GEOCHEMISTRY OF ST. JOHN AND INFLUENCE ON MARINE SYSTEMS

1988

BIOSPHERE RESERVE REPORT NO. 28

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(NPS CONTRACT NO. CX-0001-3-0048)

ABSTRACT

This study was conducted to determine if three geochemical anomalies in St. John, USVI contribute significant amounts of heavy metals to near shore marine ecosystems. Stream water, sea water, marine sediments, and marine organisms from five watersheds were analyzed for Fe, Mg, Mn, Cu, Cr, Ni, and Zn in order to determine the transport of the metals.

Metal concentrations in stream water were typical of small, unpolluted streams, and only iron exceeded the U.S. Environmental Protection Agency (EPA) water quality standard. Magnesium was transported primarily in the dissolved phase, and iron and manganese were transported in the particulate phase. The streams did not appear to have consistently lower or higher concentrations of the metals, but Coral Bay had markedly higher iron and copper than the other streams.

Annual metal export was estimated for Fish Bay Gut. Mg and Fe were exported in quantities greater than 100 kg; the other metals only rarely exceeded this quantity. There was great variability in annual export rates depending primarily on the magnitude and frequency of rain events.

Sea water samples also had low metal concentrations, but iron and manganese exceeded U.S. EPA water quality standards. There was considerable variability in metal concentrations among the sampling sites.

Marine sediments also had low concentrations and high variability among the samples. Intensive sampling conducted in Fish Bay showed that Mn, Ni, and Fe were horizontally zonated with respect to the discharge point of Fish Bay Gut. The high concentrations found in sediments make this sample type the easiest compartment for heavy metal monitoring.

Snails, crabs, and sea urchins from Fish Bay were analyzed. Snails and crabs appear to be good indicator organisms because the levels of heavy metal present in their tissue is well above the detection limit of the standard analytical techniques.

The geochemical anomalies do not pose a serious threat to the marine ecosystems of St. John island.

ACKNOWLEDGEMENTS

We would like to express our gratitude to Mr. Gary Owen of the Caribbean Research Institute for his help during the critical moments. Additional field support was provided by Mrs. Kristen Canoy and her assistants, Vincent and George, of the Virgin Island Environmental Research Station at St. John.

We would also like to thank our friends and colleagues at the Center for Energy and Environment Research (CEER), Lourdes Prieto, Iván Rosa, and Ileana Mejía for their valuable help during this project.

Partial funding for this project was provided by the University of Puerto Rico.

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INTRODUCTION

On a geological time scale, bedrock weathering and tectonic activities have been the largest sources of trace metals entering surface waters (Williams, et al. 1974). These natural inputs may lead to environmental concentrations of trace metals comparable to those produced by anthropogenic pollution. Miller et al. (1982) found dissolved copper concentrations of 4100 and 1300 ug/l in streams overlying or peripheral to large copper deposits, whereas concentrations ranged from 0.8 to 2.6 ug/l in nearby control areas.

A recent study by the US Geological Survey identified several metal deposits in St. John, US Virgin Islands (Tucker, et al. 1985). Researchers discovered anomalously high concentrations of copper, lead, iron, barium, bismuth, and tin. These metals were not restricted to the bedrock, but were also detected in high concentrations in the nearby soils and stream sediments. This geochemical data suggests that bedrock-bound metals are entering the aquatic environment, where they may pose a potential threat to the biota. This study was conducted to provide additional information concerning the potential impact of these heavy metals on marine ecosystems.

Source

St. John's geology was described by Donelly (1957). The Water Island formation, which crops out along the southern slopes, is composed chiefly of keratophyre flows and tuffs (Figure 1). Also of volcanic origin, the Louisenhoj formation overlies the Water Island formation and is composed of augite andesite breccias and tuffs with intercalated conglomerates. The Outer Brass Limestone overlies the Louisenhoj formation and is thin-bedded, silicified limestone. The Tutu formation is coarse volcanic wacke, composed almost entirely of weathered debris from the Louisenhoj formation.

Tucker, et al. (1985) concluded that these formations were not the principal source of the metals. Instead they identified three geological anomalies which they believe to be the source of the metals (Figure 2). They postulate that these anomalies were formed by the emplacement of intrusive bodies of molten lava which flowed through the existing bedrock. The anomalies are metal rich and are characterized by the presence of iron enrichment, copper minerals, alunite, and gossan.

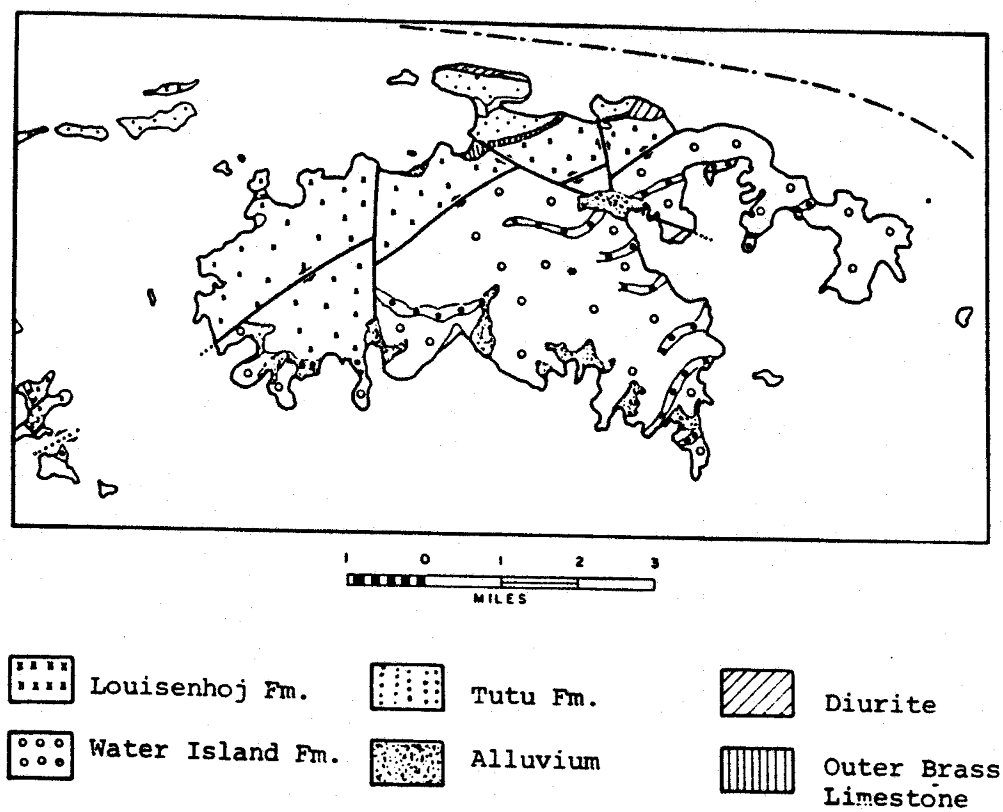

Figure 1. Geology of St. John. Adapted from Donelly (1957).

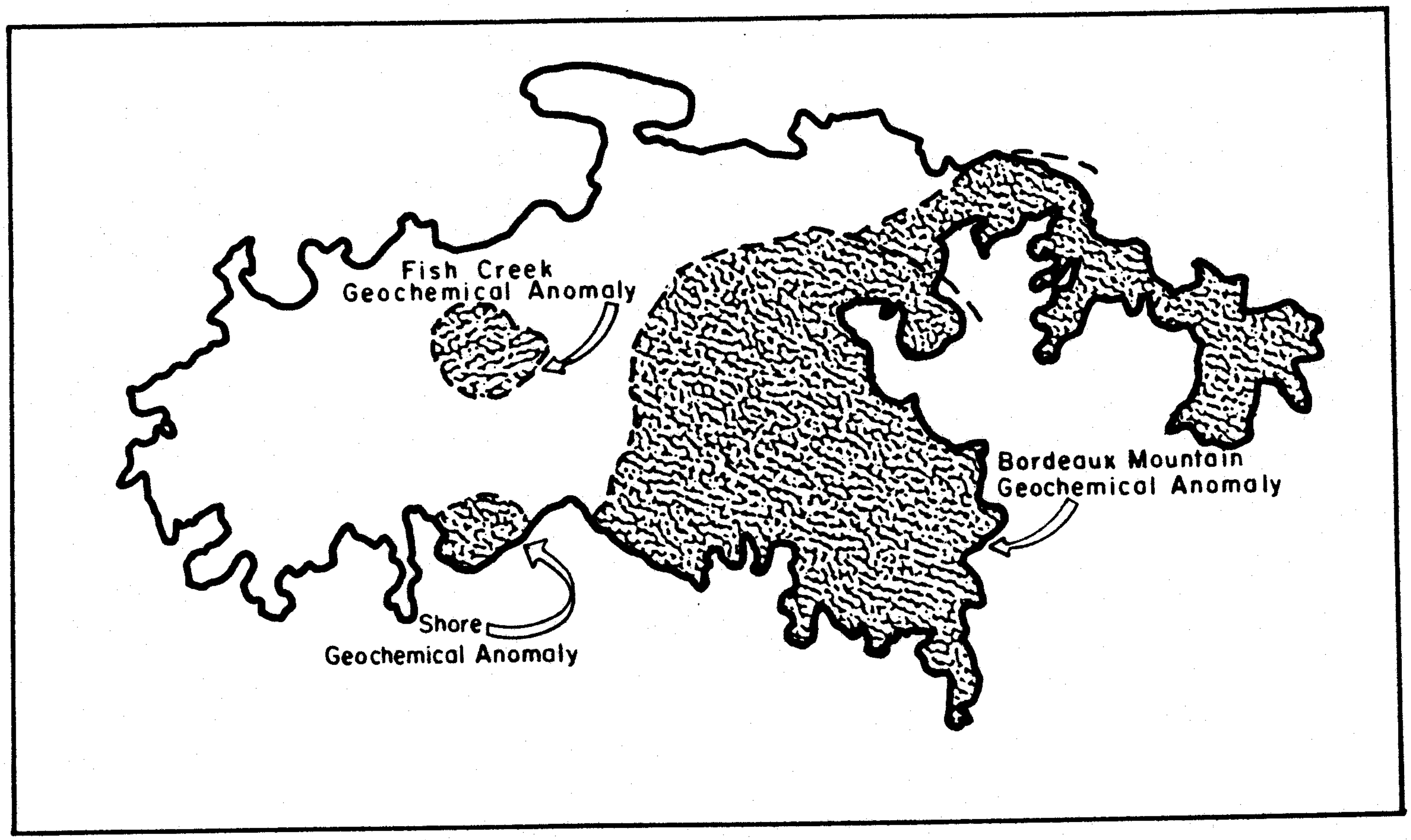

Figure 2. Metal-rich geological anomalies of St. John. Adapted from Tucker, et al. (1985).

The largest anomaly is centered around Bordeaux Mountain and extends from the crest of the mountain to the sea. The authors suggest that a large body of magma flowed through the already deposited bedrock. This anomaly contains intensely argillized areas and nearly vertical iron oxide veins. Many of the streams draining the area contain sediments high in Ag, Bi, Sb, Ba, Cu, and Pb. The second largest anomaly is centered around Fish Bay Creek and is also characterized by high concentrations of Ag, Bi, Sb, Ba, Cu, Pb, and Se in a small area. This anomaly may have been caused by a small metalization zone, possibly related to a geological fault. The third anomaly, the Shore anomaly, is characterized by gossan and intrusive rock containing pyrite.

Transport

Trace metals are affected by various factors as they are transported through streams, lakes, and estuaries on their way to the sea. Metals in stream or sea water may be either dissolved or associated with suspended solids (generally by adsorption). Equilibrium conditions exist between the two phases depending on parameters such as pH, oxidation reduction potential, salinity, and concentration of suspended solids (Williams, et al. 1974, Salomons 1985, Santschi 1984).

Sediments are by far the largest depository of metals transported by streams and sea water. Santschi, et al. (1984) calculated that 50 to 100% of the cadmium and lead entering Narragansett Bay became incorporated, at least temporarily, into the sediments. This retention of metals makes sediments an ideal indicator of pollution.

Of the trace metals associated with sediments, only a small fraction is released to the water column (Hunt 1983). These metals have been incorporated into the sediments by adsorption or complexation and do not form a part of the chemical lattice of the sediment particles (Chester and Voutsinou 1981, Gupta and Chen 1975). These so-called non-residual metals represent a small fraction of the total metal content of the sediments (Salomons 1985).

<u>Transport in St. John</u>: Of the factors that could potentially affect the transport of the bedrock-bound metals through the environment, St. John's climate and hydrology are most important. St. John receives very little rainfall, and drought conditions exist 66% of the time (BC&E 1979). The highest rainfall occurs from August to November (Cosner 1972), but seasonal cycles of

precipitation are hard to establish due to the annual variability (Bowden, et al. 1970).

Although St. John receives an average of 44 inches of rain annually, only 1 inch (2.3%) becomes streamflow (Cosner 1972). The net result is that the island's streams are intermittent, with long periods between flows. Bowden, et al. (1970) reported that in Charlotte Amalie, stream flow occurred in only 14 occasions in a ten-year period (1958 to 1968). These few periods of runoff were generally short lived and characterized by high flows.

The antecedent moisture conditions are very important in determining the amount of stream flow produced by a storm event. Cosner (1972) estimated that only 0.1% of rainfall became runoff when preceded by drought conditions, and 15.1% when preceded by heavy rain.

Several other factors could affect the transport of metals through the environment. Soils are clayey and range from shallow to moderately steep (Rivera, et al. 1970). More than 84% of the island has slopes greater than 30% (BC&E 1979). The combination of easily transported clayey soils and steep topography tends to accelerate soil loss, which also accelerates the loss of soil-bound metals. Fortunately, a land-use survey conducted in 1975 concluded that nearly 88% of the island was forested (BC&E 1979), which diminishes soil loss.

Biotoxicity

Trace metals are toxic to the marine organism above an availability threshold, but many are essential to metabolism at lower concentrations. The toxicity of heavy metals to marine biota will depend on chemical characteristics and on availability (Rainbow 1985, Louma 1983).

Results from several studies suggest that, for many species, there is a direct relationship between exposure to heavy metals and uptake (Bryan 1976). Uptake from solution is the major source of metals for most organisms since the bulk of the metals ingested passed through unassimilated (Pentreath 1973, Sick and Baptist 1979). The availability of free ions (a very small fraction of the total dissolved concentration) appears to control metal uptake from solution (Sunda and Guillard 1976, Anderson and Morel 1982). However, studies with deposit feeding organisms such as clams (Fowler and Unlu 1978) have found significant bioaccumulation from the ingestion of sediments. These metals are either maintained in a metabolically available form which may have toxic effects, or they may be detoxified.

The negative effects of elevated concentrations of heavy metals to marine organisms have been well documented by the use of "in vitro" tests (Louma 1983). However, the result of these laboratory toxicity tests may lead to false or misleading conclusions because the conditions of the assay do not necessarily reflect the physiochemical conditions of the natural ("in vivo") environment. Field studies such as the one conducted by Rygg (1986) have shown that elevated metal concentrations can adversely affect marine communities. Rygg found a significant negative relationship between species diversity in benthic communities and sediment concentrations of heavy metals, especially copper.

The consequences of gross heavy metal pollution in estuarine and marine environments have been frequently observed, but the detection of subtle or gradual ecological effects is difficult. Therefore, the environmental consequences of chronic metal contamination have probably gone largely unnoticed.

Objectives

This study was conducted to provide additional information concerning the potential heavy metal contamination in St. John by accomplishing the following tasks:

1. Measuring heavy metals in stream water, sea water, and marine sediments;

2. Estimating heavy metal export to marine ecosystems; and

3. Measuring heavy metal concentrations in marine organisms and estimating bioaccumulation.

MATERIALS AND METHODS

Samples were collected from several locations in St. John. Stream water, sea water, and marine sediments were taken in Fish Bay, Reef Bay, Little Lameshur Bay, Great Lameshur Bay, and Coral Bay. All sampling sites were located in watersheds draining the geochemical anomalies, and stream sediments had moderate to high concentrations of

trace metals (Tucker, et al. 1985). Most streams were located in undisturbed watersheds, but the Fish Bay and Coral Bay Guts had significant residential development upstream from the sampling sites.
More intensive sampling was conducted in Fish Bay because of strong development pressures in the area. At the time the samplings were conducted, several houses and roads were being constructed. These activities resulted in considerable soil movement to the stream channel. The location of the stream channel had recently been altered by the developers, thereby changing water movement through the mangroves.

Fish Bay's coastal zone has remained largely unaltered. A fringe of red mangrove borders the eastern half of the bay, and a rock outcrop borders the western half. Until recently, Fish Bay Gut drained into the bay at a small channel cut into the mangrove; the current discharge point is difficult to locate because the stream had not yet formed a well defined channel. The old drainage channel was used as the reference point for sample collection. Bottom sediments were uncompacted and deep. There were few rooted algae covering the bay floor, which made sediments highly susceptible to resuspension. Turbidity in the inner bay was very high, and visibility was often less than 2 feet. Aside from several sharks, there was low observable quantity and diversity of fish in the Bay.

Analytical

Trace metal concentrations were determined using an atomic absorption spectrophotometer (Perkin Elmer 2380) equipped with a deuterium lamp background corrector. Iron and magnesium were determined by direct aspiration; total chromium, copper, manganese, nickel and zinc were determined using a Perkin Elmer graphite furnace model HGA 400.

Since metal concentrations were expected to be very low, extreme care was taken to avoid contaminating the samples during sampling and processing. All samples for metal analysis were taken in 1 liter polyethylene bottles soaked for 24 hours in 50% nitric acid and rinsed with distilled, deionized water. Furthermore, samples were processed in CEER laboratories in laminar flow hoods. Acids used to digest the samples or to acidify them were either Ultrex^{R} nitric acid or Intra-analyzed^{R} hydrochloric acid. Blanks were analyzed for the different digestion techniques.

A rigorous quality control program in accordance with US EPA protocol was run with the samples to ensure the reliability of the results (EPA 1979, EPA 1983). This program included the use of blanks, duplicate and replicate analyses, standard additions, and US EPA unknowns.

Stream Water Samples

Samples from the Fish Bay (2 locations), Little Lameshur Bay, Great Lameshur Bay, Bordeaux, and Coral Bay Guts (Figure 3) were analyzed for dissolved and total metals. All samples were taken 3 meters upstream from the point where the stream intersects a road except for Little Lameshur Bay Gut, where the sample was taken at the intersection with Reef Bay trail. The Great Lameshur Bay Gut samples were taken 50 meters upstream from the Virgin Islands Environmental Research Station field station.

Samples were stored at 4 ^{o}C and processed within 48 hours. For the dissolved metal analysis, an aliquot was filtered through a prewashed 0.45 um membrane (Millipore HAWP) and acidified with concentrated nitric acid. The unfiltered portion of the sample was also acidified with concentrated nitric acid for the determination of total metals. Samples for total metals were digested using the hot concentrated nitric acid technique (EPA 1983). Particulate metals were defined as the difference between dissolved and total metals.

Samples for the determination of total suspended solids (TSS) were collected at the same time that samples for heavy metals were taken. TSS were determined gravimetrically using the glass fiber filtration technique (APHA 1980).

Sea Water Samples

Sea water samples were collected just off shore and 15 meters off shore from the gut outlets in Reef Bay, Little Lameshur Bay, Great Lameshur Bay, and Coral Bay (Figure 3). More intensive sampling was conducted in Fish Bay. When the samples were taken, there was no stream inflow. In order to minimize contamination, samples were collected by hand from a slow-moving fiberglass boat or by diving. Concentrated nitric acid and storage at 4 ^{o}C were used to preserve the samples prior to analysis.

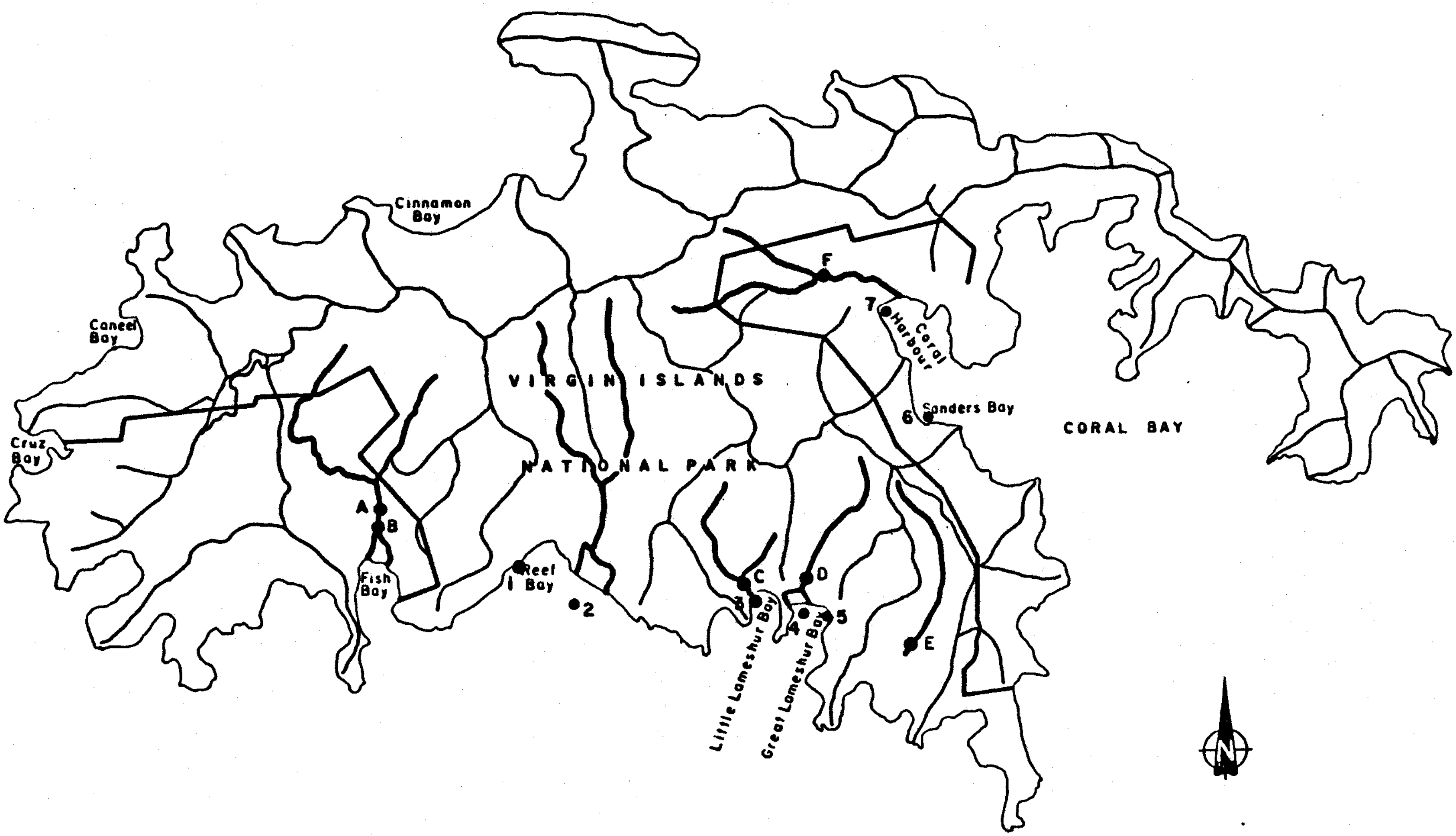

Figure 3. Sampling stations. Letters A to F indicate stream sites. Numbers 1 to 7 indicate sea water and sediment sites.

Samples were digested for the determination of total metals with the addition of 5 ml of 6N hydrochloric acid per 50 ml and heating (Brooks, et al. 1967). Iron, copper, manganese, and zinc were determined by direct aspiration (Sturgeon, et al. 1980).

Marine Sediments

Surface sediments were collected wherever sea water samples were taken (Figure 3), except in Fish Bay (Figure 6a). Sediments were obtained while diving using acid-washed plastic cores (15.2 cm long x 5.1 cm diameter).

The sediment samples were digested using the hydrochloric acid stripping method described in Wood and Acosta Cintrón (1976). Sediment cores were dried at 120 ^{o}C for 7 days. The samples were then sieved and weighed in duplicates. 175 ml of 50% hydrochloric acid was added to each sample, which was allowed to stand for 24 hours. The supernatant was decanted, and another 125 ml of acid was added. After an hour, the supernatant was decanted, and the sample was rinsed 3 times with distilled, deionized water. The digestate was taken to a final volume of 500 ml, and an aliquot was centrifuged at 3000 rpm for 5 minutes. The digestates were diluted for the determination of metals.

Marine Organisms

Invertebrates (sea urchins, crabs and snails) were caught in Fish Bay by hand and stored frozen. The crabs and snails were associated with mangroves, where they live in the roots and trunks of the trees. The sea urchins were found on a flat at the mouth of the gut. Fish traps using lettuce as bait were set up within the bay, but no fish were captured.

Soft tissues (e.g. liver, kidneys, and heart) were removed by dissection from the crabs and sea urchins; total body tissues were used for the snails. The dry ashing technique described in AOAC (1980) was used to digest the tissues. Tissue samples were oven dried at 120 ^{o}C for 24 hours and placed in a muffle furnace for 6 hours at 500 ^{o}C. 50% hydrochloric acid was added to the cool, carbon-free residue, which was then warmed for 4 hours or until the sample dissolved. The solution was later transferred to a 50 ml volumetric flask and an aliquot was centrifuged and filtered through a pre-washed 0.45 um membrane.

RESULTS

Export from the Terrestrial Environment

Heavy Metals in Stream Water: Dissolved, particulate, and total metal concentrations in stream water appear in Tables 1a and 1b. Only iron and magnesium were found in concentrations higher than 100 ug/l; manganese, copper, zinc, nickel, and total chromium content was low in all samples. Concentrations of dissolved and particulate iron varied considerably among the samples. Particulate iron concentrations, which ranged from <120 to 8,200 ug/l, were higher than dissolved concentrations, which ranged from <120 to 804 ug/l. The highest metal concentrations found in this study were dissolved magnesium, which ranged from 3,130 to 11,320 ug/l. In some cases, all of the magnesium was in the dissolved phase, and particulate concentrations were below the detection limit of 400 ug/l. None of the samples contained measurable dissolved manganese, but most contained detectable particulate manganese, which ranged from <5 to 61 ug/l. Dissolved copper concentrations were lower than 15 ug/l, and only one sample exceeded that value for particulate copper. Concentrations of zinc, nickel, and chromium were generally below the limit of detection for this study.

These values are typical of small, uncontaminated streams. They also agree with previous samplings conducted by the US Geological Survey in St. John (Robison, et al. 1973). From 1962 to 1966, the dissolved metal concentrations for Guinea Gut were: iron <10-100 ug/l, manganese <10 ug/l, and magnesium 48,000-85,000 ug/l. The large discrepancy in the magnesium values might be due to differences in land use or metal content of the bedrock. Most of the metals were below the water quality standards set by US EPA for stream water. Total copper, zinc, and chromium concentrations were much lower than the respective standards of 40, 50, and 50 ug/l. On the other hand, 17 of the 19 samples exceeded the total iron standard of 300 ug/l.

Magnesium was the only metal transported primarily in the dissolved phase (Figure 4). Iron and manganese concentrations were much higher in the particulate phase than in the dissolved phase, suggesting that transport occurred primarily associated with suspended particles. In the case of manganese, all of the detectable metal was exported in the particulate phase. Copper transport was not dominated by one phase.

Table 1a. Heavy metals in St. John streams. All concentrations are expressed in ug/l and are broken down into dissolved (D), particulate (P), and total (T) metals. TSS refers to total suspended solids.

SITE	DATE 1987	STREAM DISCHARGE	TSS (mg/L)	Iron D	Iron P	Iron T	Magnesium D	Magnesium P	Magnesium T	Manganese D	Manganese P	Manganese T	Copper D	Copper P	Copper T
Coral Bay Gut	5-8	LOW	13.70	<120	3,490	3,610	4,890	580	5,470	<5	26	31	8	11	19
Coral Bay Gut	5-14	LOW	8.54	237	1,693	1,930	5,410	<400	5,600	<5	7	12	8	3	11
Coral Bay Gut	5-18	HIGH	124.00	142	8,218	8,360	3,450	1,470	4,920	<5	61	66	11	23	34
Bordeaux Mtn. Gut	5-8	LOW	5.92	124	<120	165	7,380	<400	7,380	<5	<5	<5	4	2	6
Bordeaux Mtn. Gut	5-14	LOW	5.73	804	516	1,320	7,260	<400	7,260	<5	8	13	5	3	8
Bordeaux Mtn. Gut	5-18	HIGH	28.86	331	709	1,040	4,910	<400	5,190	<5	16	21	4	3	7
Little Lameshur Bay Gut	5-8	LOW	1.07	208	1,962	2,170	7,750	<400	7,750	<5	<5	8	6	<2	7
Little Lameshur Bay Gut	5-14	LOW	3.00			804			7,600			7			4
Little Lameshur Bay Gut	5-18	HIGH	7.35	198	2,192	2,390	3,450	1,510	4,960	<5	34	39	<2	8	10
Greater Lameshur Bay Gut	5-19	HIGH		124	<120	236	8,370	<400	8,370	<5	48	53	5	<2	5
Fish Bay Bridge	5-7	0.62	37.71	149	1,121	1,270	10,680	440	11,120	<5	24	29	5	3	8
Fish Bay Bridge	5-7	0.64	3.73	124	6,206	6,330	8,540	630	9,170	<5	44	49	14	3	17
Fish Bay Bridge	5-8	0.58		503	<120	552	10,490	<400	10,490	<5	<5	6	7	15	22
Fish Bay Bridge	5-14	0.74		<120	1,640	1,760	6,780	2,880	9,660	<5	40	45	<2	5	7
Fish Bay Bridge	5-16	0.62	7.44	198	606	804	6,260	3,020	9,280	<5	<5	10	<2	6	8
Fish Bay Bridge	5-18	2.28	37.80	<120	3,870	3,990	3,130	2,740	5,870	<5	45	50	<2	10	12
Fish Bay Pond	5-8	LOW	2.40	<120	262	382	11,320	430	11,750	<5	<5	7	5	2	7
Fish Bay Pond	5-14	LOW		124	2,786	2,910	8,010	5,830	13,840	<5	41	46	<2	14	16
Fish Bay Pond	5-16	LOW	6.33	<120	660	780	8,900	<400	9,150	<5	6	11	5	2	7
				DETECTION LIMIT=120			DETECTION LIMIT=400			DETECTION LIMIT=5			DETECTION LIMIT=2		

Table 1b. Heavy metals in St. John streams. All concentrations are expressed in ug/l and are broken down into dissolved (D), particulate (P), and total (T) metals.

SITE	DATE 1987	STREAM DISCHARGE	Zinc D	Zinc P	Zinc T	Nickel D	Nickel P	Nickel T	Chromium D	Chromium P	Chromium T
Coral Bay Gut	5-8	LOW	<5	<5	9	<5	<5	<5	<3	12	15
Coral Bay Gut	5-14	LOW	<5	<5	<5	<5	<5	<5	<3	<3	<3
Coral Bay Gut	5-18	HIGH	8	8	16	<5	6	11	<3	<3	6
Bordeaux Mtn. Gut	5-8	LOW	<5	<5	<5	<5	<5	<5	<3	<3	<3
Bordeaux Mtn. Gut	5-14	LOW	<5	<5	<5	<5	<5	<5	<3	<3	4
Bordeaux Mtn. Gut	5-18	HIGH	<5	<5	<5	<5	<5	<5	<3	<3	4
Little Lameshur Bay Gut	5-8	LOW	<5	<5	<5	<5	<5	<5	<3	<3	6
Little Lameshur Bay Gut	5-14	LOW			<5			<5			<3
Little Lameshur Bay Gut	5-18	HIGH	6	8	14	<5	<5	6	<3	<3	6
Greater Lameshur Bay Gut	5-19	HIGH	<5	<5	<5	<5	<5	<5	<3	<3	<3
Fish Bay Bridge	5-7	0.62	<5	<5	<5	<5	<5	<5	<3	<3	5
Fish Bay Bridge	5-7	0.64	<5	<5	7	<5	<5	<5	<3	7	10
Fish Bay Bridge	5-8	0.58	<5	<5	<5	<5	<5	<5	<3	<3	4
Fish Bay Bridge	5-14	0.74	<5	<5	<5	<5	<5	<5	<3	4	7
Fish Bay Bridge	5-16	0.62	<5	<5	<5	<5	<5	<5	<3	<3	3
Fish Bay Bridge	5-18	2.28	<5	<5	<5	<5	<5	6	<3	<3	6
Fish Bay Pond	5-8	LOW	<5	<5	<5	<5	<5	<5	<3	<3	4
Fish Bay Pond	5-14	LOW	<5	<5	<5	<5	<5	8	<3	5	8
Fish Bay Pond	5-16	LOW	<5	<5	<5	<5	<5	<5	<3	<3	6
			DETECTION LIMIT=5			DETECTION LIMIT=5			DETECTION LIMIT=3		

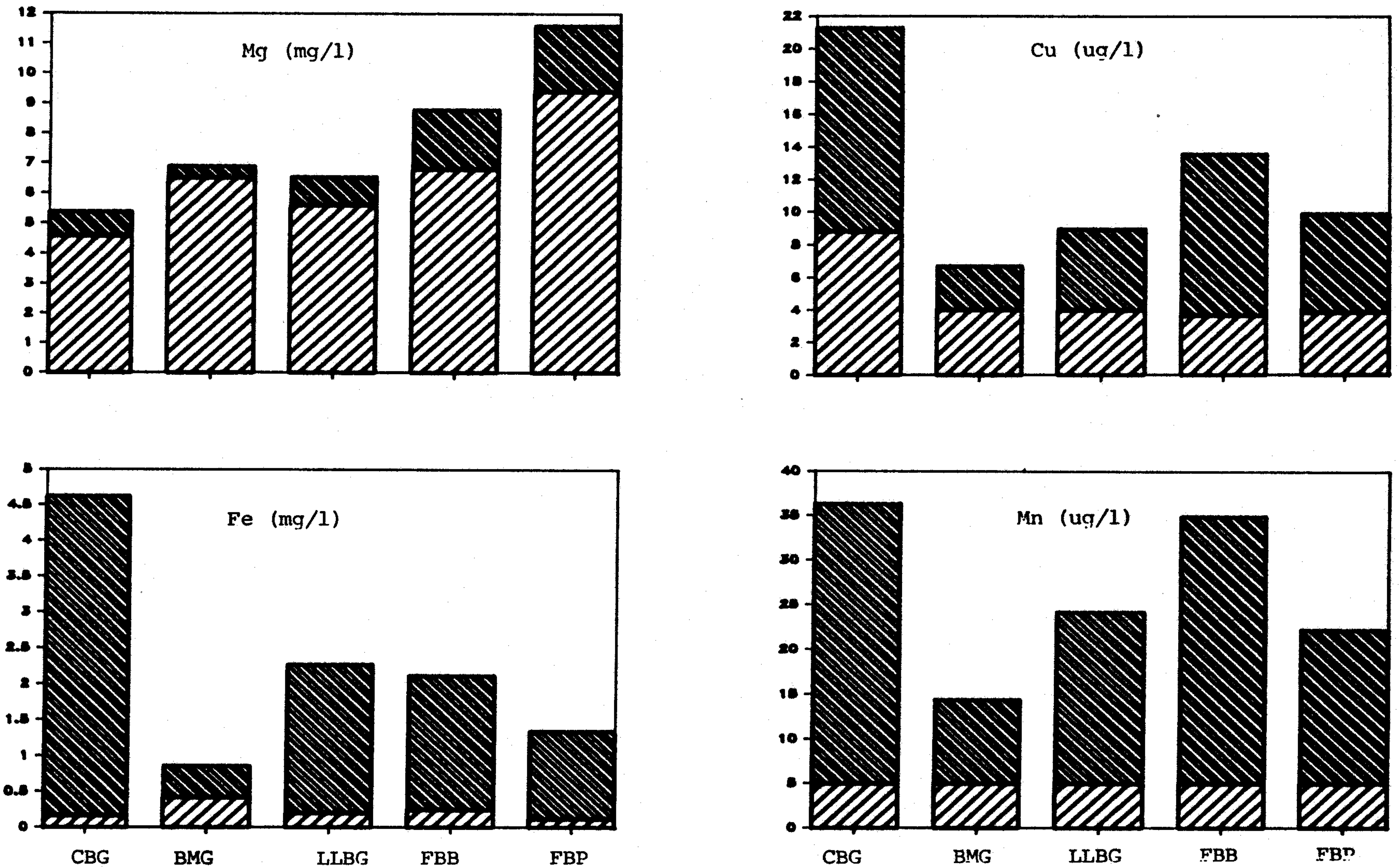

Figure 4. Heavy metal concentrations in St. John streams. Average dissolved (▨) and suspended (▩) concentrations were calculated for common sampling dates (5-8, 5-14, and 5-18). Sampling stations were: Coral Bay Gut (CBG), Bordeaux Mountain Gut (BMG), Little Lameshur Bay Gut (LLBG), and Fish Bay Gut at the bridge (FBB), and at the permanent pond (FBP).

The small number of samples taken in each gut makes it difficult to determine relationships between stream flow, suspended solids, and metal transport, but some generalizations can be made. Magnesium concentrations decreased with increasing discharge, and manganese content increased. The other metals showed no marked relationship between flow rate and metal concentration. Total suspended solids (TSS) were also higher at high flows than at low flows. TSS were positively correlated with particulate copper, manganese, and, to a lesser extent, iron (r^2= 0.854, 0.713, and 0.678, respectively). Particulate manganese and copper were also correlated with particulate iron (r^2=0.843 and 0.592, respectively).

In order to compare the heavy metal content of the guts, averages were calculated for the three sampling dates on which all guts were sampled (Figure 4). These averages showed considerable variation, which could be due to differences in metal content of the bedrock and in land use within the watershed. None of the guts appeared to have consistently lower or higher concentrations of magnesium, iron, copper, total chromium, or manganese. However, Coral Bay Gut had markedly higher copper and iron content than the other guts.

<u>Export Estimate</u>: In order to estimate heavy metal export from the Fish Bay watershed, the stream water heavy metal results were combined with estimated stream flow values. Since the Fish Bay watershed is ungaged, data from Guinea Gut were used to test the validity of hydrological models. Stream flow data for the Guinea Gut station were obtained from Cosner (1972), Curtis, et al. (1983 and 1984), and US Geological Survey preliminary data. Precipitation data were obtained from two sources: from 1963 to 1966, from the Guinea Gut watershed (Cosner 1972), and from 1983 to 1985, from the Coral Bay watershed (NOAA 1983, 1984, and 1985).

The Guinea Gut watershed data showed that export calculations should be based on annual stream runoff rather than individual storm events. The relationship between precipitation and stream runoff for individual storms was very poor (Figure 5). This great variability in the amount of runoff produced by storms of similar magnitude was probably due to the influence of antecedent weather conditions in the watershed (Cosner 1972). If a storm was preceded by drought conditions, evapotranspiration could account for almost 100% of storm waters, and stream flow would be nearly 0. Therefore, the export estimates were based on annual streamflow and precipitation, which are significantly correlated (Figure 5).

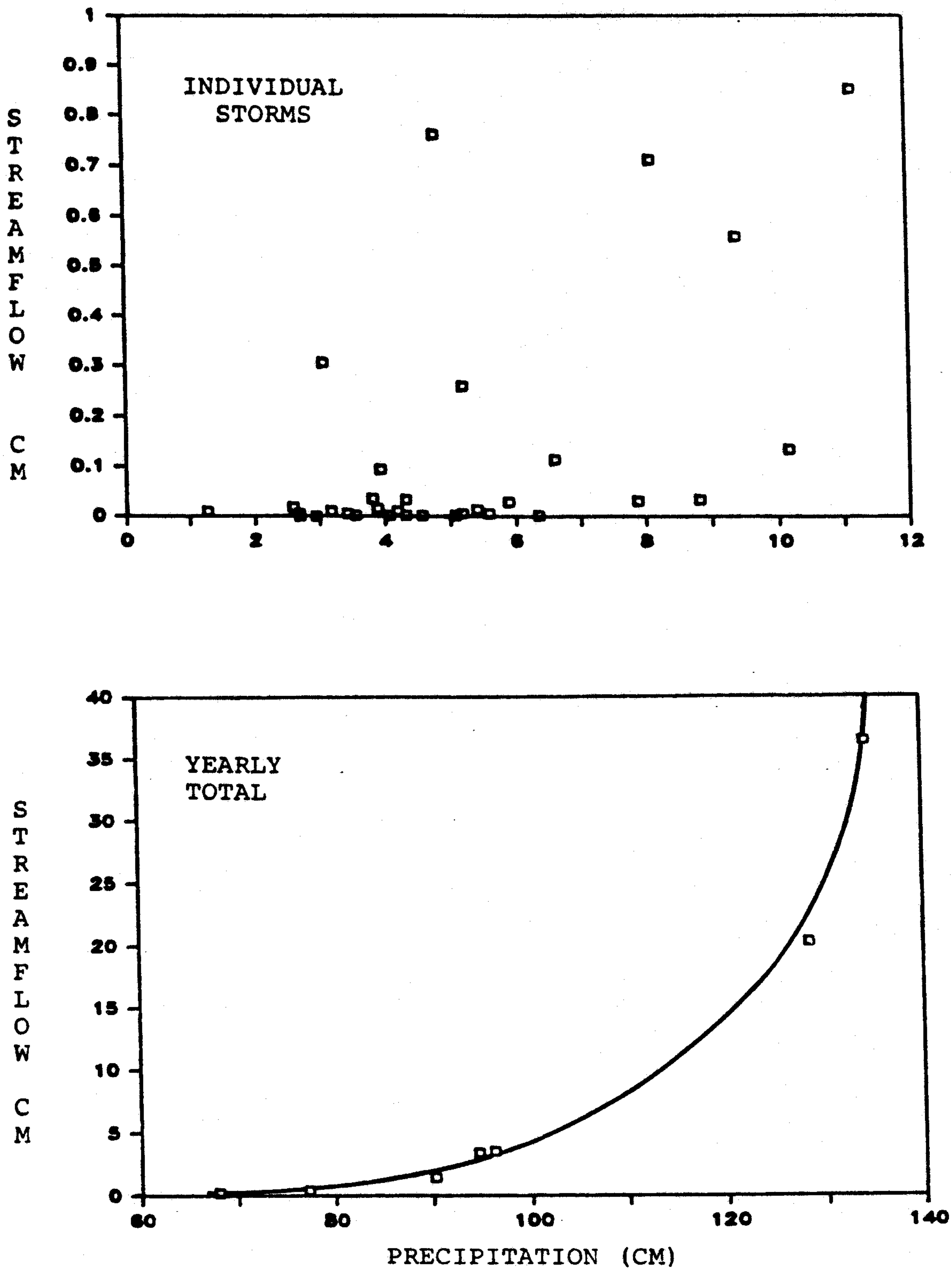

Figure 5. Relationship between precipitation and streamflow for Guinea Gut, St. John.

The next step in the calculation was to extrapolate the precipitation/runoff relationship from Guinea Gut to the Fish Bay watershed by adjusting the runoff data for the drainage area of the two watersheds (0.37 and 1.77 mi^2, respectively; Cosner 1972). Due to the sparsity of hydrological information for St. John, this manipulation represents the best estimate of runoff in Fish Bay. However, Jordan (1972) hypothesized that runoff from the major watersheds of St. John was not directly proportional to the drainage area.

The annual runoff data can be subdivided into two groups (Table 2). In some years (1964, 1966, 1983, and 1985), storm events greater than 2.6 cm (approximately 1 inch) accounted for less than 20% of yearly runoff. Most metal export in these years probably occurred over a long period of time and during base flow conditions. However, in other years (1963, 1965, and 1984), storm events greater than 2.6 cm accounted for more than 65% of yearly runoff. Most metal export in these years probably occurred at high stream flows and over a relatively short period of time. Therefore, the runoff data were divided into "base flow" and "storm flow" years, and the estimated annual runoff values for Fish Bay were multiplied by the average total metal concentrations in Fish Bay Gut during low flow conditions (5-7 to 5-16), and high flow conditions (5-18), respectively (Table 1a and 1b). Generally, there was little difference between the high flow and low flow metal concentrations, probably due to the small number of stream water samples analyzed.

There was great variability in the annual metal export (Table 2). Each year, only iron and magnesium were exported in quantities greater than 100 kg and exceeded 1,000 kg several years. The other metals only rarely exceeded 100 kg. Since zinc and nickel concentrations were generally below the detection limit, the values presented in Table 2 represent the greatest possible export (based on the results of this study). These values are comparable to export calculations made by Hart, et al. (1982) for an Australian stream.

It is very probable that only a fraction of the metals exported by a stream find their way to the near shore marine ecosystems. Many of the island's streams do not drain directly into the sea. Mangroves and salt ponds may act as heavy metal sinks by accumulating metal-rich sediments.

Table 2. Heavy metal export estimate for Fish Bay, St. John.

A. Hydrological data for Guinea Gut:

Year	Rainfall (cm)	Runoff (cm)	Number of Rain Storms <2.6 cm Per Year	% Yearly Runoff Accounted for by Storms <2.6 cm
1964	68.1	0.23	1	1
1966	77.2	0.43	5	17
1983	134.3	36.40	9	12
1985	94.6	3.43	3	2
1963	90.2	1.47	5	66
1965	96.3	3.56	7	93
1984	128.4	20.35	6	99

B. Metal Export Estimates for Fish Bay Gut:

Year	Runoff (L X 10^6)	Fe (kg)	Mg (kg)	Mn (kg)	Cu (kg)	Ni (kg)	Cr (kg)
1964	72	154	715	2.00	0.89	<0.36	0.42
1966	136	291	1,351	3.78	1.68	<0.68	0.79
1983	11,456	24,552	113,918	318.91	141.21	<57.28	66.44
1985	1,079	2,313	10,732	30.04	13.30	<5.40	6.26
1963	464	1,850	2,722	23.25	5.52	2.78	2.78
1965	1,119	4,466	6,570	56.11	13.32	6.72	6.72
1984	6,404	25,550	37,589	321.04	76.20	38.42	38.42

The quantity and chemical partitioning of the trace metals probably varied considerably in the "base flow" and "storm flow" years. Bradley (1984) concluded that the mass flow of metals is greatest during flood peaks. He also concluded that dissolved metal concentrations decrease at high flows, and the quantity of metals bound to particles increases. Therefore, export probably would be greatest during the "storm flow" years, but metals would be relatively unavailable to the environment because they would be tightly bound to suspended particles. During the "base flow" years, there would be less export, but the metals would be in the more bioavailable dissolved state.

Heavy Metals in Marine Near-Shore Environments

Sea Water: Concentrations of total metals in sea water followed a pattern similar to that observed in stream water (Table 3). Of the metals analyzed, iron had the highest concentration (range: 915 to 71 ug/l), followed by manganese (4 to 387), zinc (10 to 20), and copper (all samples <10). These values were considerably higher than the values obtained in Bermuda, and lower than those obtained in Jobos Bay, Puerto Rico (Table 4). Bermuda, like St. John, is a small island relatively free of anthropogenic contamination, whereas Jobos Bay receives the treated effluents of several industries. The difference in concentrations between Bermuda and St. John is especially interesting since it may be an indication that the metal-rich bedrock in St. John is indeed causing an increase in trace metals in coastal waters. However, the different digestion techniques utilized in the studies should be taken into consideration. The Bermuda samples were not digested, and the samples in this study were digested using 10% HCl.

Several of the samples exceeded the EPA water quality standards for coastal waters. Seven of the fifteen samples had more than 200 ug/l of iron, and four samples had more than 100 ug/l of manganese. All of the zinc and copper samples were below the 50 ug/l standards.

There was considerable variability among the sampling sites. Fish Bay apparently had higher concentrations of iron and manganese, and lower concentrations of zinc than the other bays. However, this fact is probably due to the greater number of samples taken in Fish Bay.

Table 3. Heavy metal concentrations in the coastal waters of St. John. Distance refers to the approximate distance from shore in the north/south (N/S) and east/west (E/W) axis. For ID codes refer to Figure 3.

ID Code	Site	Distance N/S (m)	Distance E/W (m)	Fe (ug/l)	Mn (ug/l)	Zn (ug/l)	Cu (ug/l)
7	Coral Bay	15	0	276	56	10	<10
6	Sanders Bay	15	0	190	9	15	<10
5	Greater Lameshur E	15	0	86	4	17	<10
4	Greater Lameshur W	15	0	162	9	10	<10
3	Little Lameshur	15	0	71	4	18	<10
2	Reef Bay E	15	0	24	12	15	<10
1	Reef Bay W	15	0	24	9	10	<10
	Fish Bay	0	0	407	387	10	<10
	Fish Bay	20	0	762	340	10	<10
	Fish Bay	40	0	915	368	10	<10
	Fish Bay	60	0	467	104	10	<10
	Fish Bay	80	0	484	73	20	<10
	Fish Bay	100	0	446	65	10	<10

Marine Sediments: The same concentration pattern that was seen in the stream and sea water samples could also be seen in the marine sediments (Tables 5 and 6). Metals could be arranged in order of decreasing concentration: magnesium (23,800-2,250 ug/g), iron (25,610-1,230 ug/g), manganese (610-4 ug/g), total chromium (388-6 ug/g), copper (33-1 ug/g), nickel (30-1 ug/g), and zinc (<35 ug/g). These values were 2 to 90 times lower than concentrations obtained for Mayaguez Bay, in Puerto Rico, which receives industrial and domestic pollution (Table 7).

Nichols and Towle (1977) studied sediment heavy metal concentrations in Benner Bay, St. Thomas. They obtained the following values: copper 140 to 0.2, and zinc 150 to 0.12 mg/g. These values are not comparable to values obtained in this study because the Benner Bay sediments were digested using hot concentrated nitric acid, which liberates matrix-bound metals in addition to the non-matrix metals liberated by leaching with hydrochloric acid.

There was considerable variation in the metal content of the sediments, possibly due to differences in factors that control adsorption, such as organic matter (Salomons 1985), manganese and iron oxides (Williams, et al. 1974), and percent non-calcareous residue (Jickells and Knap 1984). There was considerable variation in the organic matter content, sand and rock content, and vegetation of the sampling places, which could affect metal concentrations. As was the case in the stream water samples, manganese and copper were positively correlated with iron ($p<0.05$).

Table 4. Average heavy metal content of surface coastal waters. NA means not available.

	Fe (ug/l)	Mn (ug/l)	Cu (ug/l)	Zn (ug/l)	Ni (ug/l)
Bermuda[1]	1.07	0.19	0.2	0.3	0.14
St. John[2]	332	111	<10	13	NA
Jobos Bay, Puerto Rico[3]	541	252	9.6	103	NA

1. Total leachable metals (non-filtered samples without digestion) (Jickells and Knap 1984).
2. Total metals (non-filtered samples with HCl digestion). This study.
3. Dissolved metals (Puerto Rico Environmental Quality Board data for 1984).

Table 5. Leachable metals in sediment core samples from St. John island. Distance refers to the approximate distance from shore. For ID codes refer to Fig. 3.

ID CODE	SITE	DISTANCE (m)	Fe (ug/g)	Mg (ug/g)	Mn (ug/g)	Cu (ug/g)	Zn (ug/g)	Ni (ug/g)	Cr (ug/g)
1	REEF BAY W	15	1,230	12,660	4	7	<35	30	12
2	REEF BAY E	15	1,440	10,630	9	4	<35	15	9
3	LT LAMESHUR	0	1,450	4,700	25	1	<35	6	58
3	LT LAMESHUR	15	2,050	7,300	14	1	<35	16	60
4	GT LAMESHUR W	0	7,440	10,710	131	5	<35	10	49
4	GT LAMESHUR W	15	4,150	5,030	21	9	<35	1	6
5	GT LAMESHUR E	0	5,720	7,630	83	6	<35	13	10
5	GT LAMESHUR E	15	6,430	4,470	41	4	<35	1	8
6	SANDERS BAY	0	3,060	2,930	18	3	<35	5	15
6	SANDERS BAY	15	7,020	9,430	111	22	<35	10	15
7	CORAL BAY	0	7,780	7,110	64	9	<35	4	85
7	CORAL BAY	15	7,220	7,090	46	12	<35	4	13

Table 6. Leachable metals in sediment core samples from Fish Bay, St. John island. Distance refers to the approximate distances from the point of discharge of Fish Bay Gut in the north/south (N/S) and and east/west (E/W) axis. NA means non-available data.

DISTANCE N/S (m)	E/W (m)	Fe (ug/g)	Mg (ug/g)	Mn (ug/g)	Cu (ug/g)	Zn (ug/g)	Ni (ug/g)	Cr (ug/g)
10	0	14,590	9,930	480	13	<35	8	NA
20	0	9,310	8,640	222	5	<35	8	28
50	0	17,280	10,730	186	28	<35	11	388
60	0	11,190	23,800	135	15	<35	6	194
80	0	2,420	2,250	40	4	<35	1	6
90	0	11,160	6,660	362	20	<35	2	NA
100	-60	19,490	11,020	185	33	<35	11	33
100	-40	16,620	10,070	510	27	<35	9	32
100	-20	15,230	7,220	601	21	<35	8	20
100	20	12,730	8,800	145	14	<35	7	25
100	40	10,560	9,580	76	13	<35	5	29
100	60	8,770	10,040	160	15	<35	10	21
150	0	6,590	10,280	42	7	<35	3	23
200	-50	6,280	11,490	54	7	<35	2	17
200	0	5,190	9,740	54	5	<35	2	16
200	50	9,970	10,180	53	17	<35	5	33
200	150	7,400	9,900	35	16	<35	3	23
300	-50	25,610	17,400	248	28	<35	12	365
300	0	5,430	7,920	37	7	<35	2	18
300	50	9,680	10,780	67	15	<35	4	30
300	100	9,260	10,400	48	12	<35	5	31
300	200	10,110	12,650	53	16	<35	5	35

An intensive sampling effort was conducted in Fish Bay to determine if superficial sediment-linked metals were stratified in relation with the gut's discharge point. Three of the six metals studied showed a slight horizontal zonification. Manganese, nickel, and to a lesser extent, iron had markedly higher concentrations in the samples taken within 100 meters of the gut's discharge area than in more distant samples (Figure 6a and b). There were no discernible horizontal patterns for magnesium, copper, or chromium (Figure 6b and 6c). The lack of a strong pattern is not surprising since the stream runoff events that bear metals to the bay occur only 1 to 7 times per year. Post-depositional mixing of particles by physical and biological mechanisms could then affect the original heavy metal imprint on the sediments (Santschi, et al. 1984, Polprasert 1982). The water circulation pattern within the bay, which is yet unknown, may also affect the deposition pattern of the metals.

Samples taken in other bays had lower concentrations of iron, magnesium, manganese, copper, and total chromium than samples taken in Fish Bay (Tables 5 and 6). This difference is probably due to the unequal sample sizes at each site. The greater number of samples taken in Fish Bay permitted samples with higher concentrations to appear in the study.

<u>Marine Invertebrates:</u> Concentrations of manganese, copper, magnesium, and iron for several species of snails, crabs, and sea urchins are given in Table 8. Metal content varied considerably among the different organisms. The concentrations found in snail and crab tissues were generally higher than those found in sea urchins. However, this observation was not tested statistically due to the small sample size and large standard deviations.

Table 7. Heavy metal content of surface near-shore sediments.

Site	Cr (ug/g)	Cu (ug/g)	Fe (mg/g)	Mn (ug/g)	Ni (ug/g)	Zn (ug/g)
Mayaguez Bay, Puerto Rico[1]	690	31	60	827	487	70
Fish Bay, St. John[2]	68	12	9	9	7	<35

1. Adapted from Wood and Acosta Cintrón (1976).
2. This study.

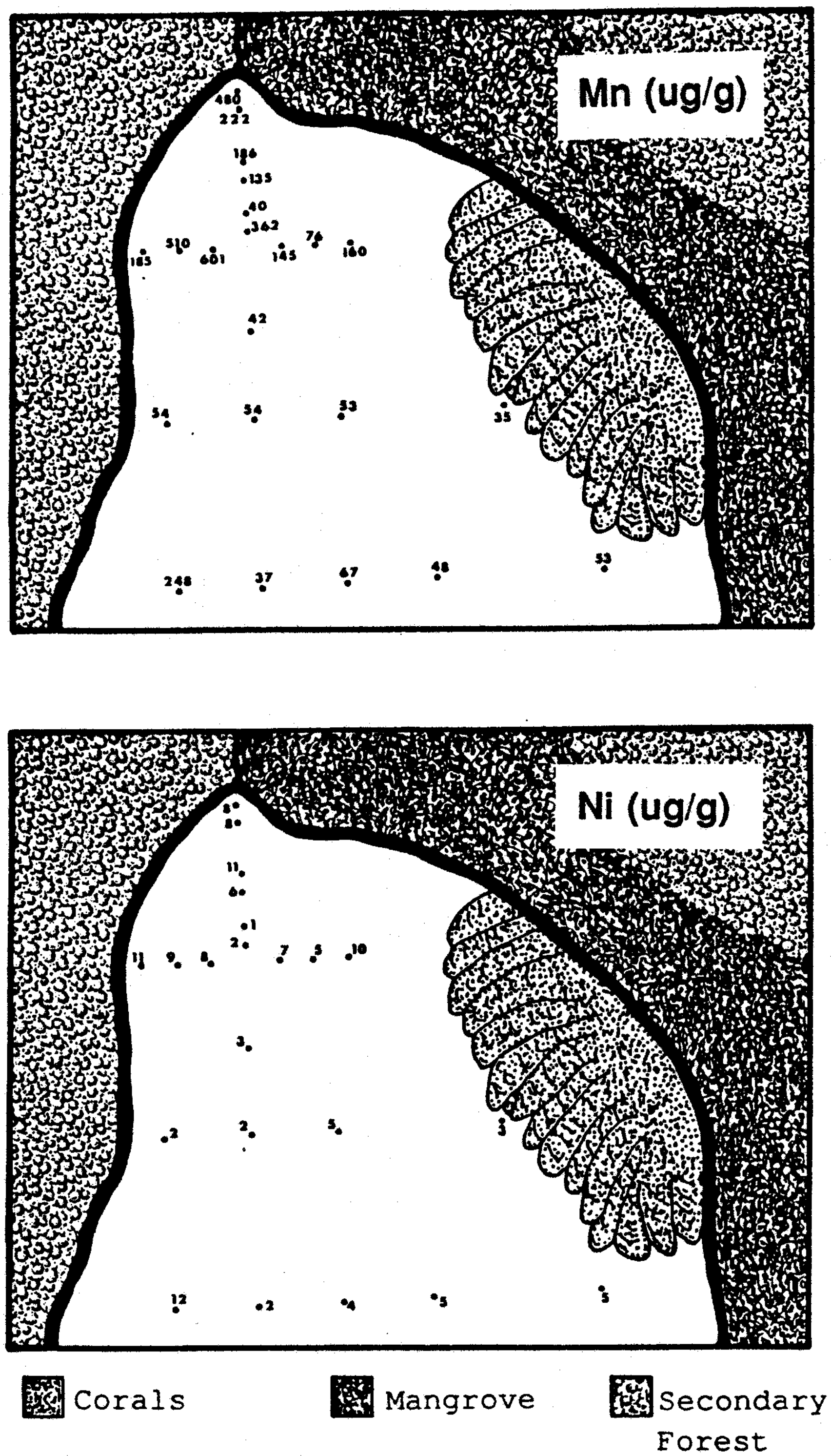

Figure 6a. Leachable metals in sediment cores from Fish Bay, St. John.

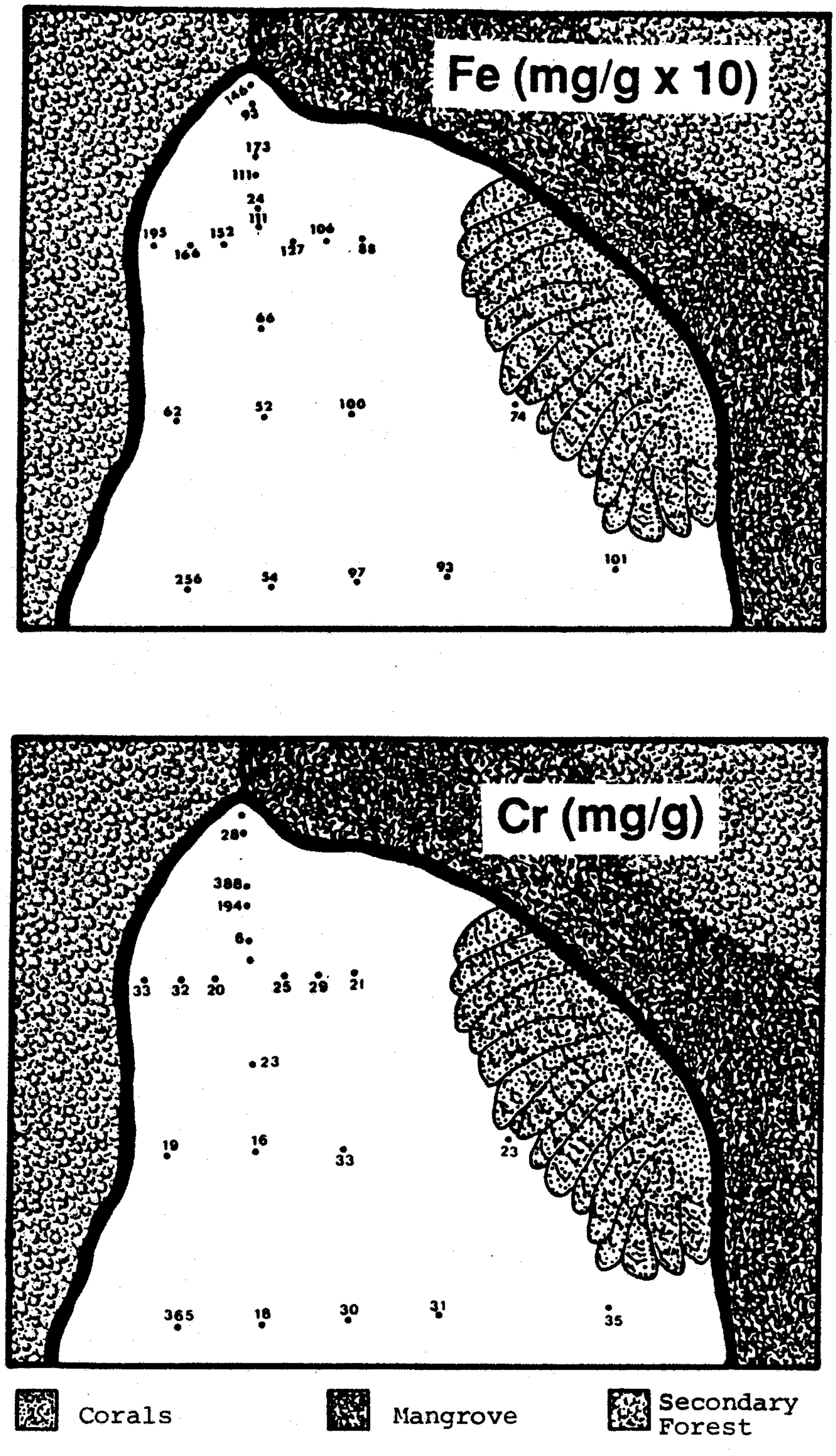

Figure 6b. Leachable metals in sediment cores from Fish Bay, St. John.

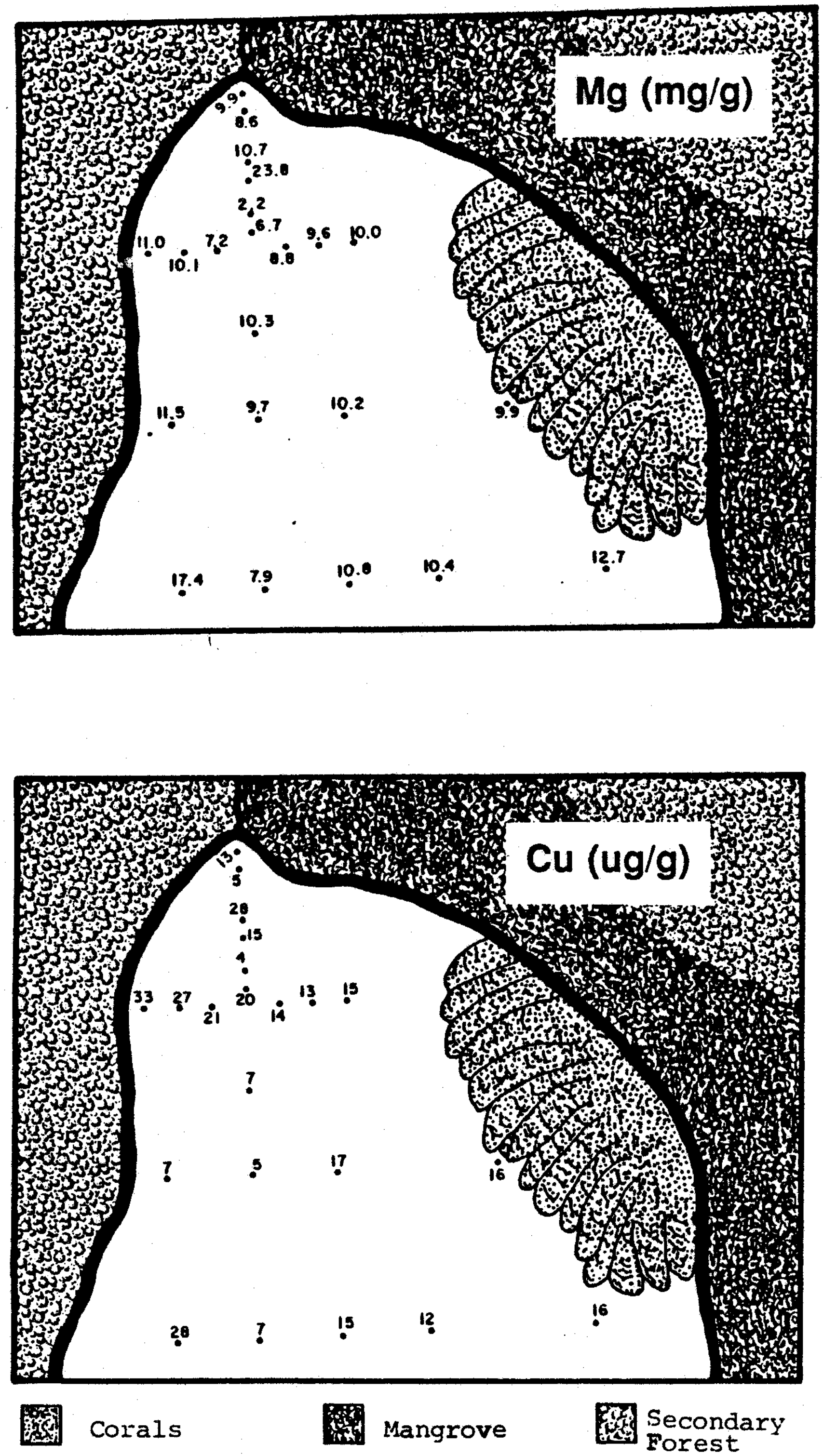

Figure 6c. Leachable metals in sediment cores from Fish Bay, St. John.

Table 8. Heavy metal content of some marine invertebrates in Fish Bay, St. John. The snail was Littorina angulifera, the sea urchin was Tripneustes esculantus, and the crabs were Goniopsis cruentata, Plagusia depressa, and Aratus pisonni. N represents the number of individuals analyzed. All values are expressed in terms of dry tissue weight.

A: AVERAGE ± STANDARD DEVIATION

	N	Wet/Dry Ratio	Fe (ug/g)	Mg (ug/g)	Mn (ug/g)	Cu (ug/g)
Snail	8	6.0 ± 1.0	1461 ± 1221	7510 ± 1900	236 ± 121	88.2 ± 58.8
Sea Urchin	4	4.8 ± 1.6	158 ± 67	8387 ± 5674	4 ± 1	3.1 ± 1.7
Crab	2	2.6 ± 0.1	133 ± 11	6906 ± 874	131 ± 29	97.9 ± 9.4

B: RANGE

	N	Wet/Dry Ratio	Fe (ug/g)	Mg (ug/g)	Mn (ug/g)	Cu (ug/g)
Snail	8	5.0 - 7.8	125 - 3818	5491 - 10124	147 - 436	2.3 - 196.7
Sea Urchin	4	3.4 - 7.0	125 - 258	5433 - 16897	2 - 5	1.1 - 5.0
Crab	2	2.5 - 2.7	125 - 140	6288 - 7524	110 - 151	91.3 - 104.6

Manganese concentrations ranged from values as high as 436 ug/g in snails to values as low as <5 ug/g in sea urchins. The same pattern was found to be true for copper and iron, with maximum concentrations of 197 and 3,818 ug/g, respectively. The concentrations of nickel and total chromium were below the analytical detection limit. The large variation in metal content of the species is not surprising since it is well known that some organisms have a significantly higher capacity to bioaccumulate metals than others due to physiological and behavioral differences (Louma 1983).

The levels of copper in crab tissue found in this study (36.4 and 38.9 ug/g wet weight) were higher than those reported by Sanders (1984) for two South Carolina estuaries (7.5 to 9.8 ug/g wet weight). This difference can be attributed to differences in methodology since Sanders analyzed only edible tissue. The tissue analyzed in this study was soft tissue which usually has higher metal concentrations.

Snails and crabs appear to be good indicator organisms since the level of heavy metals present in their tissue is well above the detection limits of the standard analytical techniques. In order to assess their suitability, information about seasonal and intra-sample variability must be generated and studied, and the implications for biomonitoring determined.

CONCLUSIONS

The geochemical anomalies identified by Tucker, et al. (1985) do not pose a serious threat to the marine ecosystems of St. John island. Heavy metals are transported by the island's streams to the sea, and can be detected in stream water, sea water, and marine sediments. However, these levels were typical of uncontaminated environments and, with the exception of iron and manganese, were mostly below water quality standards set by US EPA.

The concentrations of trace metals in these three sample types followed a similar concentration pattern: Mg > Fe > Mn > Cu > Cr > Ni > Zn. The much higher concentrations found in marine sediments make this sample type the easiest compartment for heavy metal monitoring.

Although samples from several watersheds were analyzed, no conclusions can be made concerning the relative impact of the geochemical anomalies in these watersheds due to the limited number of samples taken. Samples from Fish Bay had higher concentrations of some of the metals, but this fact can be attributed to the greater number of samples taken in Fish Bay. More intensive sampling, together with a better understanding of the role of metal sinks such as salt ponds and mangroves, are needed to address this question.

The export estimates suggest that large quantities of some metals are transported by the island's streams. More than 100 kg of iron and manganese were consistently exported by Fish Bay, and export of the other metals only rarely exceeded 100 kg. However, two factors must be taken into consideration in order to assess the potential impact of these metals. First, not all of these metals reach coastal waters because salt ponds and mangroves retard or stop metal movement. By slowing down water velocity, these ponds facilitate the incorporation of metals into the sediments. Second, the chemical partitioning of the metals determines the bioavailability to marine organisms. Dissolved ions are potentially more toxic than metals adsorbed onto particles. Only magnesium was transported primarily in the dissolved phase; iron and manganese were exported in the particulate phase.

The levels of trace metals present in the animal tissues analyzed were not dangerously high and should not pose a threat to the organisms. There was considerable difference in the metal content of the different species collected in Fish Bay, with those associated with mangroves having the highest concentrations. Snails and crabs should be considered as indicator organisms because of their abundance and the relatively high concentration of trace metals found in their tissues.

Research and Management Recommendations

1. Monitor iron and manganese concentrations in stream and sea water to determine how often the EPA standards are exceeded. Since iron is much easier to analyze and is highly correlated with manganese and copper, this metal might be used as an indicator of metal contamination.

2. Determine the transport of lead through the ecosystem. Tucker, et al. (1985) found very high concentrations of lead in the geochemical anomalies.

3. Determine the fraction of stream-transported metals that become incorporated into the sediments of salt ponds and mangroves.

4. Establish a long-term biomonitoring program. In order to assess the suitability of the indicator organisms, the intra-species and seasonal variability in metal content need to be studied.

5. Study the effects on the ecosystem of the high sedimentation and turbidity in Fish Bay; determine the relative importance of natural and anthropogenic factors in causing this sediment load.

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Funded by the U.S. National Park Service and done under the aegis of the Virgin Islands Resource Management Cooperative, VIRMC (see inside front cover of this report), the project involved more than one-half of VIRMC's members as subcontractors, drawn from a dozen different disciplines.

Island Resources Foundation (IRF) is proud of its behind-the-scene role as project organizer, prime contractor, program manager and publication series editor. We are equally proud of our role as an active member of VIRMC which offers great promise as an organizational vehicle for undertaking joint, interdisciplinary planning, research and monitoring projects.

Penultimately, a word of appreciation to five persons who have been extraordinarily helpful to Island Resources Foundation in carrying out its role as primary contractor for VIRMC's Virgin Islands Biosphere Reserve program. I am taking note of those who assisted with the overall technical and management tasks of coordinating more than twenty-five subcontracts, arranging for text and copy editing, and proof reading the thousands of pages of reports. For their many services I am indebted to Dr. Caroline Rogers, Executive Officer of VIRMC (for technical review), Phylis Rubin (manuscript copy editor), Jean-Pierre Bacle (for layout and publication coordination), Sandra Tate (for assisting with project administration and word processing) and Judith Towle (for fiscal management).

Except for further distribution of documents, the project management tasks of Island Resources Foundation are almost completed. We have, however, only laid one course of "baseline" foundation stone for the structure of the Virgin Islands Biosphere Reserve. Other builders of the information base are now needed, both in the Virgin Islands and elsewhere in the Eastern Caribbean. We hope that the spirit of cooperation implicit in VIRMC will continue.

Edward L. Towle, President
Island Resources Foundation
March 1988