NITRIFICATION IN GUAM'S SOILS AND SEDIMENTS

by

Ernest A. Matson

WERI
WATER AND ENERGY RESEARCH INSTITUTE
OF THE WESTERN PACIFIC
UNIVERSITY OF GUAM

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Ernest A. Matson

Department of Natural Sciences
and
Marine Laboratory
The University of Guam

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Nitrification in Guam's soils and sediments

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Abstract

This study was designed to evaluate nitrification in Guam's northern soils as a possible cause of the high nitrate concentrations in the aquifer system. Samples of topsoils were collected near drinking water well sites (Dededo, Mogfog, and Finegayan) after periods of dry and wet weather for one year. Nitrate production was examined in the laboratory in experimental flasks that contained *ca.* 1 g soil in 100 ml of rainwater or other media. Average nitrate production rates for soils at the three well sites were 220±320, 180±240, and 290±310 nmol NO_3^{2-} g^{-1} d^{-1} (±1 SD, n = *ca.* 44 each), respectively. Nitrification was stimulated by the addition of ammonium. These rates were sufficient to enrich the aquifer with *ca.* 200,000 time more nitrate than has been routinely observed.

To see if nitrate-rich transition zone waters could enrich the aquifer, nitrification was studied in coastal sediments. However, in coastal sediments, net denitrification occurred within 1-2 days. Stable N isotope analyses ($\delta^{15}N$) indicated that both soil and sediment N were derived from natural microbial processes and were probably not contaminated with domestic sewage.

Because laboratory flask data were much too high, nitrification was studied in an experimental soil column (170 cm^2 x 0.7 m long) constructed with topsoil and underlying carbonate from the Dededo site. An average of 146 µM NO_3^{2-} was observed in leach water from this column, which is essentially the same as that observed in the aquifer waters. At calculated average aquifer recharge rates of 1.15 m yr^{-1}, nitrification rates deduced with a mathematical model were also realistic.

The large difference between the flask rates and the soil column rates implies that potential nitrification is extremely high, but essentially all of the NO_3^{2-} is lost from the soil waters *via* denitrification prior to percolation down to the aquifer. If this is true, then it is reasonable to assume that denitrification occurred due to deoxygenation in water-logged soils. Therefore, nitrate-rich soil water that recharges the aquifer must leave the soil horizon not only devoid of O_2, but also enriched with NH_4^+, reactive P, metals, and other substances that are more soluble under anoxia. However, because aquifer waters are not anoxic but are routinely undersaturated with respect to O_2 (*ca.* 60% of saturation), they must be reoxygenated *en route* from the soil to the aquifer. Then, these substances may precipitate (*e.g.* metal-P complexes as metal apatites) in the freshly oxygenated recharge waters. Therefore, the carbonate platform below the soil horizon but above the aquifer may now be enriched with potentially harmful substances. Subsequent downward migration closer to the well waters will largely depend upon (1) their differential solubilities in oxygenated waters, (2) the mass of deoxygenated water that leaves the soil horizon, and (3) the rate at which waters migrating through the platform are being oxygenated.

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Introduction

In the tropics, nutrient cycles of both terrestrial and aquatic communities are tightly regulated by both efficient recycling and accumulation of nutrients within biomass (Wiebe 1985, Atkinson 1988, Matson *et al.* 1987). The nitrogen cycle is no exception, is mediated solely by microorganisms, and has been the subject of much study and debate. Nitrification is a required part of the N cycle: it provides for the growth and accumulation of biomass of both mixotrophic and autotrophic, free-living, soil bacteria; produces oxidized forms of N, and is usually indirectly coupled to N_2 fixation by other procaryotes, which are the only biological source of fixed N in the biosphere.

The N cycle "begins" with the enzymic reduction of N_2 to NH_4^+ by cyanobacteria and by many common genera of anaerobic and facultatively anaerobic heterotrophic bacteria. They produce about 90% of the "fixed" N on Earth. At a cost of 12 mol ATP per mol of N_2 reduced, this is an expensive process, often considered to be a good way for procaryotes to dispose of excess electrons or H_2. Regardless, the NH_4^+ (or amino groups or organic N compounds) are then excreted or leak into the environment (ammonification) where autotrophic bacteria use them for energy sources to produce ATP and to reduce CO_2 to CH_2O. These bacteria oxidize (nitrification) reduced N (oxidation state -3) to nitrite (NO_2^-, oxidation state +3) and then to nitrate NO_3^{2-} (oxidation state +5). Classically, this nitrate has been thought to be the prefered N source for plants and algae, which then take up the N to make protein (assimilatory reduction), that is released as organic matter upon death of the plant. Alternatively, facultatively anaerobic bacteria can use the nitrate, instead of O_2, as an oxidant (dissimilatory reduction) for the terminal respiration of their organic carbon sources. These modes of reduction of nitrate back to N_2 are collectively called denitrification, and comprise the major route for N return to the N_2 pool.

In contrast with ammonium, nitrate and nitrite produced in soils are exceptionally soluble and not cationically bound ("immobilized") to exchange sites in soils that are rich in clay minerals. They are easily leached from soils and have become a major pollution problem during the last two centuries of continued expedient farming practices. One common result of these microbial activities is the "contamination" with nitrate of drinking water aquifers (*e.g.*, Sahrawat 1982, Kreitler and Browning 1983, Cameron and Wild 1984, Wells and Krothe 1989), especially on tropical islands (Johannes 1980, D'Elia *et al.* 1981, Lewis 1987). The Guam Environmental Protection Agency (GEPA) has measured nitrate concentrations in Guam's aquifer waters as high as 4 mg N l^{-1} (290 μM), which is almost half of the 10 mg N l^{-1} (714 μM) upper limit recommended by the USEPA for potable waters. Zolan (1982) and Matson (1987) reported levels as high as 6.3 mg N l^{-1} (450 μM) for aquifer waters that seep out onto beaches in Tumon and Agana Bays.

Because the aquifer is Guam's only presently utilized source of drinking water, studies were recommended by the Advisory Council of the University of Guam's Water and Energy Research Institute to determine the potential source(s) of nitrate. In an earlier study of this

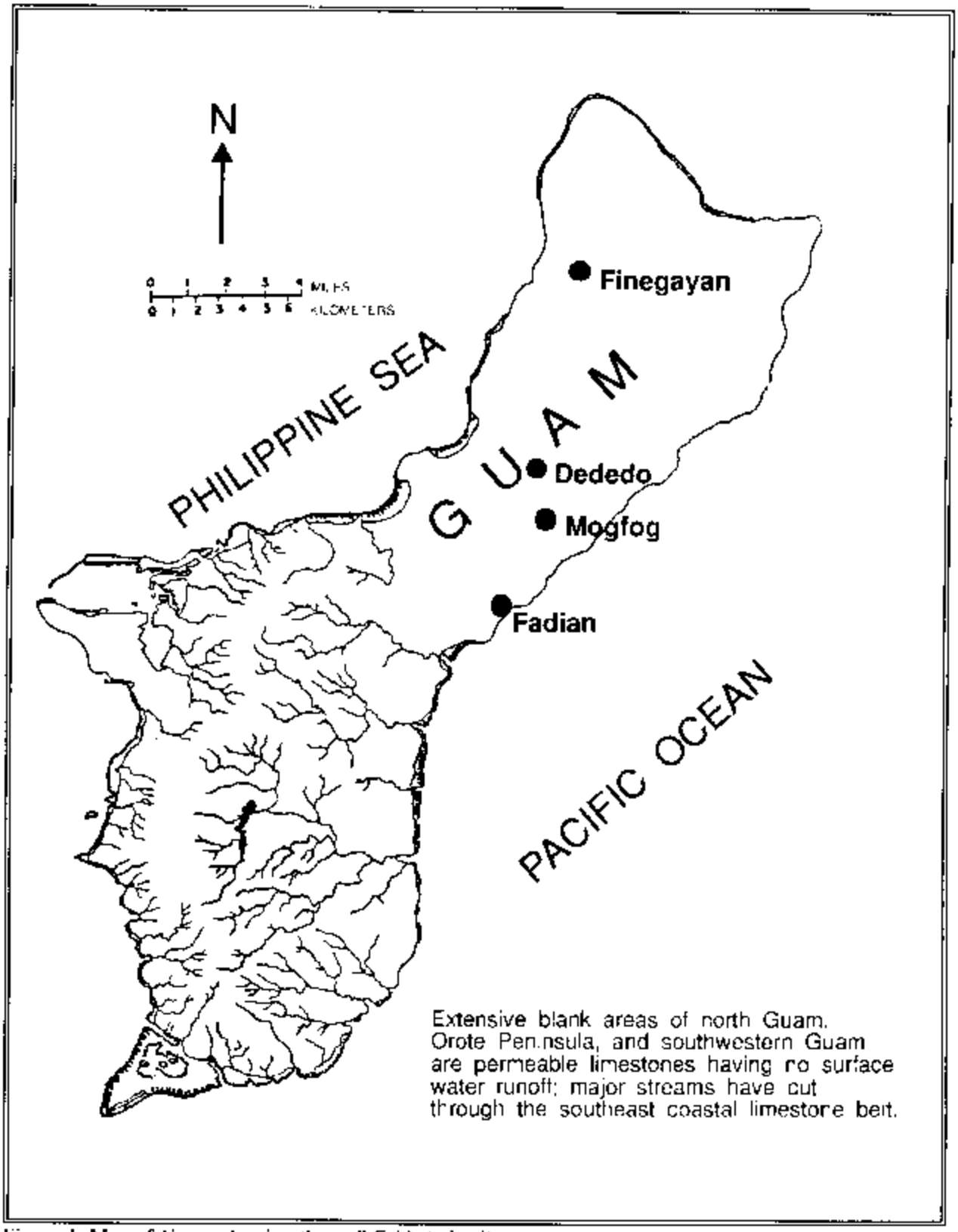


Figure 1. Map of Guam showing the well field study sites.

problem on Guam, Grosenbaugh (1979) found no evidence for the involvement of the N_2-fixing cyanobacterium *Nostoc muscorum* in the enrichment of the aquifer with nitrate.

This report includes data on the most likely source of aquifer nitrate (*i.e.*, naturally-occurring nitrification by free-living, non-photosynthetic, bacteria) that were obtained from slurries of soils collected above three major drinking water well fields. Also, calculations of net nitrate input to the aquifer were made, and nitrate (and Si) data from several subbasins of the aquifer were obtained. Stable N isotope analysis ($\delta^{15}N$) of soils and coastal sediments indicate that the nitrates do not arise from infiltration of the aquifer by sewage from homes or farms.

Materials and Methods

Study Area

Guam (area = 535 km^2) is located in the southern Mariana Islands, north of the intertropical convergence and in the southern region of the westerly trade winds (Fig. 1). The northern half of the island is a broad flat, uplifted, carbonate plateau (66 to 190 m MSL) with no rivers. The southern half is predominantly volcanic with numerous rivers, rises to 400 m MSL, and, except for a relic carbonate shelf along the southeastern coast, has very little carbonate above scalevel.

Rainfall on Guam averages 2.25 m yr^{-1}, most of which occurs in the June to December rainy season. In the northern province, thin (10 to 50 cm) lateritic soils are alternately soaked and dried over sometimes daily cycles, but can remain saturated for several weeks during the rainy season. The predominant vegetation consists of *Miscanthus floridulus* (swordgrass), *Cycas circinalis* (cycad), *Leucaena leucocephala* (tangantangan), *Casuarina* (Australian pine), *Bidens pilosa* (Guam daisy), and several types of sedges, palms, and grasses that often turn brown between January and May due to lack of water.

Nitrification in Soils and Sediments

Single kg-sized samples were obtained approximately monthly for a year beginning in May 1989 from the top 5 cm of soil within 50 m of three drinking water well sites (Dededo, Finegayan and Mogfog). In August 1990, a suite of samples was also taken from Agana Bay and Tumon Bay to determine whether nitrate was also being produced in coastal sediments or whether aquifer-derived nitrate that percolates up into them was being removed. Homogenized 1 g subsamples were suspended in 100 ml of vigorously shaken, freshly-collected rainwater (or seawater in the case of coastal sediments) or basal medium for nitrifiers (Schneider and Rheinheimer 1988) and incubated ±2 mM NH_4^+ (0.2 mM for coastal sediments) in 250 ml Erlenmeyer flasks in the dark (Nishio and Fujimoto 1990) for a week and up to a month. Aliquots of the supernatant were taken on days 0, 1, 3, 5, and 7.

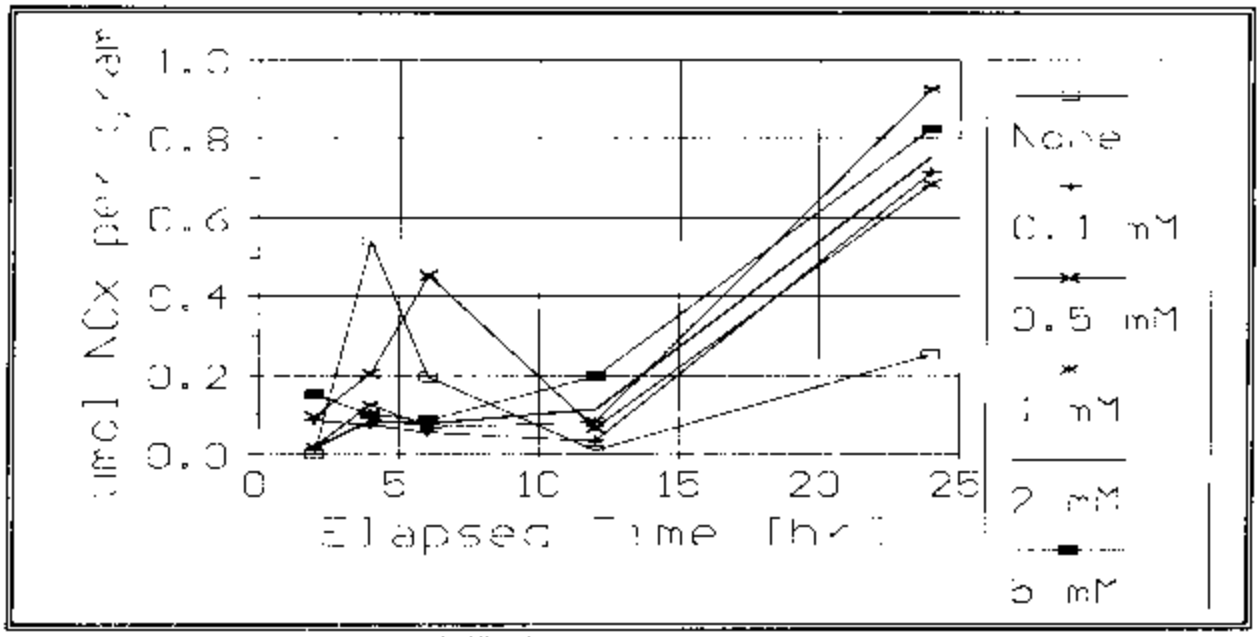


Figure 2. Effects of added NH_4^+ on nitrification.

The flasks were swirled by hand, allowed to settle for 2 h, and 7 ml aliquots of the supernatant were then filtered through pre-rinsed Millex-GS 0.22 µm pore size filters directly into tubes for separate analysis of NO_2^- and $NO_2^- + NO_3^{2-}$ (*i.e.*, NOx, *via* Cd reduction, Jones 1984). Nitrate levels in controls (water without soil) were rarely a significant digit and were subtracted from the experimental values. The effects of the experimental addition of NH_4^+ to soils (Fig. 2) indicate that up to 5 mM ammonium stimulated nitrate production. Ten-fold less ammonium was added to sediments because they contain much lower levels of naturally-occurring ammonium (Matson 1990).

An experimental soil column was built using Dededo topsoil and underlying carbonate freshly excavated from the well site. In July 1989, an opaque 70 cm length of PVC pipe (170 cm^2) was filled with carbonate and covered with 8 cm of topsoil. A PVC base plate had been cemented into the lower end of the pipe to retain the soil. About twenty 5 mm diameter holes were drilled to allow percolating rainwater to drip through. The soil column was elevated about 20 cm above the floor outdoors in direct sunlight on the lanai at the Marine Laboratory and allowed to settle and "equilibrate" until September, when heavy rains began. During this period a few sprouts of tangantangan and an unidentified grass grew in the topsoil. A 2-liter plastic bowl was placed under the bottom of the soil column to collect rain water that percolated through it. Beginning in September 1989, waters that collected in the bowl were analyzed for nitrate and nitrite.

Soil Chemistry

Subsamples of the soils used for nitrification studies were analyzed for exchangeable NH_4^+ and NO_3^- by shaking for at least 1 hr in 2 M KCl (Rosenfeld 1979, Matson 1990). Ammonium was measured with an Orion specific ion probe and exchanged nitrate was measured as described above. The signal to noise ratio was maximized by increasing the volume of soil used. Total organic N (TON) and total organic C (TOC) content of the soils were measured in duplicate or triplicate on a Carlo-Erba Model 1150 CNS analyzer with *p*-amino benzoic acid standards. The samples were combusted at 1000 °C in an oxygen stream with a tungstate-tin catalyst. Resulting CO_2 and N_2 were then measured in a downstream gas chromatograph *via* thermal conductivity in a helium stream.

$\delta^{15}N$ Analysis

Samples of topsoils from the well sites and of a transect of coastal sediments from Tumon Bay were dried and mailed to Coastal Science Laboratories, Austin Texas. There, the samples were sieved (40 mesh), treated with HCl to remove carbonates (or analyzed without acidification, see Results), and combusted (*via* catalytic reduction at 1000 °C) to produce N_2 that was directed through a mass spectrometer. Deviation from natural $\delta^{15}N$ values was calculated in reference to standard atmospheric N_2 ($\delta^{15}N = 0$ ‰), where

$R = {}^{15}N/{}^{14}N$ sample, and

$\delta R = (|R_{sam} - R_{std}|/R_{sam}) \times 10^3$, and

$R_{std} = {}^{15}N/{}^{14}N$ of atmospheric N_2

and the precision of analysis is thought to be *ca.* ±0.3 ‰ (K. Winters, Coastal Science Labs, pers. comm.)

Briefly, N_2 "fixed" (*i.e.*, reduced to NH_4^+) by procaryotes has a $\delta^{15}N$ of -2 to +2 ‰, very close to atmospheric N_2 of 0 ‰. Values that are less than *ca.* 6 to 10 ‰ are considered to be a result of natural N cycle activity. If the ratio is more positive (*e.g.*, >+10 ‰), more of the heavier, but much less abundant, ^{15}N has been incorporated into the sample. Generally, this enrichment in ^{15}N occurs for three reasons:

(1) animal waste is becoming increasingly abundant in the sample (the heavy isotope accumulates in top levels of the food "chain"), or,
(2) where N may be in low supply, and therefore limiting to biological reactions, less discrimination occurs against the heavier isotope:enzymes have no choice but to use the heavier isotope.
(3) recycling of N within an essentially "enclosed" system, such as a farm pond, lake, or other body with limited exchange or inputs of "new" N. The lighter isotopes are lost to the gas phase during denitrification.

Chemistry of Aquifer Waters

Well waters at The Fadian Aquaculture Training and Demonstration Center (Fadian), beach seeps at Tumon Bay, and other aquifer leakage sites around the periphery of northern Guam were sampled irregularly but intensively. These data have been presented elsewhere (Matson 1991b) but are summarized here to show significant differences among three aquifer subbasins. With respect to this report, this difference may be due to different rates of nitrification, different soil volumes that overlay the aquifer, and/or to different depths of aquifer water into which percolated nitrate (and other solutes) is diluted.

Results

Nitrification in Soils

Table 1. Nitrification in Guam's soils.

Date		Ded	Mfg	Fin
		nmol g^{-1} d^{-1}		
Jun	5	13		
Jul	5	32	6	18
Sep	8	3	10	59
Sep	29	330	260	420
Dec	19	40	9	130
Dec	22	40	140	220
Jan	16	830	830	910
Jan	25	970	390	880
Mar	15	160	170	340
Apr	6	150	29	120
May	22	110	63	83
Jul	11	7	4	9
Mean		**220**	**180**	**290**
±1 SD		**320**	**240**	**310**

Total net production of NOx (almost entirely as NO_3^-) over 7 days in the three well site soils incubated in rainwater only ranged from lows of 3.3 nmol g^{-1} d^{-1} in September after a long summer dry spell to 970 nmol g^{-1} d^{-1} after continued rainfall in late December and January (Table 1). By this time, soils have usually become saturated as the rainy season comes to an end. The relationship between rates of nitrification and rainfall in the previous 10 days is rather obvious (Fig. 3).

Using a measured dry bulk density of 1.35 g cm^{-3}, I integrated the rates over depth and area in an hypothetically 50-cm deep soil and obtained values of up to 360 mmol NO_3^- m^{-2} d^{-1}. These are well within the range of normal biological activity, regardless of whether the habitat is terrestrial or aquatic. Later I argue that, based on large differences between these rates of nitrate production and the ni-

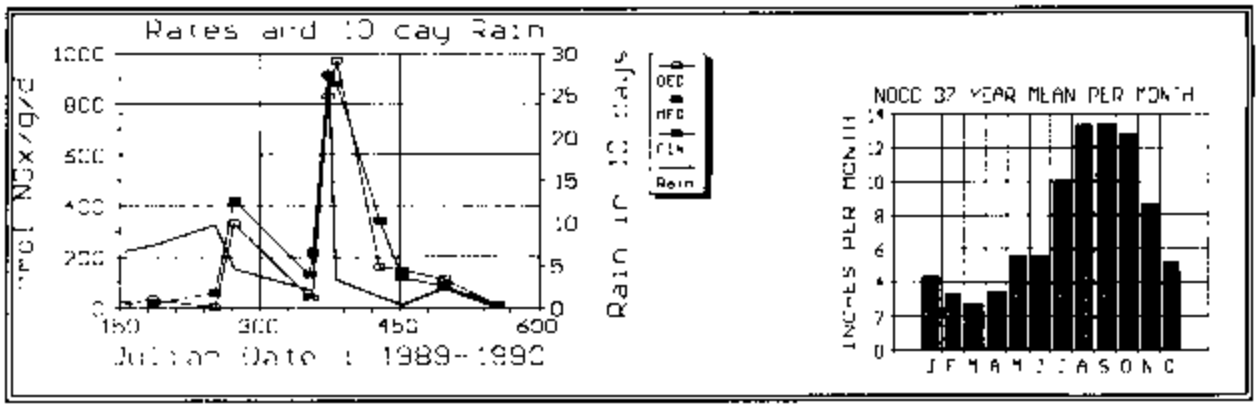


Figure 3. Nitrification rates and rainfall at NAS.

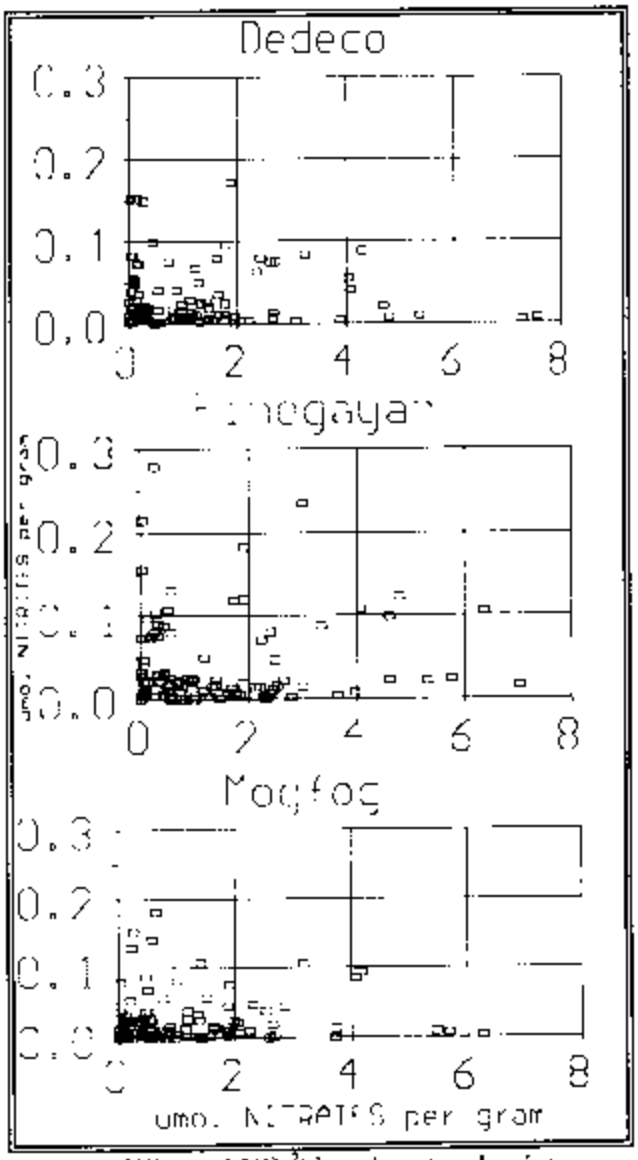


Figure 4. NO_2^- and NO_3^{2-} in rainwater slurries.

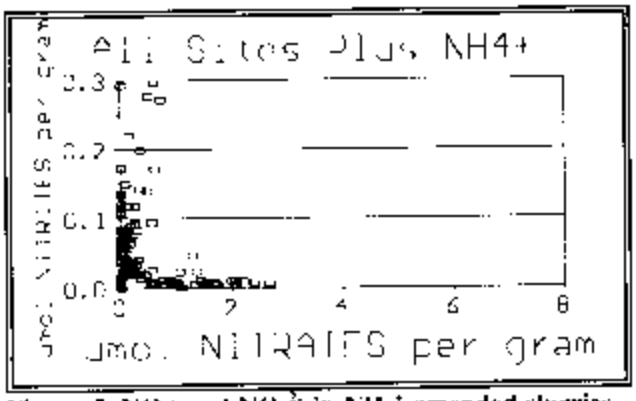


Figure 5. NO_2^- and NO_3^{2-} in NH_4^+-amended slurries.

trate content of the aquifer (it should have >100 times more NO_3^{2-}), denitrification to a gaseous form such as N_2 is a major loss from soils *in situ*. Data from soils incubated with NH_4^+ and basal medium are not given, due to significant increases in nitrification under the enriched conditions (Fig. 2).

Incubation of soils in rainwater resulted in very low levels of NO_2^- in comparison with NO_3^{2-} (Fig. 4). In contrast, the addition of 2 mM NH_4^+ increased the NO_2^- fraction and decreased the amount of total NOx produced (Fig. 5). Specifically, most NO_2^- data are clustered along the X axis (Fig. 4), while in Fig. 5 they cluster along the Y axis. Apparently, the addition of NH_4^+ to soil slurries increases the demand for O_2, which is required by the organisms for oxidation of NH_4^+ to NOx. This higher O_2 demand may inhibit the complete oxidation of NO_2^- so that it accumulates to greater levels.

Initially, however, soils *in situ* are well-oxygenated by rainwater that is saturated with air. Biological activity is stimulated but can rapidly deplete water-saturated soils of their O_2 content. Increased biological activity rapidly induces anaerobic soil conditions. Then, O_2 is not available for the second step of nitrification, which is the oxidation of NO_2^- to NO_3^{2-}. This increases the relative amount of NO_2^- at the expense of decreased NO_3^{2-} production. Also, O_2 depletion induces denitrification, which is a major loss of N (as N_2?) from these soils. Therefore, application of materials with a high O_2 demand (*e.g.*, sewage and fertilizers) can result in high levels of NO_2^- that may then percolate down to the aquifer.

Nitrification in the Experimental Soil Column

Table 2. Leach water from the soil column.

Interval Date	(days)	µM NO_2	µM NO_3	% NO_2	Volume (liters)
Sep 11	0	28	140	20	0.62
Sep 15	4	63	150	43	0.030
Oct 3	22	0.60	270	0.20	1.6
Oct 4	23	0.50	190	0.30	1.5
Nov 28	78	1.1	150	0.70	2.1
Nov 29	79	0.16	150	0.10	0.11
Jan 11	122	0.55	23	2.4	0.16
Jan 15	126	0.11	92	0.10	1.6
Average		**12**	**150**	**8.4**	**0.98**
±1 S.D.		**21**	**71**	**16**	**0.78**

Over 126 days, 7.72 liters of percolated rainwater were collected from the soil column. The average NO_3^{2-} content was 146 µM and total NO_3^{2-} output was 1.29 mmol. Although it is certain that not all water was collected, large storms were well-sampled. This rate of delivery is equivalent 9 to 65 cm of water from the 170 cm^2 column in 180 days and a total output of 0.60 mmol m^{-2} d^{-1} or 110 mmol NO_3^{2-} m^{-2} yr^{-1} over 180 days. This is much lower than the rates obtained from the soil incubations (Fig. 4) but, at an average content of 146 µM, it is precisely the order of magnitude required to maintain the nitrate concentrations that are actually observed in the aquifer (this study; Grosenbaugh 1979). Thus, the soil column used in this study appears to mimic well the "black box" of the soils and carbonate that overlay the aquifer and may be a useful tool for further studies, such as the mobility of pollutants. However, to model the field situation adequately, the 8 cm of topsoil in the experimental column should be instead underlain by at least tens of m of carbonate. Appropriate miniaturization might work, but the great distances involved between the thin topsoil and the aquifer may actually allow for reactions to occur that are incomplete within the soil, such as oxidation of nitrite, which is as water-soluble, and therefore as leachable as nitrate.

Chemistry of Well-Site Topsoils

Exchangeable ammonium in these soils generally ranges between 1 and 10 µmol g^{-1}, or 20 to 200 fold lower than the amended flasks (Matson 1989, 1990). However, the amounts of NO_3^{2-} produced in the rainwater flasks are equivalent to both the exchangeable NH_4^+ and NOx contents of the soils, but are a minor fraction of the TON content (Table 3). The use of the exchangeable N fractions could not continue for an extended length of time because the supply would be rapidly exhausted. Therefore, rainwater-saturation of soils must stimulate all biological reactions, especially the release of N fixed by other soil bacteria. In this respect, the soil N cycle is tightly coupled:water sequentially stimulates N fixation, then leakage of NH_4^+, then nitrification, and, ultimately, denitrification back to N_2. Water in excess of the moisture holding capacity then recharges the aquifer with the residual nitrate-rich soil water.

The soil column data (Table 2) then better reflect actual fields conditions in which nitrate output to the aquifer is substantially lower than rates calculated from flask experiments. Thus, soil N fractions can be sequestered (*via* N fixation or NH_4^+

Table 3. TON and TOC in Guam's soils.

Date	Site	TON	TOC	C/N
		μmol g^{-1} dry soil		
Sept 26	Fin	610	14000	23
	Ded	290	16000	54
	Mfg	290	10000	35
Dec 19	Fin	160	14000	86
	Ded	560	18000	33
	Mfg	460	13000	28
Dec 22	Fin	830	17000	21
	Ded	340	17000	51
	Mfg	580	12000	20
Jan 16	Fin	570	17000	29
	Ded	580	20000	34
	Mfg	370	12000	33
Jan 25	Fin	400	12000	29
	Ded	520	13000	24
	Mfg	410	6100	15
Mar 15	Fin	390	9300	24
	Ded	600	15000	26
	Mfg	390	8500	21
Apr 6	Fin	550	12000	23
	Ded	490	14000	29
	Mfg	280	10000	36
May 22	Fin	560	12000	22
	Ded	540	16000	30
	Mfg	650	10000	16

immobilization) to supply sufficient substrate for up to *ca.* 100 days of continued nitrification. In contrast, in the flasks, the free-living N_2-fixing bacteria were artificially stimulated by the highly aerobic conditions, which allowed for continued mineralization of organic matter and concomitant release of ammonium from it.

The flask data therefore provide estimates of maximum potential, or "gross" nitrification. Such high rates might be attained during especially heavy rainfall that saturates the soils and then percolates through them for extended periods of time. Perhaps this is why aquifer nitrate concentration data are quite variable. The high variability among the soil C and N data may also reflect a variably productive biological realm that responds rapidly and substantially to rainfall.

Nitrification in Coastal Sediments

Agana Bay and Tumon Bay sediments are not a source of the high nitrate observed in coastal waters (Figs. 6 and 7). Agana sediments contain *ca.* 10-fold less nitrate than those in Tumon Bay, which, in the nearshore, are infiltrated by nitrate-rich aquifer waters (note difference in Y scales of Figs. 6 and 7). Concentrations of sediment nitrate nearshore in both bays were much higher than those further offshore; this is a direct result of inputs of nitrate-rich aquifer (Tumon Bay) and surface drainage (Agana Bay) waters (Matson 1991b). Amendment with 0.2 mM ammonium increased the nitrate content nearshore in Agana Bay only at day 7. The sediments therefore must have a limited supply of oxidants (in contrast with Tumon Bay) and perhaps have a much higher content of organic matter and a resultingly higher demand for oxidants (Slater and Capone 1987). The removal of nitrate from these sediments in a few days shows that O_2 was used much more rapidly and promoted net denitrification sooner than in terrestrial soils.

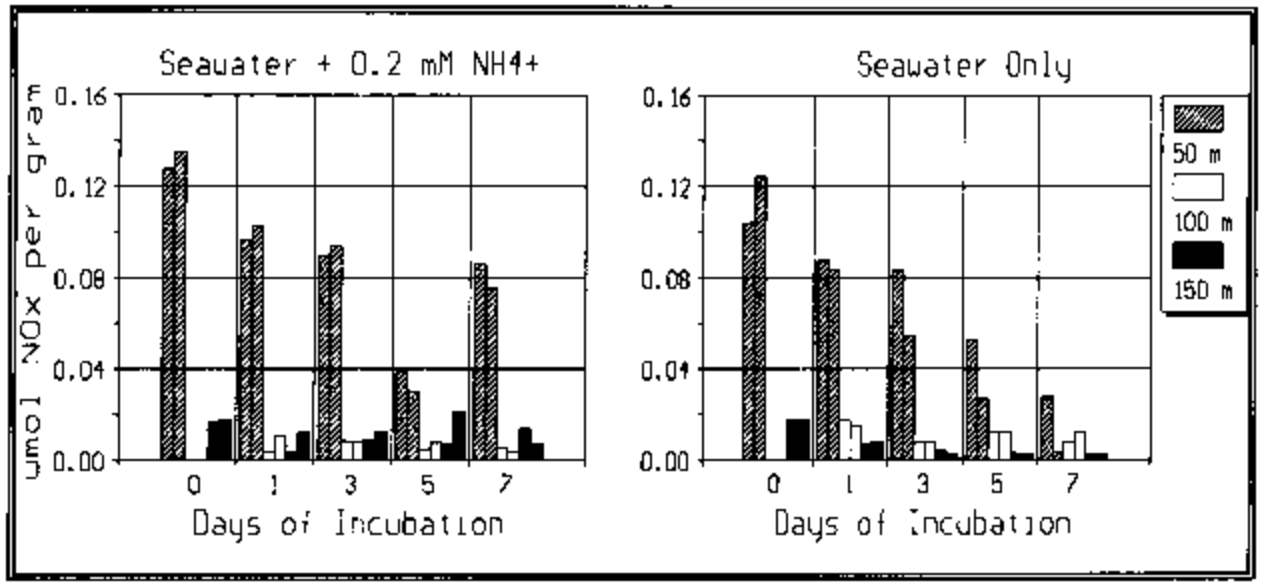


Figure 6. Agana Bay nitrification data (duplicates) from 50, 100, and 150 m offshore, with (left) and without (right) 0.2 mM NH_4^+.

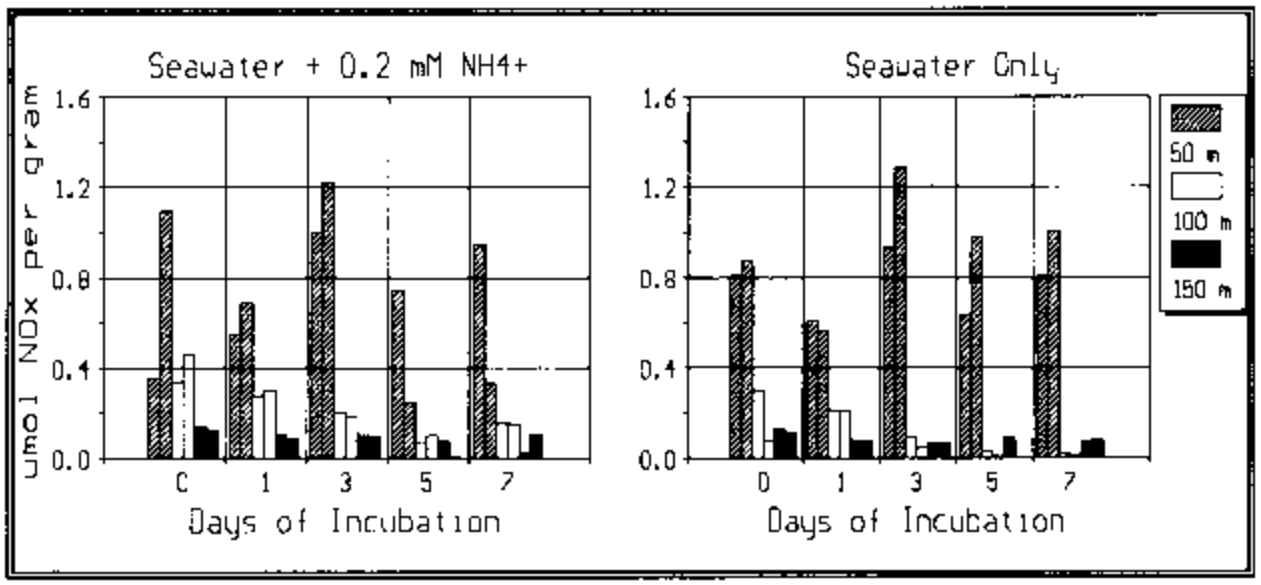


Figure 7. Tumon Bay nitrification data, as above in Fig. 6.

Stable N Isotope Analyses

Table 4. $\delta^{15}N$ data for soils and Tumon sediments.

δ15N values of Total Nitrogen				
Terrestrial Soils:				
	Dededo	Finegayan	Mogfog	
26 Sep 89	+4.5	+5.5	+6.4	
19 Dec 89	+4.4	+6.0	+6.4	
22 Dec 89	+5.2	+4.4	+6.8	
16 Jan 90	+4.5	+5.0	+6.7	
25 Jan 90	+3.8	+4.5	+7.5	
15 Mar 90	+4.1	+5.0	+7.1	
06 Apr 90	+3.7	+6.9	+6.8	
Mean	**+4.3**	**+5.2**	**+6.9**	
±1 SD	**0.5**	**0.8**	**0.4**	
NE Tumon Bay Sediments:				
	m from shore			
Apr 89	10		+0.6	
	50		+8.1	
	100		-0.4	
	150		+6.5	
Mean (±1 SD)		**+6.2 ± 4.7**		
Mar 90	0		+6.9	
	50		+5.5	
	150		+5.6	
	300		+6.0	
Mean (±1 SD)		**+6.0 ± 0.6**		
Apr 90	25	+7.8, +7.9,	+7.5	
	75	+6.4, +6.5,	+6.7	
	175	+5.7, +6.7,	+6.7	
	275	+6.4, +6.7,	+6.3	
Mean (±1 SD)		**+6.8 ± 0.6**		

$\delta^{15}N$ data for total nitrogen in soils and Tumon Bay sediments are in Table 4. The averages for Dededo, Finegayan, and Mogfog are 4.4, 5.2, and 6.9 ‰, respectively, with very little variation. These values are well within the normal range for soils (Kreitler and Browning 1983, Peterson and Fry 1987). Only slight changes occurred after rain in December and January. These, however, could be normal variations.

The Tumon Bay samples taken in 1989 are quite variable, and this may indicate that sampling resolution needs to be increased. The samples from March and April of 1990, however, do not show this wide variation. Instead, the values decrease consistently with distance from shore. The nearshore data are near the lower end of the range of ratios that signify the presence of animal waste. The two sets taken a year later do not show this nearshore enrichment, although the means are essentially the same as in 1989.

The nearshore Tumon samples are near recreational and construction sites and where abundant piles of the green macroalga *Enteromorpha* are deposited during beach "clean-up" operations. The decomposing algae may cause this nearshore enrichment in ^{15}N. Alternately, because the NE end of Tumon Bay has a rather low exchange rate with oceanic waters (Matson 1991a) and because of the frequent occurrence of "red tides" in the area we sampled (Matson 1991a), this nearshore enrichment in heavier N may simply reflect efficient recycling of a sedimentary N pool in spite of the continuous supply of aquifer nitrate in the beach seeps. Thus, the difference between these two Tumon data sets could be due to the occurrence of blooms or runoff from construction. For now, however, there is no strong isotopic evidence for the presence of animal wastes in soils near the three drinking water well sites or further from shore in Tumon Bay.

Chemistry of Selected Aquifer Waters

Table 5. NO_3^{2-} and Si in aquifer subbasins.

Site	m	b	r^2	n
Nitrate:				
Northwest coast	-0.16	89	0.90	71
Double Reef	-0.18	95	0.91	42
Fadian wells	-0.22	130	0.91	152
Tumon Bay	-0.24	130	0.95	123
Silica:				
Northwest coast	-0.016	9.9	0.81	71
Fadian wells	-0.087	55	0.76	152
Tumon Bay	-0.030	18	0.76	86

The data in Table 5 (of the form Y=mX+b, where X=mM Cl- and Y=μM NO_3^{2-} or Si) are summarized from a recent report (Matson 1991b) and are included here to illustrate the accumulation of solutes in and differences among several subbasins of the northern aquifer. The regressions are strong, and have been almost equally weighted with samples taken at high salinities (*i.e.*, coastal waters with which aquifer waters mix). Obvious and significant differences among the nitrate and silica contents occur from the southern (Tumon Bay and Fadian) to the northern end of the northern plateau of Guam. For example, Si levels at Fadian average *ca.* 6 times higher than at seeps in cracks along shore at Double Reef and Artero's beach (NW coast). Likewise, nitrates in NW coastal seeps are about 70% of those at Fadian. These data support the contention (Matson 1991b) that the aquifer is divided into subbasins that are differentially affected by both soil biochemistry and by the composition of any basalts that appear above sealevel. These differences among coastal seep waters are use ful in the identification of waters from distinct subbasins. However, aquifer waters further inland may not show these differences.

Spatial Variability Within Subbasin Chemistry

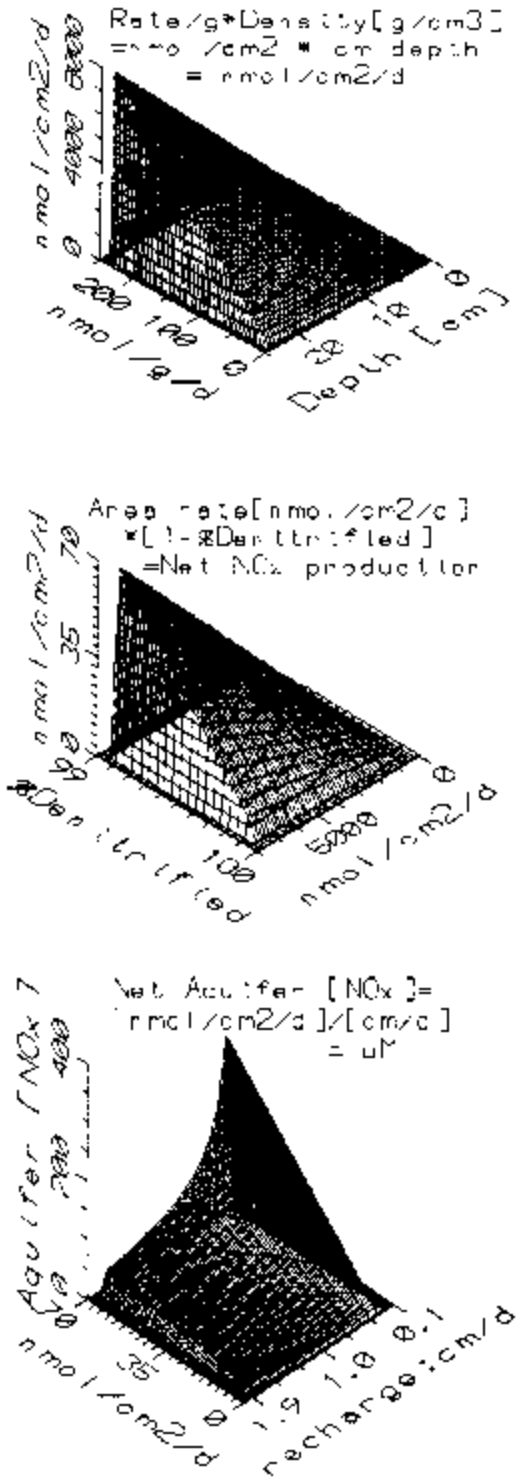
Table 6. Chemical variation among beach seeps.

Seeps were sampled in 2 hr over a 280-m reach of Tumon Bay. C.V.=±1 S.D. (n=20) as % of the mean. All in μM, except for Cl-[mM] and pH.

	Mean		C.V.
Chloride	78	± 13	17
Oxygen	131	± 12	9.2
Nitrite	0.06	± 0.077	117
Nitrate	115	± 6.5	5.7
Reactive P	0.76	± 0.18	24
Fe	0.20	± 0.19	95
pH	7.37	± 0.09	1.2

Data from a 2 hour survey of the variability among 20 discrete beach seeps in Tumon beach seep are presented in Table 6. The variation in O_2, NO_3^{2-}, and pH is very low. These dominant features are strongly regulated by geochemical and hydrological processes, perhaps something as simple as transition zone mixing and conservative dilution. In contrast, Fe, P, and NO_2^- vary remarkably within this 280 m stretch of beach. These components of seep water are biochemically and geochemically much more reactive to changes in salinity (Eckert and Scholkovitz 1976, Morris *et al.* 1978), such as within the transition zone. Whether this type of variability also occurs within the aquifer proper is presently unknown. However, high variability in the concentrations of chemical active components is not unexpected within the mixing zone.

Figure 8. A summary of a model of gross potential nitrification integrated over variable soil depths, depleted by denitrification, and leached in recharge water to the aquifer.



The lower rates of NO_3^- production observed in field slurries (Table 1) and in the soil column (Table 2) are used to calculate "Gross" production of NO_3^- in field soils. These are then normalized to area rates (nmol cm^{-2} d^{-1}) with dry bulk density (1.35 g cm^{-3}). These "GROSS", area integrated rates can range up to 1.4 mol m^{-2} d^{-1}, but the lower rates are used here as described below.

To obtain realistic values for "NET" NO_3^- production, an estimate of denitrification within the field soils must be made. These, however, are actually obtained empirically and backwards: *i.e.*, the NO_3^- content of aquifer waters is much less than what it should be based on "Gross" nitrification data. Thus, the data to the left are calculated from the difference between production in soils, above, and enrichment of the aquifer, below. This logic is explained more fully in the text.

Regardless of how much NO_3^- is actually produced or is lost to the atmosphere during denitrification, the aquifer is enriched with the residual soil NO_3^- by water that can percolate down through the carbonate plateau after soil saturation and after loss due to evapotranspiration; these, however, are critically affected by the rate of rainfall. Rapid soil flooding can increase recharge and decrease both nitrification and evapotranspiration. This may be why aquifer NOx concentrations are variable.

Finally, aquifer nitrate and recharge data are both reasonably sound and are therefore used, together with the flask and column nitrification data, to "force" the denitrification estimates so that nitrate recharge equals aquifer contents at steady state. Recharge largely occurs within the middle of the rainy season, and averages about 0.6 cm d^{-1} over 180 days.

Discussion

Estimates of Nitrification

The nitrification data presented here should be considered to be "gross" or "net potential" rates due to the lack of inhibition of simultaneous denitrification and to the incubation of soil suspensions in excess amounts of well-oxygenated water rather than in moist soils at their water holding capacity. Also, it is difficult to model the essentially flow-through system that occurs in the field when rainfall rapidly supplies sufficient moisture to reach and exceed the capacity of the thin (10 to 50 cm) soils. The experimental soil column therefore supplied much more realistic data.

In the wet season, soils are almost always moist to saturated. Rainfall in excess of that capacity percolates through the soils, bringing with it the acquired solutes. Subsequent dry weather (for 2 or 3 days at most in the wet season) stops biological activity as well as percolation. Both recharge of the aquifer and enrichment of it with nitrate largely occurs during saturating events, which usually occur in the rainy season only. In this way, the use of soil suspensions is not considered to be very different from actual field conditions except for the fact that the flasks were not experimentally de-oxygenated after several hours or days of incubation. This procedure would have more realistically reflected conditions *in situ*, as mentioned above and discussed below. Finally, the rates obtained are, however, within the same order of magnitude as those from other *in situ* and experimental studies in a variety of conditions (Webb and Wiebe 1975, Matson *et al.* 1987, Nishio and Fujimoto 1990).

Enrichment of The Aquifer With Nitrate

I summarize the approach used to calculate nitrate enrichment of the aquifer in Fig. 8. The data most critical to accurate estimation are relatively sound:the total potential rate of nitrification and the actual rate of percolation (*i.e.*, aquifer recharge) have been measured or are otherwise known within one order of magnitude or better. However, because the observed nitrate concentration in the aquifer is 5 orders of magnitude lower (*i.e.*, 20,000-fold less) than the potential input, one or both of two critical data are either missing or grossly inaccurate. Either (1) the aquifer volume is much greater than presently estimated, so that large amounts of nitrate are diluted to the lower concentrations that are observed, and/or (2) a substantial amount of nitrate is lost to the atmosphere as N_2 or N_2O, which are the major end-products of denitrification under conditions of excess NO_3^{2-}. The data obtained from the experimental soil column clearly show that free-living soil bacteria can easily supply all of the nitrate that is observed in the aquifer waters. The flask data, however, show that potential nitrification is several orders of magnitude higher than what is required to produce these observed concentrations in the aquifer or in the experimental soil column.

Gross potential rates of aquifer recharge and NO_3^{2-} production data can then be used to predict how much NO_3^{2-} could potentially be delivered to the aquifer. Using the

assumptions in Fig. 8, and an estimated median production value of 220 nmol g^{-1} d^{-1} from per day rates in unamended rainwater, I calculate that about 150 mmol m^{-2} d^{-1} is produced to a depth of 50 cm:

$$[220 \text{ nmol } g^{-1} d^{-1}] * [1.35 \text{ g } cm^{-3}] = 297 \text{ nmol } cm^{-2} d^{-1}$$

(to a depth of 1 cm in the soil), and

$$[297 \text{ nmol } cm^{-2} d^{-1}] * [10^4 \text{ cm}^2 \text{ m}^{-2}] * [50 \text{ cm deep}] = 149 \times 10^6 \text{ nmol } m^{-2} d^{-1},$$

or *ca.* 27 mol N m^{-2} $year^{-1}$

(for the six-month rainy season only).

According to estimates by the Public Utility Agency of Guam (PUAG), and evapotranspiration data in Matson (1991b), recharge of the aquifer is about 1.15 m yr^{-1} (Table 7). If all this nitrate produced (27 mol m^{-2} yr^{-1}) is dissolved into this recharge water, the NO_3^- concentration of aquifer waters, at steady-state, would be about:

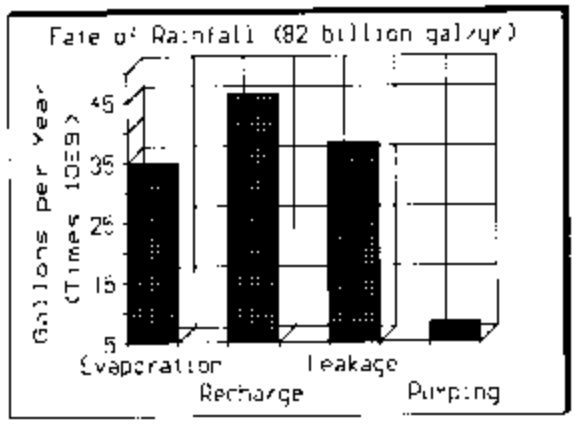
27 mol m^{-2} yr^{-1} / 1.15 m^{-1} yr^{-1} = 23 mol m^{-3} (23,000,000 µM), or about 2 x 10^5 times as great as the average value (*ca.* 110 µM) for nitrate in both the column leach water (Table 2) and the aquifer waters (Table 5).

That nitrite was a small fraction of the total NOx produced when soils were incubated in rainwater only implies that, during the wet season in the field, the process is probably limited by the availability of O_2. After rainfall stops, soil-water could be rapidly depleted of O_2 by respiration, which would then stimulate both denitrification and ammonification but also inhibit ammonium oxidation, which requires O_2. In turn, this reduces the total amount of

Table 7. A first-order water budget for Guam.

Rainfall data from NOCC at NAS; withdrawal (@30 mgd) and aquifer area data from PUAG; leakage calculated by difference and evapotranspiration by monthly mean runoff/rainfall ratios for the Ugum River as in Matson (1991b,c). Budget is for the parabasal aquifer only (area = 134 km^2), the total aquifer area = 176 km^2, and the northern plateau is 256 km^2.

Item	Annual Rate (Millions) Gal	m^3
Rainfall (2.25 m yr^{-1})	8150	302
Evapotranspiration (43%)	450000	130
Recharge (1.15 m yr^{-1})	46500	172
Withdrawal	8300	31
Leakage to coast	38200	141



NOx in soil water (regardless of whether NO_2^- or NO_3^{2-} is the end-product), but could provide relatively NO_2-rich and O_2-poor water to the aquifer. However, because nitrite is very low (*ca.* 0.066 µM) in aquifer waters (Table 6), it is likely that nitrification is completed after export of soluble inorganic N from the soils but before these ions (*i.e.*, NO_2^-) arrive at the aquifer. The fact that aquifer waters are only *ca.* 60% saturated with O_2 does not mean that 40% has been removed in the aquifer to drive nitrite oxidation to nitrate. This is because *ca.* 100 µM O_2 (the missing percentage) is insufficient by orders of magnitude to oxidize mM levels of nitrite except if the waters were continuously reoxygenated (during turbulent flow) before arrival at the aquifer. This could possibly occur during percolation through the 60 to 200 m of porous carbonate *en route* to the aquifer. In other types of aquifers, however, denitrification can be a significant N loss, especially in those that staturate finer-grained and unconsolidated soils (Smith and Duff 1988).

Thus, about 99.9995% of the NO_3^{2-} produced in soils does not appear in the aquifer waters and is lost from soil water either *in situ* or *en route* to the aquifer. It is not lost within the aquifer because the O_2 content there is too high to allow for denitrification (Table 6). Under field conditions, nitrite would accumulate only when denitrifying organisms are supplied with excessive amounts of oxidant (nitrate) and much lower levels of reductant (organic matter). In these situations bacteria generally reduce nitrate only to nitrite, not to N_2 or NH_4^+ as they would if nitrate itself were the limiting factor.

If the "missing" mM levels of NO_3^{2-} were to be lost *en route*, equal amounts of dissolved organic matter (DOM) would have to occur in the percolating soil water. However, because the beach seep waters and leach water from the experimental soil column contain very little dissolved UV-fluorescent material (indicative of high DOM levels) this situation is highly unlikely. Also, some wells that are shallow or of low volume would then have DOM levels that are greater than the limits for potable waters.

Aquifer Turnover Times

These and other data are useful for calculations of aquifer response and turnover. For example, a storm in February of 1988 produced large and rapid changes in the nitrate, silica, and chloride content of beach seep water in Tumon Bay and in the freshwater well at Fadian (Matson 1989). Response time to this "event" was calculated to be on the order of hours to days. This is not unrealistic when conservative values for hydraulic conductivity of 100 m d^{-1} for carbonate platforms similar to these (Mink 1976, Oberdorfer and Buddemeier 1985) are used. Dr. L. Heitz (UOG Water and Energy Research Inst., pers. comm.) estimated hydraulic conductivities of from 600 to 3600 m d^{-1} (vertical) and .3 to 3 m d^{-1} (horizontal).

However, perhaps rapid changes in chemistry occur only in waters that may literally "pour" off the top of the aquifer at the nearshore transition zone (Fig. 9). These waters respond to sudden events such as the storm in February discussed above. They cannot represent the "homogenous" waters that, inland, are up to 60 m deep (Fig. 10). Thus, mixing

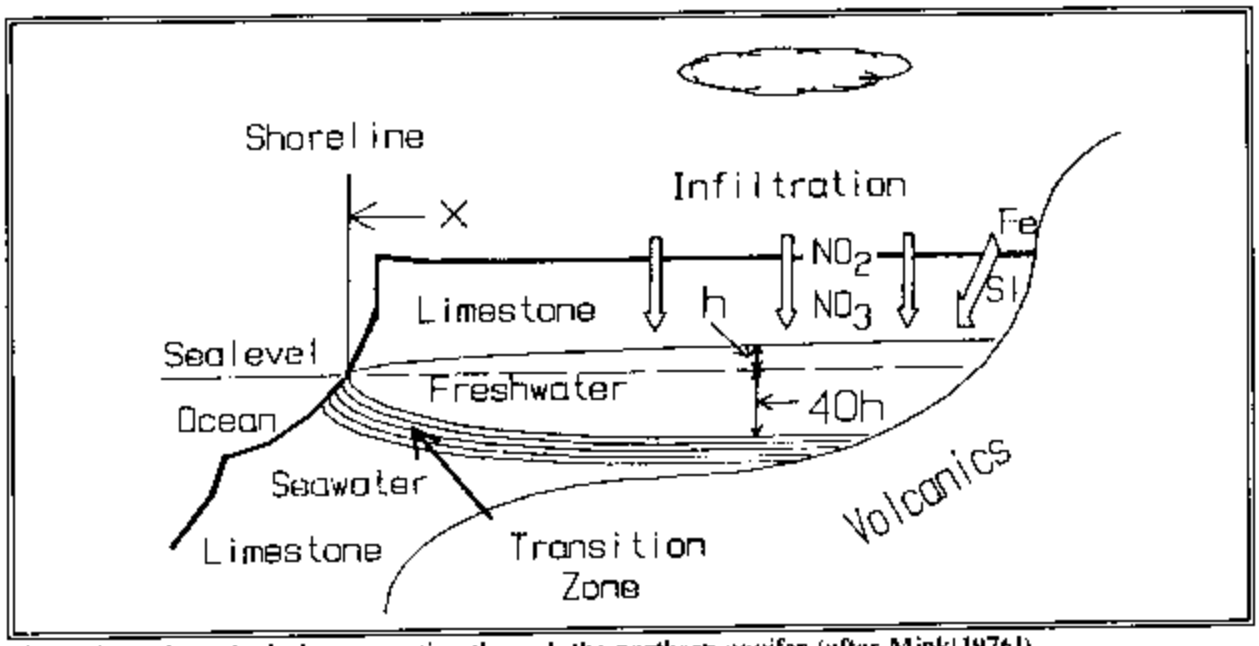


Figure 9. An hypothetical cross-section through the northern aquifer (after Mink[1976]).

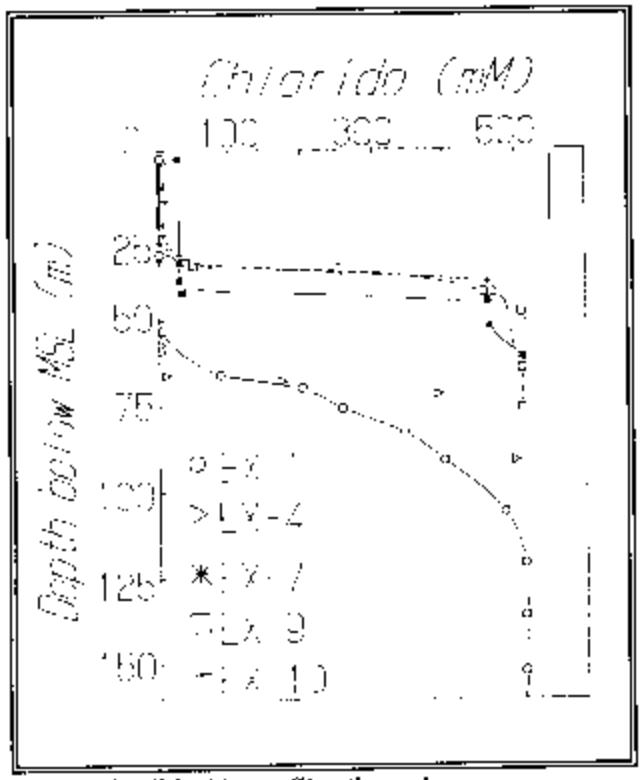


Figure 10. Chloride profiles through some experimental wells, after Contractor and Srivastava (1989). Full-strength seawater has 550 mM Cl.

of "new" surface aquifer waters with those in the deep layer must be somehow restricted.

Therefore, data from the three Fadian wells were used to see if conservative mixing does occur within the aquifer layers. If the data infer that advective (and conservative) rather than diffusive mixing occurs, then the aquifer waters must mix (1) relatively rapidly, and (2) in response to some advective force that physically moves water around within the basin. In this respect, Contractor and Srivastava (1989) showed that fluctuations of up to 1.2 m can occur in the level of well waters, apparently due to tides. Other forces that could drive mixing include lateral exchange in tidal waters, internal ocean waves, rapid changes in atmospheric pressure, and "streamflow" of recharge water within the carbonate plateau *en route* to the aquifer (Valiela *et al.* 1980, Contractor *et al.* 1981, Matson 1989, 1991c).

As it turns out, conservative mixing does occur (note the r^2 value for Fadian slopes in Table 5), at least at Fadian, but which is essentially within the nearshore transition zone (Fig. 9; Matson 1991c). Because both nitrate and silica are rather conservatively mixed in the three layers of the Fadian wells (Fadian data in Table 5 are from all three wells), we can calculate a residence time by dividing mean depth (*ca.* 25 m, Fig. 10) by recharge (1.15 m yr^{-1}, Table 7). This gives a net residence time of *ca.* 22 years for the entire freshwater layer.

Mean depth can also be approximated using the Ghyben-Herzberg model (Mink 1976), where

$q = 41*k*h^2/2x$, and
q = discharge (m^3 m^{-1} of shoreline d^{-1}),
k = 100 m d^{-1},
x = distance (m) inland from the coast, and,
41 = the sum of the ratio of 1 unit freshwater height above sealevel and 40 is the depth of freshwater below MSL.

Heads of 2 to 3 m have been commonly observed at well sites 3 to 5 km inland (Contractor and Srivastava 1989). A freshwater head of 2 -3 m then implies that 80 -120 m of freshwater occur down to the mixing zone. Thus, turnover time would be on the order of 70 to 100 years. In either case, this is a long time for a dangerous pollutant. This may be especially problematic because drinking waters are drawn from nearer the surface of the freshwater layer to prevent coning of seawater layers. This layer may be part of the aquifer that has a low residence time. Therefore, a potential pollutant could be withdrawn into wells and/or exported to the coastal zone very quickly.

Conclusions and Recommendations

Natural rates of nitrification in soils near three drinking water wells above Guam's northern aquifer is sufficient to supply much more nitrate to the aquifer than what it presently contains. Coastal sediments, however, are not a direct source of high nitrate levels in coastal waters;they serve as a conduit for nitrate rich aquifer waters that percolate through them.

Percolation rates are sufficiently great (hours to days) through the carbonate plateau, especially from saturated soils, that drinking waters could quickly be contaminated with pollutants long before detection by monitoring agencies.

An experimental soil column, constructed with field soils, can adequately model nitrate flux to the aquifer and may be used effectively for other solutes.

No evidence was found for inclusion in aquifer water of N from animal waste, except nearshore in Tumon Bay.

Commercial, industrial, and residential development in northern Guam should be restrictively zoned and extremely well-regulated in order to prevent contamination of the aquifer.

Monitoring agencies should, in the immediate future, determine the actual response time of aquifer waters to changes in rainfall, percolation, and tides. Also, the chemical signature of well waters in all major subbasins of the aquifer should be precisely identified. This will assist in studies of the turnover time of waters in each subbasin, knowledge of which is critical to effective protection and management.

Monitoring agency personnel should devise a sampling regime that includes DAILY monitoring of representative wells in all well fields and acquire and be trained to use automated analytical equipment to obtain "real-time" data.

Part of a thorough study of the dynamics of the northern Guam lens should include a search for potentially toxic substances that may have precipitated within the carbonate platform above the aquifer. Such a study should be especially designed for platform materials near existing and historical dumps.

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References

Atkinson M.J. 1988. Are coral reefs nutrient limited? Proc. 6th Int. Coral Reef Symp. *1*:157-166.

Cameron, K.C. and Wild, A. 1984. Potential aquifer pollution from nitrate leaching following the plowing of temporary grassland. J. Env. Qual. *13*:274-278.

Contractor, D.N., J.A. Ayers, and S.J. Winter. 1981. Numerical modeling of salt-water intrusion in the northern Guam lens. Univ. of Guam Water and Energy Res. Inst. Tech. Rpt. 27, UOG Station.

Contractor, D.N. and R. Srivastava. 1989. Calibration of a saltwater intrusion model for the northern Guam lens using a microcomputer. Univ. of Guam Water and Energy Res. Inst. Tech. Rpt. 69, UOG Station

D'Elia, C.F., K.L. Webb, and J.W. Porter. 1981. Nitrate-rich groundwater inputs to Discovery Bay, Jamaica: A significant source of N to local coral reefs? Bull. Mar. Sci. *31*:903-910.

Eckert, J.M. and E.R. Sholkovitz. 1976. Flocculation of iron, aluminum, and humates from river water by electrolytes. Geochim. Cosmochim. Acta *40*:847-848.

Grosenbaugh, D. A. 1979. Role of the blue-green alga *Nostoc muscorum* as a possible nitrate source to the groundwaters of Guam. Univ. Guam Wat. Energy Res. Inst. Tech. Rpt. 9.

Johannes, R.E. 1980. The ecological significance of the sub-marine discharge of groundwater. Mar. Ecol. Progr. Ser. *3*:365-373

Jones, M.N. 1984. Nitrate reduction by shaking with cadmium : Alternative to cadmium columns. Wat. Res. *18*:643-646.

Kreitler, C.W. and L.A. Browning. 1983. Nitrogen-isotope analysis of groundwater nitrate in carbonate aquifers:Natural sources versus human pollution. Jour. Hydrol. *61*:285-301

Lewis, J.B. 1987. Measurements of groundwater seepage flux onto a coral reef:Spatial and temporal variations. Limnol. Oceanogr. *32*:1165-1169.

Matson, E.A. 1987. Groundwater intrusion into coral sediments and a reef moat of Guam. Eos *68*:1689 (abstr).

Matson, E.A. 1989a. Aquifer nitrate in the coastal zone: Changes associated with rainfall and tides. Proc. Ann. Mtg. Amer. Soc. Limnol. Oceanogr., Fairbanks (abstr).

Matson, E.A. 1989b. Biogeochemistry of Mariana Island coastal sediments:terrestrial influence on $\delta^{13}C$, Ash, $CaCO_3$, Al, Fe, Si, and P. Coral Reefs 7:153-160.

Matson, E.A. 1990. Significance of runoff and terrestrial erosion to the nutrient status of the estuaries of Guam. Univ. of Guam Water and Energy Res. Inst. Rpt. 70, UOG Station.

Matson, E.A. 1991a. Water chemistry and hydrology of the "Blood of Sanvitores": a Micronesian red tide. Micronesica *24*:91-111

Matson, E.A. 1991b. Nutrient chemistry of the coastal waters of Guam. Micronesica *24*:113-138.

Matson, E.A. 1991c. Nitrate flux through soils and the aquifer to the coastal zone of Guam, Mariana Islands. Limnol. Oceanogr. revision in review

Matson, P.A., P.M. Vitousek, J.J. Ewel, M.J. Mazzarino, and G.P. Robertson. 1987. Nitrogen transformations following tropical forest felling and burning on a volcanic soil. Ecol. *68*:491-502.

Mink, J.F. 1976. Groundwater resources of Guam: occurrence and development. Univ. of Guam Water and Energy Res. Inst. Tech. Rpt. 1, UOG Station.

Morris, A.W., R.F.C. Mantoura, A.J. Bale and R.J.M. Howland. 1978. Very low salinity regions of estuaries: Important sites for chemical and biochemical reactions. Nature *274*:678-680.

Nishio, T. and T. Fujimoto. 1990. Kinetics of nitrification of various amounts of ammonium added to soils. Soil Biol. Biochem. *22*:51-55.

Oberdorfer, J.A. and R.W. Buddemeier. 1985. Coral Reef Hydro-geology. Proc. 5th Int. Coral Reef Symp. *3*:307-312.

Peterson, B.J. and B. Fry. 1987. Stable isotopes in ecosystem studies. Ann. Rev. Ecol. Syst. *18*:293-320

Rosenfeld, J.K. 1979. Ammonium adsorption in nearshore anoxic sediments. Limnol. Oceanogr. *24*:356-364.

Sahrawat, K.L. 1982. Nitrification in some tropical soils. Plant Soil *65*:281-286.

Schneider, J. and G. Rheinheimer. 1988. Isolation methods. pp. 73-94 In: B. Austin (ed.). Methods in aquatic bacteriology. Wiley Interscience, G.B.

Slater, J.M. and D.G. Capone. 1987. Denitrification in aquifer soil and nearshore marine sediments influenced by groundwater nitrate. Appl. Environ. Microbiol. *53*:1291-1297.

Smith, R.L. and J.H. Duff. 1988. Denitrification in a sand and gravel aquifer. Appl. Environ. Microbiol. *54*:1071-1078.

Valiela, I., J.M. Teal, S.B. Volkman, C.M. Cogswell, and R.A. Harrington. 1980. On the measurement of tidal exchanges and groundwater flow in salt marshes. Limnol. Oceanogr. 25:187-192.

Webb, K.L. and W.J. Wiebe. 1975. Nitrification on a coral reef. Can J. Microbiol. *21*:1427-1431

Wells, E.R. and N.C. Krothe. 1989. Seasonal fluctuations in $\delta^{15}N$ of groundwater nitrate in a mantled karst aquifer due to macropore transport of fertilizer-derived nitrate. J. Hydrol. *112*:191-201

Wiebe, W.J. 1985. Nitrogen dynamics on coral reefs. Proc. 5th Int. Coral Reef Symp. *3*:401-406.

Zolan, W.J. 1982. A preliminary study of natural aquifer discharge on Guam. Univ. Guam Water and Energy Res. Inst. Tech. Rpt. 34, UOG Station.