

Other issues that complicate this matter include (a) the unknown lateral flux of nitrate-rich seawater that underlays Guam's aquifer and (b) the largely unknown flux of river water seaward of the reef front. For example, the deep seawater well at the Fadian Aquaculture Demonstration and Training Center (windward) is located ca. 25 m from shore and 25 m below MSL, averages >95% seawater, but contains 32 times more nitrate than offshore surface waters (Table 6). In other experimental wells, essentially full-strength and presumably equally-enriched seawaters occur between 75 and 110 m below MSL (Contractor & Srivastava 1989). "Outwelling" of this subaquifer, nutrient-rich, deep seawater therefore occurs up to 75 m above the open water thermocline (100 m below MSL) and is a potentially large source of nutrients to both coasts.

Second, the major rivers, all of which are on the southeastern windward side, enrich the estuaries with NH_4^+, Fe, Si^-, and P. While outwelling of nutrient-enriched waters from these estuaries has not been measured (except as given in Figs. 15, 16), it is presumed to occur and can enrich those waters that travel south from the northern plateau along the coast. This is in contrast with leeward waters that are also driven and entrained southward, but which are not affected by either rivers or aquifers once they move past Tumon Bay. Thus, both water masses are transported southwest away from the carbonate plateau, but to windward, they are continuously enriched, adjacent to land, by runoff. In contrast, leeward waters are not enriched by terrestrial runoff, but may be more enriched by upwelling of thermocline waters along shore.

Finally, I and others observe that the total area of bottom that is covered by coral/algal communities north of Fadian on the northeast (windward) coast is significantly less than on the leeward side. To windward, large areas of scoured or otherwise bare bottom occur well within diving depths north of Fadian point and massive corals are comparatively rare. In contrast, to leeward, extensive reefs that include massive and branching corals occur well past diving depth. Weather

that is sufficiently calm for safe handling of small boats rarely occurs to windward. Thus, orientation into tides, currents, and winds may play a significant role in the determination of nutrient and biological regimes here as elsewhere (Welsh et al. 1982).

For these reasons, I suggest that, an island mass effect occurs downwind of Guam and it is caused by a complex set of factors. Waters downwind of northern Guam are predicted to be more nutrient-depleted and plankton-enriched than those downwind of southern Guam. For the latter, downwind offshore waters should have higher nutrient levels, fewer plankton, but contain more detrital particles that are derived from estuaries.

Conclusions

The nutrient chemistry of Guam's coastal waters is remarkably variable due to high nutrient fluxes from northwestern aquifers (constant and greater than from northeastern aquifers), southeastern rivers (seasonal and restricted to ca. 10 km of southeastern coast), and to potentially greater nutrient uptake, recycling, and offshore transport of plankton on the leeward side. Upwelling of both nutrient-rich thermocline waters and outwelling of aquifer waters affect the nutrient regime to a greater extent to leeward than to windward, but windward waters transported southwest around Guam's southern tip may accumulate large amounts of plankton nutrients and detrital particles from estuaries.

Several hypotheses can be constructed about biological communities on both sides and for each end of the island, but they are probably untestable because of the important and substantial effects of wind direction, upwelling, wave action, surge, water residence time, surface current flow, and differences in the chemistry of water from rivers and aquifers.

This large, nutrient-rich island leaks volcanic Fe, Si^{-}, (and many other elements that were not measured) as well as red clay and aquifer-derived nitrate into the surface and deep waters of the north equatorial currrent. A chemical "island mass effect" occurs: a study of its biological significance should be done.

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