



SIGNIFICANCE OF RUNOFF AND TERRESTRIAL EROSION TO THE NUTRIENT STATUS OF THE ESTUARIES OF GUAM

by

Ernest A. Matson

Technical Report 70

June 1990



WERI

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

**SIGNIFICANCE OF RUNOFF AND TERRESTRIAL EROSION
TO THE
NUTRIENT STATUS OF THE ESTUARIES OF GUAM**

by

Ernest A. Matson

UNIVERSITY OF GUAM
DEPARTMENT OF NATURAL SCIENCES
AND
MARINE LABORATORY

June 1990

Technical Report No. 70

of the

WATER AND ENERGY RESEARCH INSTITUTE
of the
WESTERN PACIFIC

Project Completion Report

for

**SIGNIFICANCE OF RUNOFF AND TERRESTRIAL EROSION TO THE
NUTRIENT STATUS OF THE ESTUARIES OF GUAM**

Project No. 14-08-0001-G1417

Principal Investigator : Ernest A. Matson

Project Period : June 1987 to June 1988

The work on which this report is based was supported in part by funds provided by the United States Department of Interior as authorized under the Water Research and Development Act of 1978.

ABSTRACT

Coastal sediments of Guam were analyzed for excess accumulations of N from terrestrial sources. Sedimentary aluminum and iron were used as tracers of terrestrial soils in nearshore sediments.

Total organic nitrogen (TON) accounted for >98% of coastal sedimentary N in almost all cases, and ranged from 8 to 100 $\mu\text{mol N g}^{-1}$ dry sediment (average of ca. 30), while KCl-exchangeable NH_4^+ and NO_x (nitrite plus nitrate) were almost always less than 0.6 and 0.04 $\mu\text{mol g}^{-1}$, respectively. In most cases, Al and Fe levels reflected erosion of nearby Al- and Fe-rich sources but were not related to the amount of any N fraction in any easily described manner. Regardless of the presence of nearby sources of terrestrial material, coastal environments that are naturally depositional generally contained fine grained sediments with greater amounts of particulate Al, Fe, TON, and NH_4^+ and very low or undetectable NO_x . Organic matter in coastal sediments does not contain any terrestrial signal until the TON contents increase to >100 $\mu\text{mol N g}^{-1}$. In many cases, aluminum is a better tracer of terrigenous material than iron because of preferential sequestering of iron in biochemical reactions.

Natural or accelerated runoff from land does not produce a persistent N signal in sediments as strong as that of Fe and provides relatively little N that persists in sediments compared with N from in situ fixation and oceanic import. Seepage and infiltration of nitrate-rich aquifer water from the northern carbonate platform appears to be the single largest source of terrestrial nutrients to the coastal zone.

If nutrients are in fact "enriched" in Guam's coastal zone, they do not appear in the sediment and may be already incorporated into biomass, which was not measured in this study. Alternatively, eroded particulate nutrients may be rapidly mineralized and exported from coastal areas in dissolved form.

TABLE OF CONTENTS

Abstract..... iii

List of Figures v

List of Tables..... vi

Introduction..... 1

Materials and Methods..... 2

Results and Discussion..... 4

Conclusions..... 18

Recommendations..... 20

Acknowledgements..... 21

Literature Cited.. 22

Appendix I. Terrestrial soil and Agana Bay data..... 24

LIST OF FIGURES

1. Study areas in Guam..... 5

2a. Iron, aluminum, and total organic N in terrestrial soils..... 6

2b. Iron, aluminum, and exchangeable ammonium in terrestrial soils..... 6

3. Iron, aluminum, and total organic N in a core of the Agana River Estuary near the Paseo..... 7

4a. Iron and aluminum vs. distance from shore at the Dungcas River delta..... 9

4b. Ammonium and total organic N vs. distance from shore at the Dungcas River delta, as in Fig. 7a.... 9

4c. Iron and aluminum vs. distance from shore at the NAS storm drain..... 10

4d. Ammonium and total organic N vs. distance from shore at the NAS storm drain, as in Fig. 7c..... 10

5. (left) Iron, aluminum, and total organic N and (right) exchangeable ammonium and nitrate vs. distance normal to shore from a leaking sewer manhole on Alupang Beach..... 12

6. Iron, aluminum, and total organic N from all Agana Bay sites..... 12

7. Iron, aluminum, and total organic N in Tumon Bay sediments..... 13

8. Pore water nitrate content of five cores taken on a transect normal to shore in Tumon Bay in front of the south lawn of the Okura Hotel..... 16

9. Pore water ammonium and nitrate content of cores from the (a) NAS storm drain and (b) Dungcas River deltas..... 16

10. Exchangeable ammonium vs. iron in coastal sediments from (a) Guam, and (b) other Mariana Islands..... 17

11. (top) Organic C ($\mu\text{mol g}^{-1}$) and (middle) the stable C isotope ratio ($\delta^{13}\text{C}$) of OC vs. TON ($\mu\text{mol g}^{-1}$) and (bottom) the $\delta^{13}\text{C}$ of OC in sediments ($\mu\text{mol g}^{-1}$) vs. OC content, all from Ylig River estuary and Cocos Island lagoon..... 19

LIST OF TABLES

1.	Habitat descriptions for sample sites.....	3
2.	Nitrogen fractions and Fe in Guamanian sediments of two transects at three sites in Tumon Bay, and from Pago Bay, Anae Island, and Cocos Island lagoon.....	14
3.	Mean (± 1 S.D.) of all TON, exchangeable NH_4^+ and NO_x , and E-Fe data.....	15

INTRODUCTION

Nearshore sediments generally contain an integrated record of material that has accumulated from a variety of sources. Depending upon the morphology of adjacent land masses and orientation to prevailing winds and tides, material from land and offshore may accumulate in coastal sediments. This may add to material that accumulates there due to natural and autochthonous biochemical reactions, regardless of the presence of land. A terrestrial signal may be detected if sediment contains a particular element or compound that is not expected to occur in the marine environment. In earlier reports (Matson 1986, 1989), it was shown that iron and aluminum, above certain low levels, were good tracers of the occurrence terrigenous material in the coastal zone of Guam and Saipan. Neither autochthonous accumulation nor import from offshore could provide HCl-extractable Fe and Al concentrations in coastal sediments higher than ca. 3 and 20 μmol per gram, respectively. Higher levels would thus indicate the presence of terrigenous material. Here, this technique is used to determine whether terrigenous N, in several forms, is present in amounts in excess of natural accumulation. Influx of terrigenous material could have a substantial effect on the nutrient status of Guam's estuaries and coastal lagoons. This effect could be a stimulation of coral growth or a change in community structure to macroalgae.

In shallow water tropical environments where there is sufficient solar energy to fix large amounts of C into biomass and hard skeletons, the availability of N and Fe may regulate community production and/or structure (Entsch *et al.* 1983b, Wiebe 1985). However, procaryotes may fix sufficient N_2 into biomass using energy derived either directly or indirectly from sunlight, the N of which then becomes available to the community *via* detrital or trophic webs. Although a consensus has not been reached on whether the availability of any element serves to "regulate" or "limit" productivity or other community characteristics (Entsch *et al.* 1983a, Smith 1984, Wiebe 1985, Cook and D'Elia 1987), only a few reports describe the distribution and abundance of these nutrients, especially in the sediments (*e.g.*, Entsch *et al.* 1983b, Corredor and Morell 1985, Matson 1989). The availability of P is not considered to be critical due to its rather uniform distribution in Guam's nearshore sediments at ca. 10 $\mu\text{mol g}^{-1}$, although a large influx of N may induce removal of P (Matson 1986).

For these reasons, a survey of the Fe and N contents was performed at several different sites on Guam and compared with Al contents as a potential indicator of the occurrence of terrestrial N. In order to determine whether erosion of Guam's soils adds to the nutrient regime, (and, hence, stimulate productivity in the coastal zone), I studied the distribution and abundance of three soil and sedimentary N fractions: total organic N (TON),

and KCl-exchangeable NH_4^+ and NO_x (i.e., $\text{NO}_2 + \text{NO}_3$), and the concentrations of labile Al and Fe fractions that readily (ca. 24 h) dissolve in 20% HCl. The effects of accelerated terrestrial erosion on nutrient content of coastal sediments are distinguished from those of natural accumulation by the lack of a detectable N signal from N-rich terrestrial soils despite some obvious accumulations of terrigenous Al and Fe.

MATERIALS AND METHODS

Study Area

The terrestrial soils of Guam can be generally divided into two major groups, and detailed soils maps are available from the Soil Conservation Service. In northern Guam, a thin (ca. 10 to 50 cm) veneer of mixed carbonate and laterite overlays up to several hundreds of meters of carbonate platform. This material is heavily weathered and has relatively low levels of Fe, Si, and Al in comparison with the rich deep red lateritic soils of southern Guam. Also in the south, deep alluvial deposits occur in flood plains of the many rivers. Northern Guam has no rivers and therefore no alluvium.

Coastal study sites were chosen based on their proximity to or isolation from terrestrial runoff. As extremes, Cocos Island and Tumon Bay receive very little surface runoff, while the outwash deltas in Agana Bay are built by such runoff. The Agana River estuary is a deposition zone for material exported from Agana Swamp. The sites are further described below.

Sampling Sites

Single 0.25 kg sediment samples were taken from the top 5 cm with an 8 cm diameter PVC core liner at nearshore sites shown in Fig 1 (dates given in Tables and Figures). A suite of samples was also taken from land in northern Guam (data from southern areas reported earlier [Matson 1986] are also included in discussion), within a reef moat (Tumon Bay), a reef moat with substantial runoff from culverts (Agana Bay), an offshore atoll lagoon (Cocos Island), an offshore island near river runoff (Anae Island), and a windward reef crest near an estuary (Pago Bay). A list of habitat types is given in Table 1. In most cases, samples were obtained from moat water less than 2 m deep on or behind barrier reefs.

All samples were placed in either Zip-Loc or Whirl-Pac bags, kept at ambient temperature in the shade, returned to the University of Guam Marine Laboratory, and dried at 50 °C after the supernatant waters were decanted. The sediment samples were not rinsed to remove associated interstitial (pore) water. Thus, a small fraction of the exchangeable NH_4^+ and NO_x (described below)

Table 1. Habitat descriptions for sample sites.

Site	Characteristics
Cocos Island	Offshore, pristine, barrier reef lagoon (atoll)
Anae Island	Coastal leeward island near lateritic runoff
Pago Bay	Windward fore reef and reef flat estuary
Tumon Bay	Leeward fringing reef estuarine moat with up to 15% NO_x -rich aquifer water
Agana Bay	Leeward fringing reef estuarine moat with storm drainage culverts and sewage

was due to these associated waters in coastal sediments. The terrestrial soil samples (top 5 cm) were comparatively dry when obtained (February 1988), so little, if any, soil water is included.

A sediment core of the Agana River Estuary was obtained with a PVC core liner with rubber stoppers. Holes in the top stopper allowed for supernatant water escape, and the core was sectioned and processed the same day. Pore waters from Agana and Tumon bays were obtained with a sediment spear similar in design to that of Corredor and Morell (1985). A 3 cm diameter PVC pipe was cut obliquely at one end and a plastic shield with 1 mm holes was glued over that end. Approximately 50 cm distal from that end, a 60 cm length of aquarium tubing (that holds 5.5 ml) was inserted through the side of the pipe. The tubing extended to the inside end of the pipe so that a 60 cm³ syringe attached to the distal end could be used to suck pore water from the end of the pipe inserted in the sediment. The exterior of the pipe was marked at 5 cm intervals to establish the depth in the sediment from which the pore waters were obtained. The samples were immediately filtered through Millex 0.22 μm syringe filters into another syringe that was then stored in the shade. Later that day at the Marine Laboratory, the samples were analyzed for NH_4^+ , NO_x , and Cl^- (Haake-Buchler Digital Chloridometer, $\pm 0.9\%$ relative precision).

Nitrogen Analyses

For analysis of exchangeable ammonium and nitrate, two to five gram subsamples of homogenized and dried sediment were shaken on a rotary shaker in 2.0 M KCl (Kodak) for at least two hours (Rosenfeld 1979). Ammonium in both the KCl extract and blank were measured with an Orion ammonia probe, standardized each time in 2 M KCl. The limits of detection varied between 1 and 10 μM NH_4^+ , and the sample and extract volumes were adjusted to keep the signal/noise ratio > 5 . Nitrite plus nitrate (NO_x)

in the KCl extract was quantified with the spongy cadmium shaking method of Jones (1984). Because of the frequently low amounts of nitrate, detection limits ($0.0005 \text{ umol N g}^{-1}$) were often approached, except for some sediments from Tumon Bay that are infiltrated by nitrate-rich aquifers.

Total organic nitrogen ("organic nitrogen" because of the relatively minor contribution of NH_4^+ and NO_3^- , see results) was quantified in duplicate on a Carlo-Erba model 1150 CNS analyzer at 1000°C , with p-amino benzoic acid (PABA) standards. The sampler tins for the CNS analyzer hold a maximum of about 180 mg dry carbonate sediment, and the minimum detectable signal was about 1.5 umol N . Thus, some of the data presented are close to two times the detection limit (8.3 umol g^{-1}) of the method. However, most data are well above this minimum value, and soil levels were much higher.

Iron and Aluminum Analysis

Dried and homogenized 10 gram subsamples of soils and sediments were extracted in sufficient 20% HCl ("Baker Analyzed Reagent") to dissolve carbonates. Fe in this extract was determined colorimetrically with Ferrozine (Stookey 1970, Murray and Gill 1978). Neither magnetite nor pyrite, which can be common in these sediments, is included in this "labile" Fe fraction, which is operationally called extractable Fe (E-Fe). Aluminum in the same HCl extract (E-Al) was analyzed with an atomic absorption spectrometer at the Guam Environmental Protection Agency.

All data presented are single points obtained from analyses of a subsample, except for TON, Fe, and Al, which are averages of at least duplicates.

RESULTS AND DISCUSSION

N, Fe, and Al in Terrestrial Soils

Individual sites in both the northern and southern provinces of Guam may, however, have high levels of the three forms of N studied, depending upon local productivity and on the occurrence of stable forest canopies and limestone forests. Thus, the exchangeable (hereafter referred to as "E-") NH_4^+ and NO_3^- levels are quite variable (Fig. 2a), as are those for TON and Fe (Fig. 2b). No statistically significant relationship exists for these soil fractions and Al, although the Fe/Al ratio clusters around 1. Except for a few high value outliers (discussed below) this, at the outset, dismisses part of the hypothesis that terrigenous N may be distinguished by association in coastal sediments with terrigenous Fe and Al. Nonetheless, terrigenous N levels are several fold to several orders of magnitude higher than in

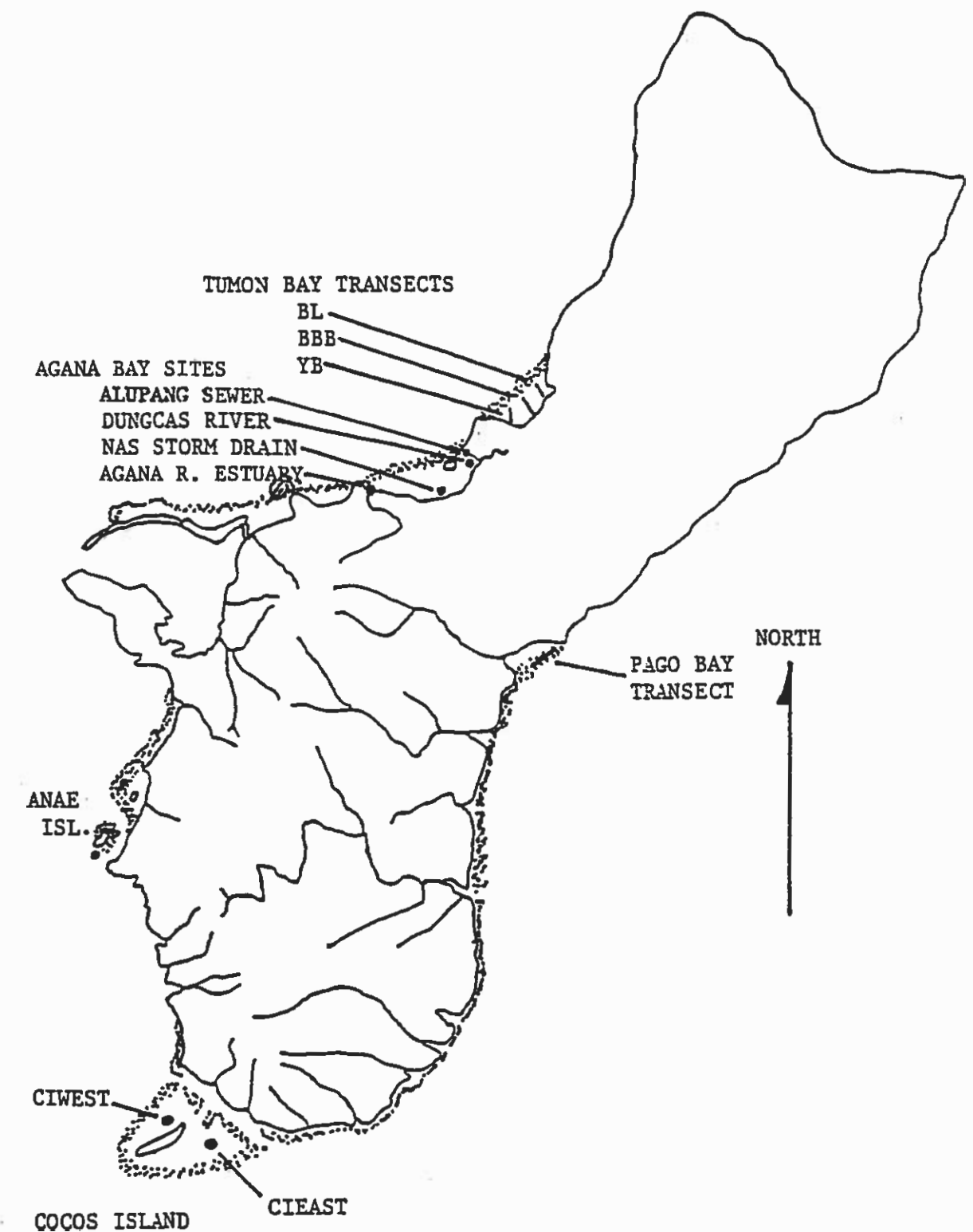


Figure 1. The study areas in Guam.

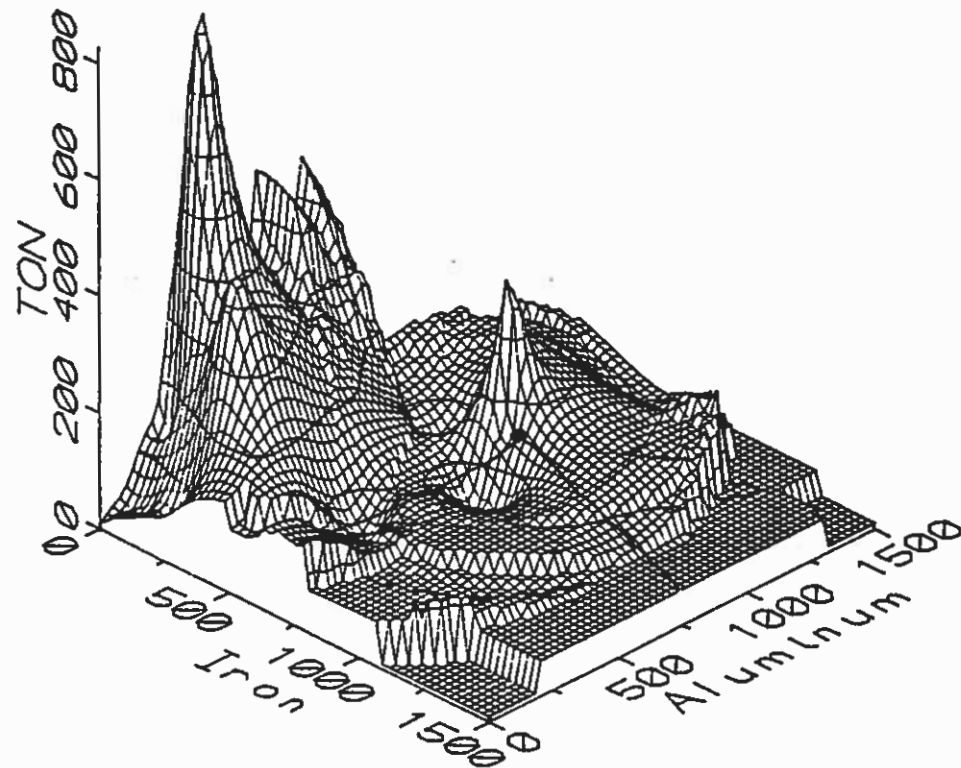


Figure 2a. Iron, aluminum, and total organic N in terrestrial soils.

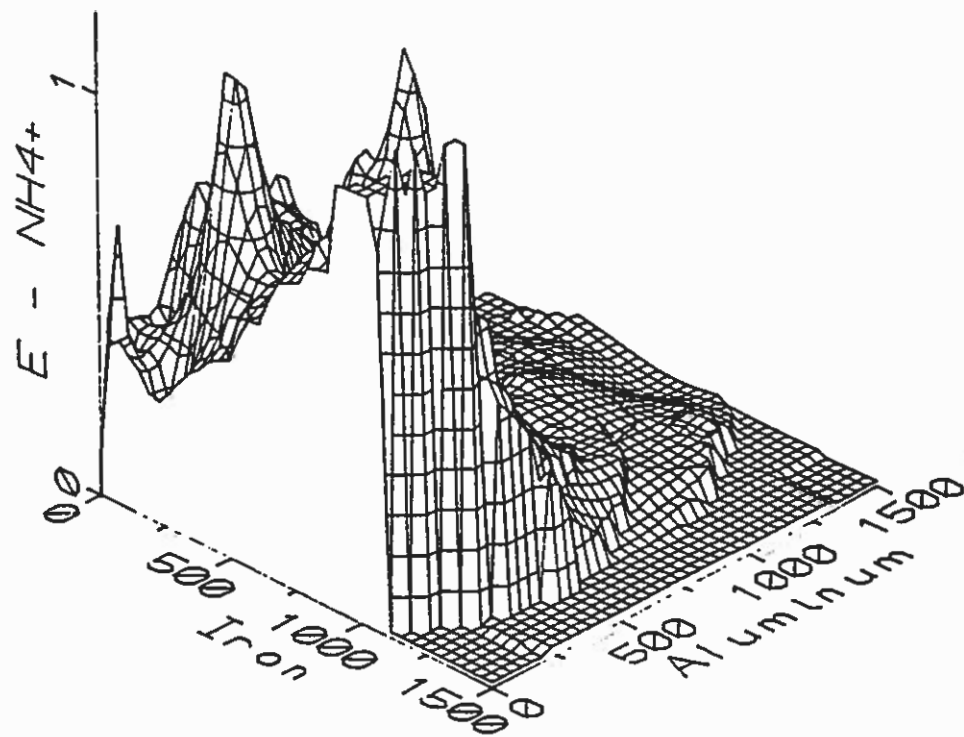


Figure 2b. Iron, aluminum, and exchangeable ammonium in terrestrial soils.

coastal sediments (discussed below). Later, an alternate hypothesis is proposed that states where both high Fe and Al fractions occur simultaneously with elevated N, the N is either also directly from land and has been preserved in deeper sediments of estuaries, or it occurs due to stimulation of N fixation *in situ* by imported terrestrial Fe.

Particulate Phase Nutrients in Coastal Zone Sediments

Such an example of natural accumulation of Fe, Al, and TON was obtained from a core of the Agana River Estuary (ca. 50 m downstream of the Rt. 1 bridge, Fig. 3). Cores such as these supply good information about terrigenous runoff as well as geochemical segregation and post-depositional (diagenetic) changes. In this core (which is typical of several taken at this site), Fe, Al, and TON increase with depth in the core to levels much higher than those in coastal surface sediments away from river influence (see Agana Bay data discussed below). What is particularly noticeable is the lack of a parallel increase in Al, which, on land, occurs in about a 1/1 ratio with Fe. This possibly occurred due to two phenomena. First, Fe coagulates and flocculates into oxyhydroxides and organic P complexes that are rapidly deposited in the mixing zone of estuaries. Next, in deeper core layers, anoxic metabolism produces sulfides that rapidly precipitate Fe into, for example, relatively inert FeS_2 .

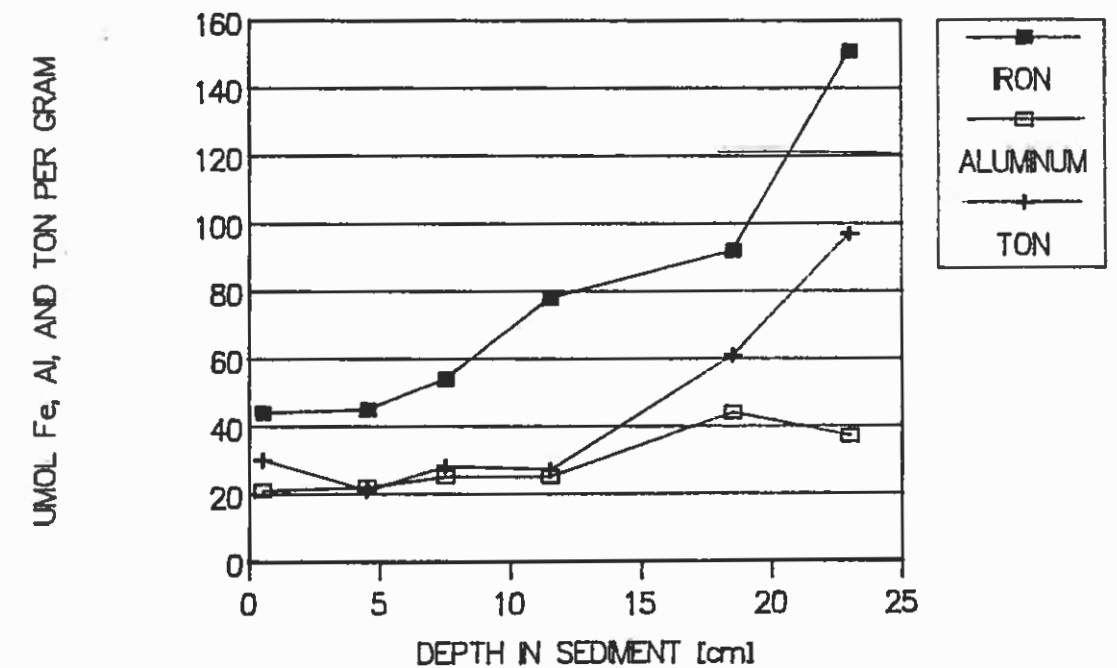


Figure 3. Iron, aluminum, and total organic N in a core of the Agana River Estuary near the Paseo.

This preferentially sequesters Fe but not Al or TON. Simultaneously, however, refractory N compounds (such as humus) may be preserved in the sediments. Al may "passively" accumulate due to simple deposition of Al rich clay minerals. Thus, the accumulation of Fe in this core is largely due to processes that occur after erosion from land, during sediment diagenesis, and before subsequent removal of this sediment from the estuary to areas further from shore during the next large runoff event. These preferential sequestering processes are not, in this case, necessarily related to the simultaneous occurrence of high levels of both Fe and N in source material. Here in the estuary, the TON contents are higher and the NH_4^+ contents lower than in culvert runoff in the same bay (discussed below).

TON, KCl-exchangeable NH_4^+ and NO_x^- , and HCl-extractable Fe values for the surface (top 5 cm) from the Agana Bay sediments impacted by terrestrial surface runoff are given in Figs. 4a-d. All samples were taken from five 120m-long transects (a-e) with a common origin at the mouth of either the Dungcas River or NAS storm drain. The five transects were taken at 30, 60, 90, 120, and 150 degrees from this point. The Dungcas Beach samples are from a depositional delta at the mouth of a small river that largely drains erosional construction areas and asphalt road surfaces. The NAS storm drain samples came from a similar delta formed by sediments from a culvert that delivers runoff from Naval Air Station, and which includes some drainage from the Guam International Airport. At both Dungcas and NAS, the 90 and 120 meter samples are well outside the region of influence of these deltas and are representative of offshore Agana Bay sediments. Nearshore, the outwash deltas expand during the "wet" season (June through December) and erode during the "dry" season (January through May). However, the only significant difference among these two periods was higher levels of ammonium in June than December (not shown). Dungcas River delta had much higher levels of ammonium. The total nitrogen data from these sites show no obvious trend with distance from shore, although it appears that nearshore sediments had higher values than those further out from the source at both sites. Total nitrogen accounted for at least 98.4% of the N fraction in these sediments and ranged from a low of 11 to a high of 53 $\mu\text{mol g}^{-1}$ dry sediment. In all nearshore sediments, both Fe and Al accumulated at all Agana Bay sites, except for an outlying peak offshore of the Dungcas River delta. Although essentially all of the iron in runoff to these sites already occurs in the particulate form (data not shown), deposition still occurs quite close to shore within the freshwater/seawater mixing zone.

Similarly, processes that preferentially accumulate N but not Fe or Al may occur. For example, in sediment collected on a transect normal to an Alupang Beach site where sewage leaks into the coastal waters, N, Al, and Fe are rapidly removed to the sediments within a few tens of meters from shore (Fig. 4a).

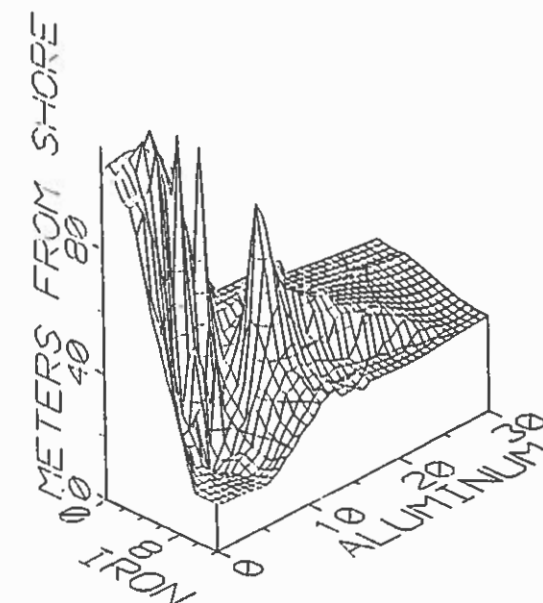


Figure 4a. Iron and aluminum vs. distance from shore at the Dungcas River delta.

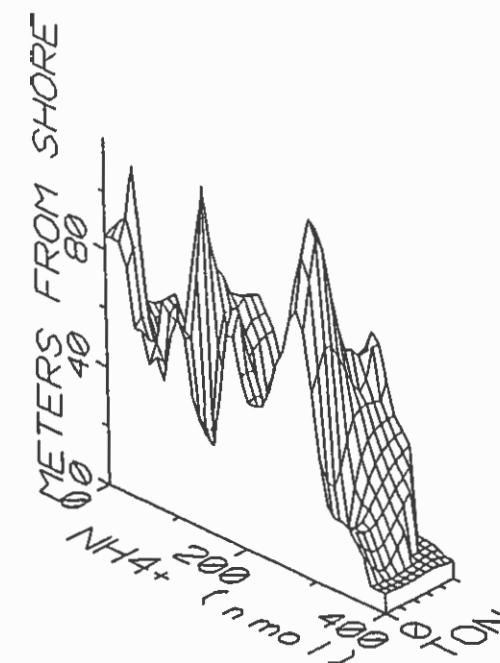


Figure 4b. Ammonium (nmol g^{-1}) and total organic N vs. distance from shore at the Dungcas River delta, as in Fig. 4a.

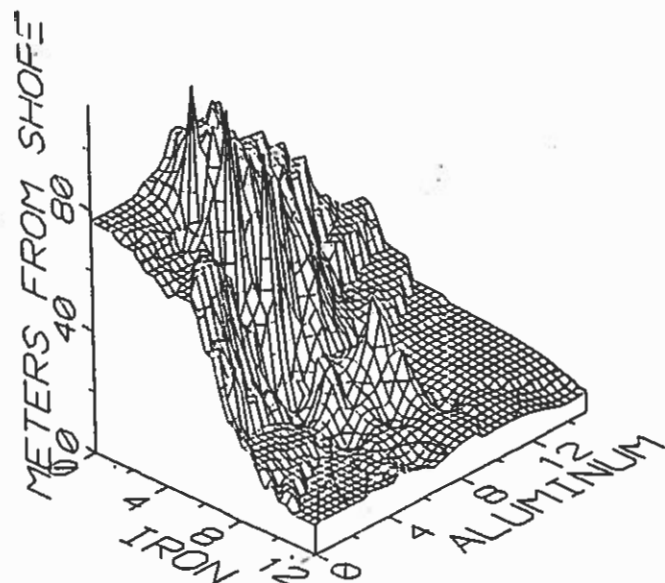


Figure 4c. Iron and aluminum vs. distance from shore at the NAS storm drain.

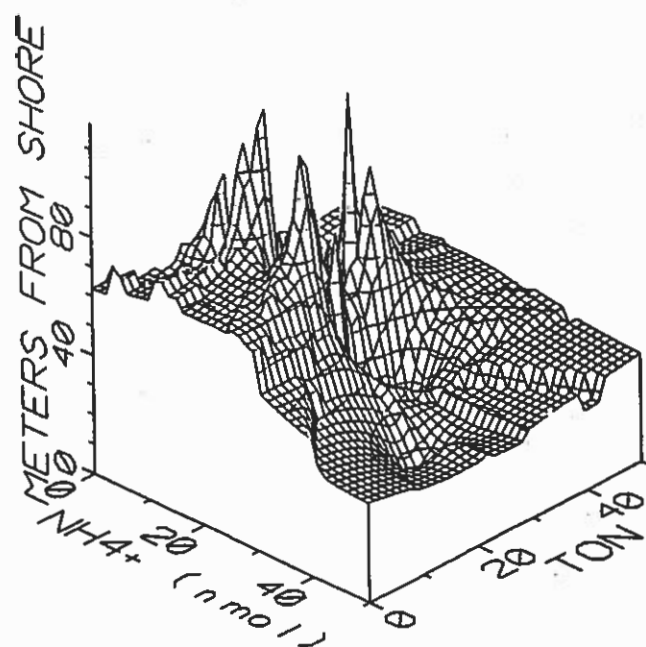


Figure 4d. Ammonium (nmol g⁻¹) and total organic N vs. distance from shore at the NAS storm drain, as in Fig. 4c.

However, the source of this material (Guam's N-rich, and Fe- and Al-poor drinking water aquifer) and its fate prior to discharge in the coastal zone (routing through homes) results in a strong N signal (especially rich in ammonium, Fig. 5) and a weak Fe and Al signal. Regardless, all three elements display parallel and rapid dissipation and dilution within the coastal mixing zone.

All Agana Bay data (except those from the Agana River estuary core) are plotted in Figure 6 for comparison with the terrestrial signal (Fig. 2) and with Tumon Bay, discussed below. The coincident Fe and Al peaks evident in Fig. 2 also occur in Agana Bay, and are later shown to be a persistent characteristic of these coastal sediments.

Nutrient levels in Tumon Bay were generally lower than at the other sites (Fig. 7). Of particular note are the familiar Fe and Al peaks of Figs. 2 and 6 that coincide with a TON peak near the axis origin. This may indicate the presence of a small and barely detectable erosional signal in this otherwise relatively clean bay. Table 2 contains the individual transect data normal to shore in Tumon Bay together with comparative data from Pago Bay, Aanae Island, and Cocos Island lagoon. In contrast with these other sites, Tumon Bay receives ca. 1 m³ sec⁻¹ of aquifer water that averages 114 μ M NO_x (Matson, 1987). Fewer of these springs exist near the BBB series, which is located in the northcentral part of the bay, while essentially no spring water discharges near the YB series in the southwestern end of the bay. Exchangeable NO_x values from the BL site were always equal to or greater than those from all other sites, while NH₄⁺ values were about the same as those from the Dungcas delta (Fig. 4b). Total ON levels were similar to those in Agana Bay, except for some inexplicably high values at 50 and 150 m at BBB in May.

Nitrogen data are given (Table 2) from two cores taken in an offshore, relatively pristine "atoll" lagoon ca. 1 km off the southern coast of Guam (Cocos Island). Total ON and exchangeable NH₄⁺ and NO_x levels were higher than or equal to those of the Agana Bay samples that are directly impacted by surface runoff. Fine grained sediments in a mound area created by Callianassa (a burrowing decapod shrimp) contained more Fe (CIE) and NH₄⁺ than did the coarse-grained sediments under a Halodule uninervis (seagrass) bed (CIW), but they had equal amounts of TON.

The N data have been recalculated to show the average contents for each major site in terms of concentration and in mass per unit area (Table 3). The shallow sediments of Agana Bay contain the lowest amounts of all N fractions measured, while the quiescent sediments surrounding Aanae Island contain the highest (except for nitrate). Tumon Bay has elevated levels of TON in comparison with Agana Bay due to the large amounts of groundwater nitrate that percolate through the sediments (discussed below), especially in the northern end of the bay (Matson 1987). Tumon

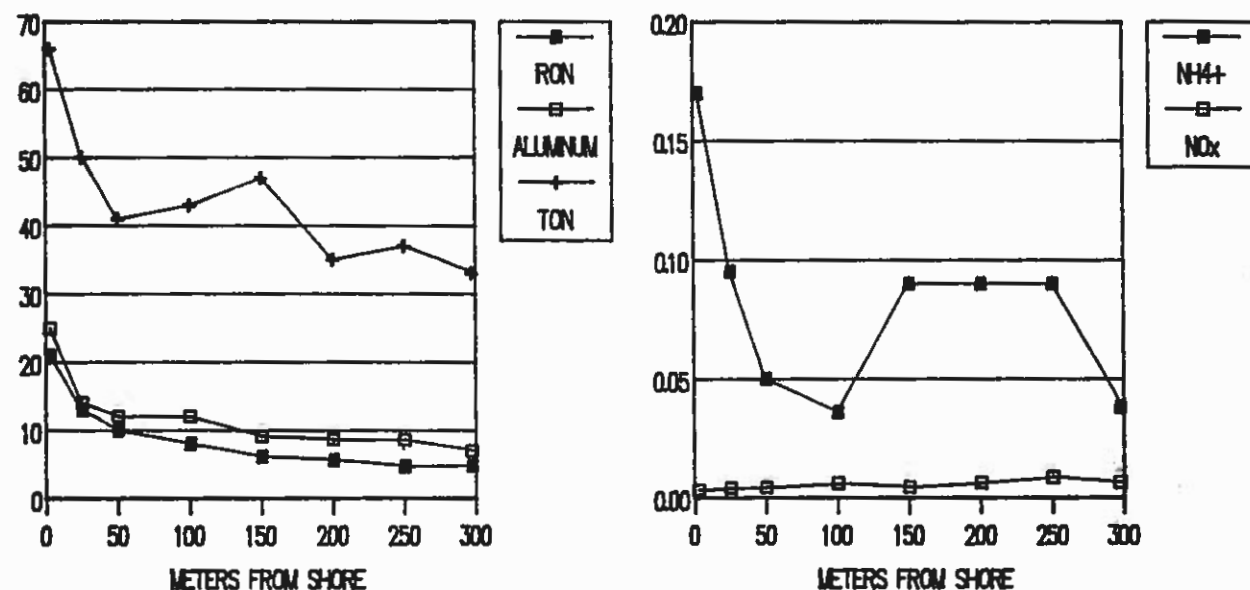


Figure 5. (left) Iron, aluminum, and total organic N and (right) exchangeable ammonium and nitrate vs. distance normal to shore from a leaking sewer manhole on Alupang Beach.

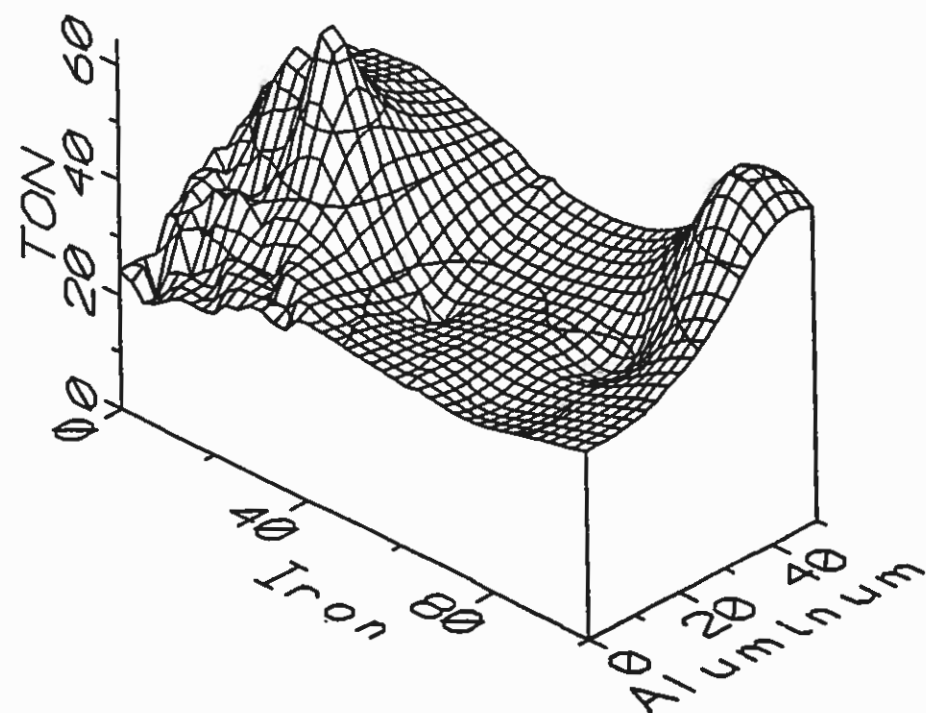


Figure 6. Iron, aluminum, and total organic N from all Agana Bay sites.

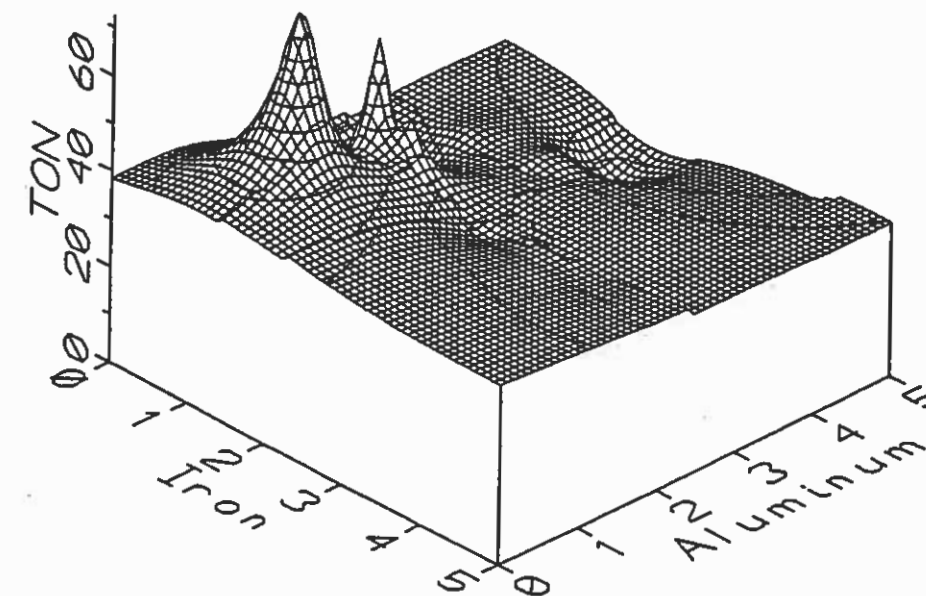


Figure 7. Iron, aluminum, and total organic N in Tumon Bay sediments.

Bay and Cocos Island have equivalent amounts of TON, but the N at Cocos is probably due to N fixation in the roots of plants and within epibenthic blooms of cyanobacteria and diatoms. Pago Bay fore reef samples are probably most representative of coral reef sediments although Fe levels of up to $11 \text{ } \mu\text{mol g}^{-1}$ imply that Pago River material has been deposited. This, however, may be a natural accumulation in this coral-rich area, especially in comparison with the CIE samples that have at least twice as much Fe in a relatively runoff-free environment.

Dissolved Nutrients in Coastal Sediments

Other types of N delivery also occur, especially in northern Guam where the aquifer leaks NO_x -rich water to the coastal zone. In this case, N enrichment occurs without simultaneous enrichment in Fe and Al simply because the aquifer waters are quite low in Fe and Al (Matson, unpublished), both of which are relatively insoluble in seawater in comparison with NO_x . An example of this enrichment is given in Fig. 8 with data from a pore water transect of Tumon Bay normal to the shore from the southwestern border of the Okura Hotel. In these pore waters, especially the ones closer to shore (10 and 50 m), nitrate levels are up to half those of the aquifer (ca. $114 \text{ } \mu\text{M}$) and over 100 times those in coastal ocean water ($0.29 \text{ } \mu\text{M}$, Lassuy 1979, Matson, unpublished). In terms of nutrient "runoff" from land, the northern unconfined

Table 2. Nitrogen fractions and Fe in Guamanian sediments of two transects at three sites in Tumon Bay, and from Pago Bay, Anae Island, and Cocos Island lagoon.

Site	TN	ENH4+	ENox	EFe
	umol/g dry sediment			
Tumon Bay (May 1987)				
BL-50 ^(a)	32	0.054	0.83	2.5
BL-150	31	0.24	0.98	2.6
BBB-50	73	0.063	0.93	1.1
BBB-150	61	0.077	0.83	1.2
YB-50	32	0.082	0.4	3.8
YB-150	18	0.063	0.9	1.9
Tumon Bay (December 1987)				
BL-50	31	0.11	3.6	1.1
BL-100	13	0.14	1.0	0.88
BL-150	11	0.14	1.6	0.91
BBB-50	46	0.29	0.1	1.5
BBB-100	31	0.15	2.6	0.87
BBB-150	31	0.27	0.6	1.1
YB-50	31	0.14	0.45	1.9
YB-100	26	0.13	1.0	1.4
YB-150	22	0.12	0.5	0.9
Pago Bay Fore Reef (May 1989)				
PB-1	20	0.20	0.0024	11
PB-2	35	0.23	0.0018	4.9
PB-3	28	0.39	0.0018	5.6
PB-4	30	0.36	0.0012	5.3
Anae Island (May 1989)				
AI-1	44	0.31	0.00029	27
AI-2	149	1.21	0.0024	44
AI-3	98	0.94	0.0016	23
AI-4	88	0.33	0.0023	29
AI-5	31	0.10	0.0015	17
Cocos Island cores (December 1987)				
CIE A-2 ^(b)	36	0.58	0.036	18
CIE B-9	31	0.47	0.041	19
CIE C-16	31	0.71	0.050	23
CIE D-21	31	0.31	0.027	20
CIE E-24	32	0.57	0.036	20
CIW A-2	33	0.36	0.050	2.9
CIW B-4	30	0.17	0.038	2.5
CIW C-9	30	0.16	0.040	2.3
CIW D-13	28	0.19	0.050	2.9
CIW E-17	33	0.17	0.044	3.5

^(a) numbers for Tumon Bay refer to distance (m) from shore.
^(b) numbers for Cocos Isl. refer to depth (cm) in sediment.

Table 3. Mean (± 1 SD) of all TON, exchangeable NH₄⁺ and NO_x, and extractable Fe data.

Sample Group	TN	ENH4+	ENox	EFe
	umol/g dry sample			
Dungcas Beach	25(7.2)	0.078(0.074)	0.0096(0.0081)	4.1(1.7)
NAS storm drain	24(5.2)	0.014(0.0071)	0.0058(0.0044)	4.9(2.5)
Tumon Bay	33(16)	0.14 (0.072)	1.1 (0.88)	1.6(0.83)
Anae Island	82(42)	0.58 (0.42)	0.0020(0.0013)	28 (10)
Pago Bay	28(5.3)	0.30 (0.081)	0.0018(0.00042)	6.7(2.9)
Cocos Island	32(2.1)	0.37(0.19)	0.041 (0.0071)	11 (9.1)
	mmol/m ² to a depth of 40 cm			
Dungcas Beach	7,400	23	2.8	1190
NAS storm drain	7,100	4.1	1.7	1420
Tumon Bay	9,800	41	330	460
Anae Island	24,000	168	0.58	8120
Pago Bay	8,120	87	0.52	1940
Cocos Island	9,500	110	12	3190

^(a) mol/m² to 40 cm calculated from average dry densities of 1.35 g/cm³.

aquifer is a major source of fixed N for the coastal zone. When the aquifer leaks through cracks and fissures in the limestone, the pore waters may then contain variable amounts of Fe and Si which are indicative of either (1) the type of soil that overlays the aquifer and/or (2) whether percolating rainwater intercepts volcanic layers that enrich in Fe and Si prior to arrival at the aquifer.

In sediments that are not infiltrated by the oxygenated aquifer waters, the pore waters may accumulate high levels of ammonium but not nitrate, probably due to a combination of denitrification and mineralization of organic N in fine-grained sediments (Fig. 9). Such sediments are common in Agana Bay near the storm drain from Naval Air Station (NAS) and the delta of Dungcas River. At both sites, fine-grained sediments accumulate that induce anoxic conditions and hence, ammonium accumulation. This is in contrast with the coarser, aquifer-infiltrated Tumon Bay sediments that are rich in oxygen, nitrate and poor in iron.

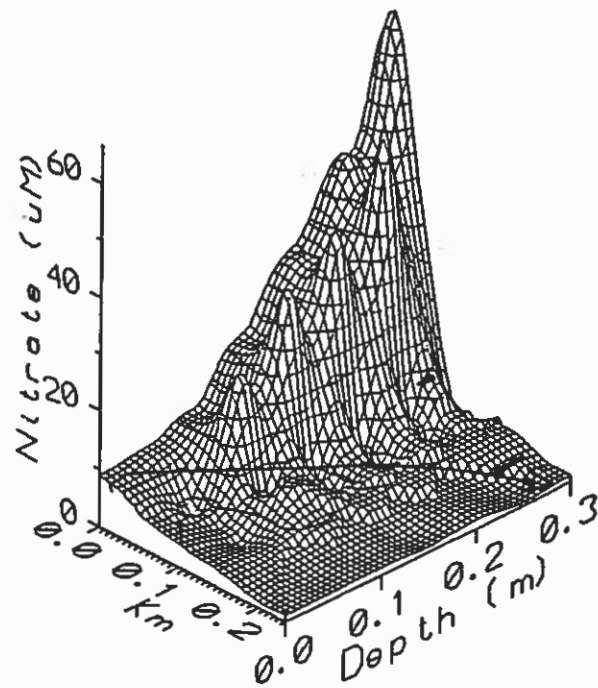


Figure 8. Pore water nitrate content of five cores taken on a transect normal to shore in Tumon Bay in front of the south lawn of the Okura Hotel.

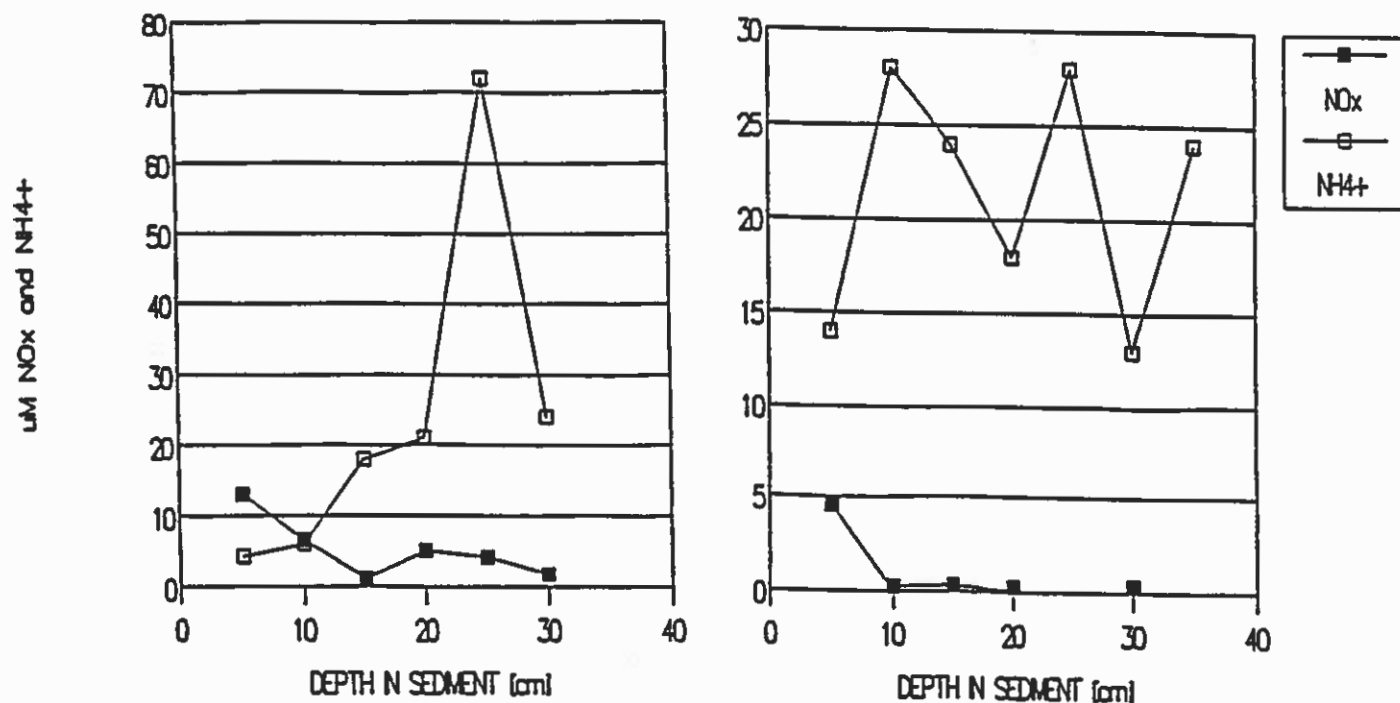
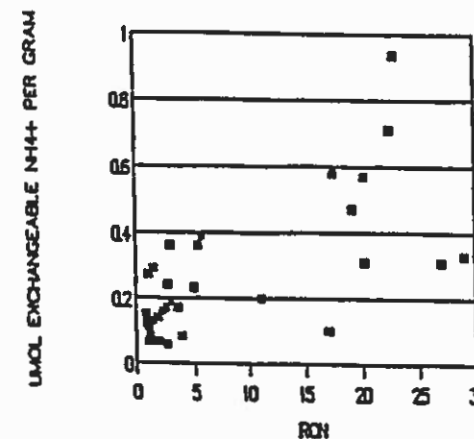


Figure 9. Pore water ammonium and nitrate content of cores from the (a) NAS storm drain and (b) Dungcas River deltas.

Comparison with other Mariana Islands

Some of these data are plotted in Fig. 10 to show the generally rather weak relationship among Fe and N in the coastal sediments, especially from other Mariana Islands (discussed elsewhere). All the data with Fe values above $10 \mu\text{mol g}^{-1}$ are from CIE (little runoff) and Anae Island (significant erosion). The plots do not include Agana Bay data where obvious runoff occurs. For Guam data, regression implies a 46% covariance between iron and exchangeable ammonium, and the value for the other Mariana Islands (Saipan, Rota, Chuuk, and Belau) is 0.07%. Similar plots for TON against iron had R^2 values of 0.19 and 0.26, for Guam and the other Mariana Islands, respectively. It appears then that the simultaneous accumulation of N and Fe in coastal sediments may occur in a statistically significant fashion in sites where little, if any, deposition of terrestrial material occurs (e.g., CIE). However, some sites such as the Anae Island samples show obvious effects of nearby erosional sites, especially in depositional areas where those samples were obtained. Where obvious accumulation was anticipated, such as in Agana Bay, none was evident. Accumulation may therefore depend upon the morphology of the particular sampling area and whether the site is naturally productive.

$$\text{ENH4+} = (0.015) * \text{Fe} + 0.142 \quad R^2 = 0.46$$



$$\text{ENH4+} = -(0.018) * \text{Fe} + 0.2 \quad R^2 = 0.07$$

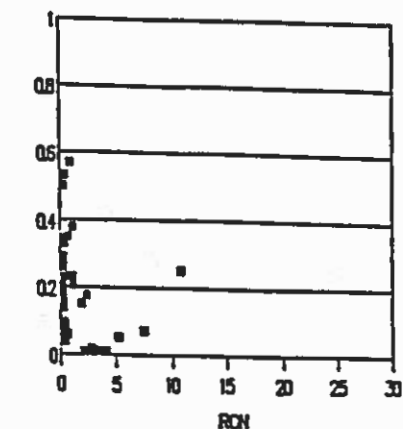


Figure 10. Exchangeable ammonium vs. iron in coastal sediments from (a) Guam, and (b) other Mariana Islands.

This complex relationship is perhaps best described by replotting previously reported stable C isotope data (Matson, 1986, 1989) against C and N values recently obtained on the same samples (Fig. 11). Isotopically heavy C (a relatively high stable C isotope ratio that implies marine origin) only occurs where there are low amounts of C and N. Also, C and N vary strongly together and the C/N ratio of these samples is on the order of 20 to 30, especially in the terrestrial range of stable isotope values (ca. -20 and lower). These values are indicative of the accumulation of terrestrial plant material (Fry and Sherr 1983, Matson and Brinson 1990). The "marine" samples are from Cocos Island Lagoon, and are low in N and have a heavy (more positive) isotopic signature. Thus, in spite of high iron values at Cocos Island, the OC is definitely of marine origin. Further, a ten fold increase in Fe at CIE was not associated with an increase in TON over than at CIW. The iron probably accumulated due to natural biochemical processes that have occurred in this relatively quiescent lagoon.

CONCLUSIONS

With the exception of broken sewerage (Alupang), a volcanic island near runoff (Anae Isl.), and a few samples at storm drain culverts, there was no evidence of significant nutrient enrichment associated with runoff or erosion. Some sites have aesthetically unpleasant characteristics (e.g., the deltas in Agana Bay) that might be corrected by diverting runoff, which would also possibly prevent a problem that might develop over periods of time longer than this study.

The occurrence of levels of Al and Fe above those previously described as "background" (Matson 1986, 1989) may or may not imply the accumulation of other terrigenous nutrient in this suite of samples. Natural marine biochemical processes may enrich sediments with either or both Fe and N, especially in areas that have high water residence times. The entire suite of samples described here was obtained from nearshore where terrigenous influence might have been predicted. However, the large amounts of N on land appear to be (1) retained on land (except in transport through aquifers), (2) distributed through the coastal zone in soluble form, or (3) sequestered in live biomass. If (2) were important, post-depositional mineralization processes should then provide a soluble N signal in the coastal waters. However, that signal requires the use of other techniques, such as analysis of dissolved N fractions in the surface waters (to establish concentrations) and stable N isotope analysis (to distinguish terrestrial from marine sources). Preliminary data from an ongoing project in our laboratory may provide such evidence.

Actually, even in the presence of obvious accumulations of terrigenous Al and/or Fe, many sediments did not show a propor-

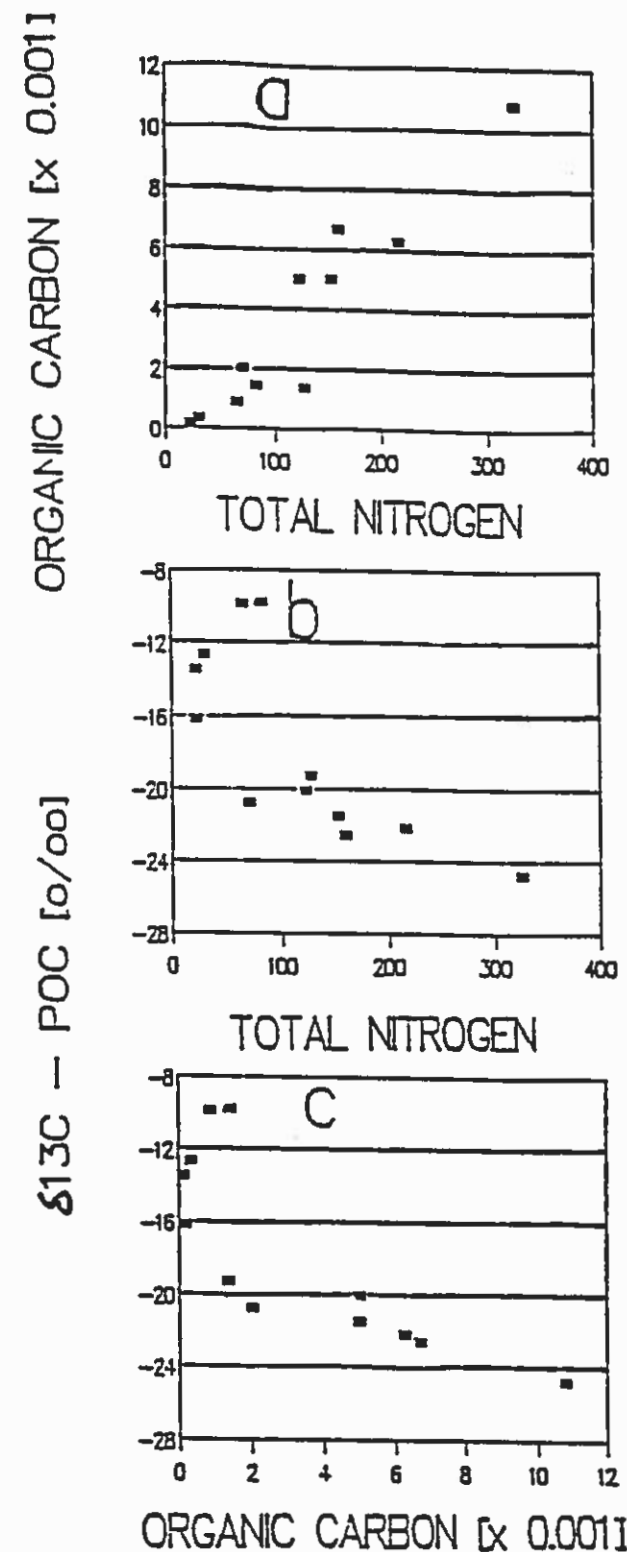


Figure 11. (top) Organic C ($\mu\text{mol g}^{-1}$) and (middle) the stable C isotope ratio ($\delta^{13}C$) of OC vs. TON ($\mu\text{mol g}^{-1}$) and (bottom) the $\delta^{13}C$ of OC in sediments ($\mu\text{mol g}^{-1}$) vs. OC content, all from Ylig River estuary and Cocos Island lagoon.

tional increase in N. It appears as though tropical environments such as these have already dealt with the "problem" of nutrient availability. Now that Guam has become a high island (elevated from a submarine shoal), these "extra" nutrients, when they occur, have no impact on sediment chemistry that is detectable by the methods used in this study. It is quite possible, especially in the light of reports of efficient nutrient recycling, that any "excess" N and Fe have been sequestered in biomass or exported offshore in soluble form. However, offshore export from Guam has been previously dismissed in first-order calculations (Matson 1989). In any case, accumulation in the sediments has not generally occurred, and a distinct terrestrial signal of nutrient enrichment does not occur at the sites studied.

RECOMMENDATIONS

The possibility for nutrient enrichment of tropical coastal waters exists, especially where major changes in land use occurs. Substantial erosion from land could cause large accumulations nearshore, because this material does not travel very far from rivers, culverts, and other sources of runoff (Matson, 1989). However, a persistent signal, such as one in the sediments, is difficult to detect and may require analyses other than those described here. Particular sites, such as the Agana River and culverts and sewers that drain into Agana Bay are potentially important sources of material that could affect community structure over longer periods of time. The diversion of runoff into small moats and bays is a potentially dangerous practice that should be avoided. Likewise, extreme care and forethought should be used in changing the land use of the Agana River watershed. This area has the potential to export large amounts of terrestrial materials that have accumulated for long periods in the swamp.

ACKNOWLEDGEMENTS

I thank Butch Irish, Serge Quenga, Rick Wood, Cathy Cráwford, and Sharon Britos for valuable assistance with field and laboratory work. Chuck Birkeland, Dick Randall, and Gary Denton provided constructive comments on an earlier draft. Ken Morpheau and Mila Pador of the Guam Environmental Protection Agency kindly made available the use of their laboratory for aluminum analysis. The research was also supported in part by an equipment grant from the National Science Foundation, and by the Marine Laboratory and Department of Natural Science of the University of Guam.

LITERATURE CITED

- Cook, C.B., D'Elia, C.F. (1987) Are natural populations of zooxanthellae ever nutrient limited? *Symbiosis* 4:199-212.
- Corredor, J., Morell, J. (1985) Inorganic nitrogen in coral reef sediments. *Mar. Chem.* 16:379-384.
- Entsch, B., Boto, K.G., Sim, R.G., Wellington, J.T. (1983a) Phosphorus and nitrogen in coral reef sediments. *Limnol. Oceanogr.* 28:465-476.
- Entsch, B., Sim, R.G., Hatcher, B.G. (1983b) Indications from photosynthetic components that iron is a limiting nutrient in primary production on coral reefs. *Mar. Biol.* 73:17-30.
- Fry, B., Sherr, E.B. (1984) $\delta^{13}\text{C}$ measurements as an indicator of carbon flow in marine and freshwater ecosystems. *Contr. Mar. Sci.* 27:13-47.
- Jones, M.N. (1984) Nitrate reduction by shaking with spongy cadmium. *Wat. Res.* 18:643-646.
- Lassuy, D. R. (1979). Oceanographic conditions in the vicinity of Cabras Island and Glass Breakwater for the potential development of ocean thermal energy conversion on Guam. Univ. Guam Marine Laboratory Tech. Rpt 53, UOG Station.
- Matson, E.A. (1986) Terrigenous material in coastal zone sediments of Guam and Saipan. Univ. of Guam Water and Energy Res. Inst. Tech. Rpt. 69, 33 pp.
- Matson, E.A. (1987) Groundwater nitrate intrusion into coral sediments and a reef moat of Guam. *Eos* 68(50):1689.
- Matson, E.A. (1989) Biogeochemistry of Mariana Islands coastal sediments: Terrestrial influence on $\delta^{13}\text{C}$, Ash, CaCO_3 , Al, Fe, Si, and P. *Coral Reefs* 7:153-160.
- Matson, E.A., Brinson, M.M. (1990) Stable carbon isotopes and the C:N ratio in the Pamlico River and Neuse estuaries, North Carolina. *Limnol. Oceanogr.* 35:in press.
- Murray, J.W., Gill, G. (1978) The geochemistry of iron in Puget Sound. *Geochim. Cosmochim. Acta* 42:9-19.
- Rosenfeld, J.K. (1979) Ammonium adsorption in nearshore anoxic sediments. *Limnol. Oceanogr.* 24:356-364.
- Smith, S.V. (1984) Phosphorus versus nitrogen limitation in the marine environment. *Limnol. Oceanogr.* 29:1149-1160.

- Stookey, L.L. (1970) Ferrozine-A new spectrophotometric reagent for iron. *Anal. Chem.* 42:779-781.
- Wiebe, W.J. (1985) Nitrogen dynamics on coral reefs. *Proc. 5th Int. Coral Reef Symp.* 3:401-406.

Appendix I. Terrestrial soil and Agana Bay data.

Sample and source	E-Fe	E-Al	E-NH4+	E-NOx	TON
<u>umol per gram dry soil or sediment</u>					
<u>Southern terrestrial soils</u>					
Ylig R. Watershed	751	825	0.170		124
Ylig R. Watershed	800	729	0.011		37
Ylig R. Watershed	707	1428	0.023		49
Ylig R. Watershed	1370	758	0.027		61
Ylig R. Watershed	739	713	0.019		32
Ylig R. Watershed	629	1006	0.170		250
Ylig R. Watershed	720	870	0.170		405
Ylig R. Watershed	507	884	0.019		16
Mt. Alutom A	741	465	1.200	0.012	111
Mt. Alutom B	649	369	0.950	0.020	46
Mt. Alutom C	495	400	0.180	0.011	12
<u>Northern terrestrial soils</u>					
Mt. Santa Rosa	102	43	0.360	0.051	36
AAFB South	79	321	0.710	1.250	840
YIGO PARK A	30	38	0.800	0.064	19
YIGO PARK B	49	61	0.180	0.180	21
AGFGUM-A	55	42	0.480	0.045	36
B	3.8	4.8	0.070	0.002	8.1
NAVY PP	286	242	1.100	0.151	445
Y. SENG SONG A	548		1.300	0.930	288
Y. SENG SONG B	44	210	0.340	0.570	105
Happy Landing Road	210	53	0.220		51
<u>Agana Bay sediments</u>					
Agana River Estuary					
0 cm	73	7	0.190		27
0.5 cm	44	21			30
4.5 cm	45	22			21
7.5 cm	54	25			28
11.5 cm	78	25			27
18.5 cm	92	44			61
23 cm	151	37			97

Appendix I., continued

Sample and source	E-Fe	E-Al	E-NH4+	E-NOx	TON
<u>umol per gram dry soil or sediment</u>					
<u>Alupang leaking sewer pipe</u>					
0 m	21.0	25	0.170	0.003	66
6 m	13.0	14	0.095	0.004	50
12 m	10.0	12	0.050	0.004	41
30 m	8.0	12	0.036	0.006	43
60 m	6.1	9.1	0.090	0.004	47
90 m	5.6	8.6	0.090	0.006	35
120 m	4.7	8.6	0.090	0.009	37
150 m	4.8	6.9	0.038	0.006	33
<u>Duncgas' River Delta</u>					
June 1988					
DB A-1 6 m	6.2	6.3	0.120	0.003	32
-2 12 m	6.7	6.6	0.320	0.003	16
-3 30 m	5.2	4.9	0.140	0.004	16
-4 60 m	3.2	4.7	0.100	0.004	11
-5 90 m	3.3	3.6	0.180	0.006	8.3
-6 120 m	2.9	4.0	0.280	0.005	23
B-1 6 m	6.2	6.6	0.190	0.000	31
-2 12 m	9.7	6.3	0.210	0.003	27
-3 30 m	5.4	5.3	0.062	0.004	24
-4 60 m	5.1	6.5	0.072	0.008	29
-5 90 m	2.3	2.6	0.037	0.008	23
-6 120 m	2.8	3.1	0.055	0.005	22
C-1 6 m	5.9	5.3	0.145	0.004	23
-2 12 m	4.0	4.3	0.048	0.001	22
-3 30 m	5.8	3.5	0.036	0.000	20
-4 60 m	5.1	6.8	0.040		20
-5 90 m	2.9	4.2	0.036	0.013	17
-6 120 m	2.1	3.7	0.025	0.009	20
D-1 6 m	4.4	7.4	0.380	0.003	31
-2 12 m	3.7	6.8	0.080	0.001	36
-3 30 m	5.0	6.2	0.044	0.001	26
-4 60 m	4.4	5.3	0.054	0.001	31
-5 90 m	2.6	3.7	0.055	0.004	24
-6 120 m	1.8	3.2	0.110	0.005	30
E-1 6 m	3.3	4.3	0.042	0.002	42
-2 12 m	4.5	5.1	0.080	0.003	32
-3 30 m	4.1	8.6	0.034	0.004	36
-4 60 m	4.0	6.2	0.088	0.002	26
-5 90 m	1.9	4.3	0.200	0.005	20
-6 120 m	1.1	4.5	0.110	0.010	33

Appendix I., continued

Sample and source			E-Fe	E-Al	E-NH4+	E-NOx	TON
umol per gram dry soil or sediment							
December 1988							
DB	A-1	6 m	4.4	3.6	0.035	0.009	18
	-2	12 m	4.3	4.2	0.098	0.010	24
	-3	30 m	4.4	5.6	0.050	0.009	20
	-4	60 m	4.1	5.4	0.053	0.017	25
	-5	90 m	2.4	2.9	0.047	0.016	21
	-6	120 m	2.8	3.2	0.037	0.027	22
	B-1	6 m	3.1	4.1	0.025	0.016	26
	-2	12 m	5.3	6.1	0.048	0.012	24
	-3	30 m	5.0	6.9	0.105	0.009	22
	-4	60 m	2.6	4.8	0.095	0.009	30
	-5	90 m	2.5	5.3	0.028	0.011	18
	-6	120 m	2.1	5	0.063	0.019	22
	C-1	6 m	6.8	4.9	0.029	0.011	22
	-2	12 m	4.1	5.8	0.025	0.010	19
	-3	30 m	5.2	9.2	0.050	0.006	28
	-4	60 m	3.5	6.1	0.030	0.043	25
	-5	90 m	2.5	6.3	0.032	0.023	25
	-6	120 m	3.1	5.4	0.053	0.022	21
	D-1	6 m	4.1	5.2	0.022	0.029	26
	-2	12 m	4.0	6.3	0.050	0.012	23
	-3	30 m	3.5	4.7	0.022	0.008	23
	-4	60 m	3.9	7.4	0.044	0.012	23
	-5	90 m	2.1	5	0.024	0.016	30
	-6	120 m	2.5	4.8	0.038	0.013	28
	E-1	6 m	4.9	7.2	0.023	0.007	27
	-2	12 m	4.4	7.6	0.029	0.007	34
	-3	30 m	11.0	28	0.037	0.006	56
	-4	60 m	4.1	6.1	0.035	0.009	30
	-5	90 m	6.0	11	0.027	0.026	34
	-6	120 m	3.2	7.7	0.031	0.017	26
NAS STORM DRAIN							
June 1988							
NAS	A-1	6 m	9.2	10	0.025	0.006	32
	-2	12 m	8.4	8	0.016	0.002	23
	-3	30 m	8.0	8.9	0.026	0.007	24
	-4	60 m	7.1	8.7	0.015	0.010	27
	-5	90 m	3.5	5.6	0.018	0.007	22
	-6	120 m	2.7	4	0.014	0.009	17

Appendix I., continued

Sample and source		E-Fe	E-Al	E-NH4+	E-NOx	TON	
umol per gram dry soil or sediment							
B-1	6 m	11.0	6.5	0.013	0.003	24	
-2	12 m	7.2	6.8	0.040	0.005	20	
-3	30 m	4.0	4.9	0.045	0.005	20	
-4	60 m	2.8	4	0.008	0.002	23	
-5	90 m						
-6	120 m	2.8	4.5	0.023	0.000	16	
C-1	6 m	8.2	5.7	0.023	0.003	26	
-2	12 m	5.6	5.4	0.021	0.005	18	
-3	30 m	2.3	3.8	0.018	0.008	21	
-4	60 m	2.6	3.3	0.005	0.006	18	
-5	90 m	3.0	3.7	0.020	0.006	24	
-6	120 m						
D-1	6 m	4.8	5	0.018	0.002	24	
-2	12 m	5.2	4.9	0.020	0.004	21	
-3	30 m	3.7	5.7	0.009	0.005	20	
-4	60 m	2.9	4.1	0.006	0.001	22	
-5	90 m	2.5	4	0.004	0.003	20	
-6	120 m						
E-1	6 m	6.1	5.1	0.009	0.004	34	
-2	12 m	4.7	6.2	0.009	0.000	32	
-3	30 m	4.0	4.3	0.009	0.000	28	
-4	60 m	2.4	2.8	0.005	0.003	30	
-5	90 m	2.5	3.3	0.009	0.003	29	
-6	120 m						
December 1988							
NAS	A-1	6 m	7.1	9.6	0.014	0.000	30
	-2	12 m	7.3	10.5	0.012	0.003	31
	-3	30 m	5.8	6.7	0.012	0.007	32
	-4	60 m	3.6	5.8	0.012	0.006	27
	-5	90 m	3.6	5.8	0.018	0.003	33
	-6	120 m	4.2	5.5	0.014	0.011	33
	B-1	6 m	12.0	14	0.012	0.003	18
	-2	12 m	5.3	6.5	0.013	0.004	20
	-3	30 m	4.3	7.2	0.011	0.005	16
	-4	60 m	2.4	5	0.009	0.004	19
	-5	90 m	3.3	6.7	0.014	0.016	21
	-6	120 m	2.4	4.9	0.014	0.004	18
	C-1	6 m	7.8	9.8	0.012	0.002	19
	-2	12 m	7.0	9.1	0.018	0.003	20
	-3	30 m	3.5	3.7	0.016	0.000	24
	-4	60 m	2.0	3.4	0.014	0.006	26
	-5	90 m	3.0	5.7	0.012	0.007	16
	-6	120 m	1.9	3.9	0.013	0.011	15

Appendix I., continued

<u>Sample and source</u>		<u>E-Fe</u>	<u>E-Al</u>	<u>E-NH₄⁺</u>	<u>E-NO_x</u>	<u>TON</u>
<u>umol per gram dry soil or sediment</u>						
D-1	6 m	8.7	7.7	0.008	0.002	23
-2	12 m	6.5	9.6	0.011	0.006	25
-3	30 m	6.7	6.4	0.012	0.007	26
-4	60 m	3.9	5.1	0.011	0.015	21
-5	90 m	2.6	4.7	0.011	0.009	32
-6	120 m	2.8	4.3	0.011	0.006	26
E-1	6 m	5.4	5.6	0.014	0.003	24
-2	12 m	10.0	11	0.015	0.017	32
-3	30 m	3.9	5.3	0.011	0.005	30
-4	60 m	4.6	5.1	0.012	0.014	32
-5	90 m	2.9	4.6	0.014	0.014	26
-6	120 m	3.4	4.3	0.015	0.020	25

N.B. For the Dungcas' River and NAS storm drain data, letters A - E refer to the five transects taken 30, 60, 90, 120, and 150 degrees normal to shore from the center of the deltas at shore.