#### **INFORMATION TO USERS**

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

# UMI®

Bell & Howell Information and Learning 300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA 800-521-0600 •

#### A NUTRIENT MASS BALANCE FOR NITROGEN AND PHOSPHOROUS FOR THE NEARSHORE WATER OF THE WEST COAST OF BARBADOS, W.I. (July, 1996 to May 1997).

by Christine Wellington

Department of Biology McGill University, Montreal

January, 1999

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of Master of Science (Biology).

© C.Wellington, 1999.



### National Library of Canada

#### Acquisitions and Bibliographic Services

395 Wellington Street Ottawa ON K1A 0N4 Canada Bibliothèque nationale du Canada

Acquisitions et services bibliographiques

395, rue Wellington Ottawa ON K1A 0N4 Canada

Your file Votre rélérence

Our file Notre référence

The author has granted a nonexclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission. L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-55098-2

## Canadä

#### ABSTRACT

A mass balance approach was used in an attempt to quantify nutrient flux to the nearshore at the West Coast, Barbados, W.I. Total nitrogen and total phosphorous levels of the groundwater at inland pumping stations and above beach margins, as well as in the water of the nearshore zone and approximately 2 km offshore, were obtained. Nearshore groundwater seepage rates and salinity data were also taken. This study attempted to use this raw data to estimate flushing rates, nutrient loading rates, and nutrient loss rates, to ultimately create a picture of the fate of nutrients as they travel in groundwater into the nearshore zone. Annual loading for the entire West Coast was calculated at 1.46 x 10<sup>5</sup> kg  $NO_3$ -N for nitrogen and 1.19 x 10<sup>3</sup> kg PO<sub>4</sub><sup>3</sup>-P for phosphorous. Mean nutrient levels in groundwater above the beach margin were estimated at 969.83 µM for nitrogen and 3.63 µM for phosphorous. For nitrogen and phosphorous respectively, these levels were twice and three times higher than at the pumping stations farther inland; and there was also a fourfold and fivefold drop in nitrogen and phosphorous, respectively, in the nearshore zone relative to this groundwater above the beach margin. This indicated that the dense coastal population at the West Coast was adding significant amounts of nutrient to groundwater after it had left the inland pumping stations. There were no patterns of gradation in nutrient concentrations detected within the immediate nearshore, making completion of an accurate mass balance impossible, though indicating that there was significant advection of submarine groundwater offshore, beyond the study zone. This may contribute to the poor health of West Coast reefs, where sewage and fertiliser leaching and runoff are suspected as the primary sources for nutrient input to submarine groundwater to the south and northern parts of the West Coast, respectively.

İİ

#### RÉSUMÉ

Un bilan massique a été utilisé dans le but de quantifier les flux des nutriments vers les rives de la Côte Ouest, Barbades, W.I. La concentration d'azote total et de phosphore total ont été déterminées sur des échantillons de la nappe phératique prélevés à la station de pompage et à la limite de la plage, ainsi que sur des échantillons d'eau prélevés à proximité de la rive et à environ 2 km vers le large. Le taux de percolation de l'eau souterraine de la rive et le niveau de salinité ont également été déterminés. Ces données ont été utilisés pour estimer les taux de dilution, d'apport et d'exportation des nutriments afin de déterminer le sort de ces nutriments lorsqu'ils sont transportés de l'eau souterraine vers les berges. L'apport annuel d'azote était de 1.46 x  $10^5$  kg NO<sub>3</sub><sup>-</sup>N et de phosphore était de 1.19 x  $10^3$  kg PO<sub>4</sub><sup>3</sup>-P pour la Côte Ouest. La concentration moyenne de nutriments dans les eaux souterraines à la limite de la plage était de 969.83 µM pour l'azote et 3.63 µM pour le phosphore. Ces valeurs étaient respectivement deux et trois fois plus élevé pour l'azote et le phosphore par rapport à la station de pompage; il y avait également une diminution de l'azote et du phosphore par un facteur de quatre et cinq, dans la zone près des berges par rapport à la limite de plage. Ceci indique que la dense population à la Côte Ouest rejète une quantité significative de nutriments dans les eaux souterraines une fois qu'elles ont quitté les stations de pompages. Aucun gradient de nutriments n'a été détecté au niveau de la rive, ce qui empêché de développer un bilan massique précis. Ces résultats suggèrent toutefois qu'il y avait un apport important de nutriments des eaux souterraines sous-marine par advection provenant d'une zone éloignée des sites échantillonnés durant cette étude. Ceci pourrait contribuer à la détoriation des récifs coraliens de la Côte Ouest, où la fuite des égouts dans le sud et le ruissellement des fertilisant dans le sud représentent la source principale des nutriments pour l'eau souterraine sous-marine de la Côte Ouest.

#### **TABLE OF CONTENTS**

AB	STRACT	ii
RE	SUME	iii
TA	BLE OF CONTENTS	iv
LIS	ST OF FIGURES	vi
LIS	ST OF TABLES	vii
PR	EFACE	ix
AC	KNOWLEDGEMENTS	x
1.0	INTRODUCTION	1
2.0	REVIEW OF LITERATURE	3
3.0	METHODS	8
	3.1 Mass Balance Rationale	8
	3.1.1 Components of the mass balance	10
	3.2 Description of Sites Sampled	13
	3.3 Description of Physical Data Collection & Water Sampling	17
	3.3.1 Collection of Seepage Rate Data	18
	3.3.2 Collection of Salinity & Temperature Data	18
	3.3.3 Collection of Water Samples for Nutrient Analyses	19
	3.4 Collection of chemical data	20
4.0	RESULTS	22
	4.1 Physical data	22
	4.1.1 Seepage rates	22
	4.1.2 Calculation of Q <sub>M</sub>	22
	4.2 Chemical data	24
	4.3 Calculations of nutrient loading	25
	4.4 Calculation of the term for clearance mechanisms or loss, K <sub>i</sub>	27
	4.5 Assembling picture of nutrient movement into the coastal zone	28
5.0	DISCUSSION	30

5.1 Technical Discussion
5.1.1 Estimates of Rates of Seepage and Coastal Discharge30
5.1.2 Salinity Measurements
5.1.3 Estimates of $Q_M$
5.1.4 Estimating Patterns of Movement of Fresh Groundwater
relative to Marine Discharge
5.1.5 Compared Nutrient Levels & Estimation of Nutrient Loading
to the Coast34
5.1.6The Mixing Phenomenon and Advection of Nutrient Offshore.35
5.1.7 Subsurface Behaviour of Nitrate and Phosphate
5.1.8 Attempts to Calculate Loss Term, Ki
5.1.9 Limitations in the Literature and of this Study
5.2 Non-technical Aspects and Summary
6.0 APPENDIX: Tables 1 to 1043
7.0 REFERENCES

•

#### LIST OF FIGURES

Figure 1	BARBADOS - Public water supply wells, nearshore and	
	offshore study sites and population highlighted ( adapted from	n
	Harries, 1997)	5
Figure 2	Schematic representation of submarine groundwater flow	
	(adapted from Johannes, 1980)	7
Figure 3	Proposed schematic representation of the nutrient mass	
- igui e 5	Toposod sonomatio representation of the natione mass	
	balance for the West Coast of Barbados, W.I	)

#### LIST OF TABLES

- Table 4: Averaged total phosphate values (10<sup>-1</sup>μM) for samples at all sites.
   BRI = Brighton/Spring Garden; PAY=Payne's Bay;
   HOL=Holetown; MUL=Mullins. N.D.- No data. Average totalP

#### PREFACE

#### Statement of Contribution

The ideas for this research were developed jointly by myself and my supervisor, Professor Joseph Rasmussen. I was responsible for sampling design, data collection, nutrient and data analyses, and for the initial drafting of this thesis. The final draft of the thesis benefitted in large part from editorial inputs from my supervisor.

#### Statement of Originality

This study represents the first attempt to construct a mass balance model of the nutrients nitrogen and phosphorous in the nearshore marine environment of the West Coast of Barbados. It also represents the first time that total nitrogen and total phosphorous data has been collected for these marine waters and local groundwaters.

#### Thesis Format

This thesis has been formatted according to the guidelines for thesis submission of McGill University, and mirrors that which was submitted by Patrick Allard (1993) to the Faculty of Graduate Studies and Research, McGill University, in partial fulfillment of the requirements for the degree of Master of Science.

#### ACKNOWLEDGEMENTS

I wish to thank my supervisor Professor Joseph Rasmussen for the hours of long-distance brainstorming, faxing and e-mailing of ideas with me, allowing me to see the completion of this thesis. I also wish to thank him for personally bringing to Barbados some of the equipment crucial to data collection in this study, and for facilitating (sometimes in somewhat orthodox, though perfectly legal, fashion!) my obtaining various supplies I would not have otherwise been able to source in Barbados.

I wish to sincerely thank Andrea Jordan (formally of the Government Analytical Service), and others from the Government Analytical Service, Ministry of Agriculture and the University of the West Indies, who provided me with invaluable advice for the nutrient analyses of water samples, as well as with temporary supplies of materials.

I am especially grateful to Wayne Hunte, Honor Wiltshire, Chris Parker and Sophia Pollard and the entire staff of Bellairs for their friendship and support throughout my period of study.

I would like to thank Lynda McNeil, formally of Graduate Studies (Biology), McGill University, who was truly invaluable in lending much support and advice.

I am indebted also to my family and friends, who all took turns acting as field assistants. I would especially like to mention my father who passed away during this study. Thanks Dad for the physical and moral support. I would also like to thank my uncle, Arthur Atkinson, who effortlessly and expediently produced the figures for this thesis, despite having his own deadlines to meet. And to my family as a whole, thank you for putting up with the highs and lows associated with this process.

This research was supported in part by personal loans, as well as a McGill Major Fellowship Award (1996/97).

#### **1.0 INTRODUCTION**

Land use changes in coastal watersheds from agricultural to residential development with on-site sewage disposal represent a potential change in both the quantity and quality of nutrient inputs to coastal marine systems (Weiskel et. al., 1992). Especially sensitive are coralline islands with highly porous carbonate platforms, that discharge more groundwater than surficial runoff to the coastal marine environment (Matson, 1993). In the Caribbean and the Bahamas, such land masses are found in abundance, and are often highly populated and prone to the direct discharge of both fertiliser and sewage to the carbonate aquifer (D'Elia et. al., 1981; Lewis, 1987; Matson, 1993; Simmons et. al., 1994). The nutrient-enriched groundwater then percolates up through coastal sediments and discharges into the coastal marine environment (Matson, 1993).

Economic development and urbanisation in the Caribbean constitute an important environmental stress on coastal zones, which are important both as a tourist attraction, and as a source of food to subsistence fishermen. Water quality surveys for the coast of Barbados have shown that coastal waters are experiencing nutrient and suspended particulate matter contamination as a result of wastewater discharge (Faruqui et. al., 1995). Hotels and industries in fast-developing coastal areas use septic systems or package wastewater units with ground disposal; and therefore comprise an important source of waste effluents to the soil environment and groundwater in these areas (Faruqui et. al., 1995; Hagedorn et. al., 1981).

Caribbean hotels especially have problems with the regular clean-out of septic systems during peak tourist season (Faruqui et. al., 1995), and indeed there is a lack of information concerning what exactly some major hotels do with their sewage (Rasmussen, 1994). In Barbados, there are many unsubstantiated local reports of covert discharge of raw sewage directly into the nearshore or into coastal waterways. Delcan Ltd. (1994), suggests that the observed rise in groundwater nitrates at West Coast supply wells to the north of the island is due to the leaching of fertilisers in agricultural areas, rather than from domestic wastewater. However, work by Cabana (Ph.D. thesis, McGill, 1996) indicates

that sewage-derived nitrogen is being heavily incorporated into the fringing reef food-chain off the more densely populated southern half of the West Coast. Barbados like many other coralline islands, with its extremely porous, unconfined, limestone aquifer system, is prone to both agricultural and urban groundwater contamination, with subsequent discharge of this high nutrient freshwater as a submarine flux into the nearshore coastal zone. And the latter probably acts as the major source of nutrient loading to the marine system off the west coast of Barbados (Lewis, 1987; Harries, 1997).

Nutrient-enriched groundwater discharge into the coastal environment can have significant eutripyhing influences on the receiving systems. Not only can one observe an elevation of nearshore nutrient concentrations ( Johannes, 1980; Capone et. al., 1985; Simmons et. al., 1994; Faruqui et. al., 1995 ), but there is often a eutrophication response, usually in the form of a loss of species diversity, by benthic and/or pelagic biota ( D'Elia et. al., 1981; Sewell, 1982; Lee, 1985; Tomascik et. al., 1987; Allard, 1993 ).

This thesis represents an extensive collection of water quality data, attempting for the first time the construction of a mass-balance model of the nutrients nitrogen and phosphorous in the nearshore marine environment. The primary aims of this study were: (i) to estimate the rate at which nitrogen and phosphorous are being loaded to the nearshore zone via groundwater discharge; (ii) to calculate the rate of 'flushing' for these nutrients, ie. how quickly the nutrients are advected outward from shore by nearshore circulation of the ocean; and (iii) to identify the location and relative magnitude of any important biotic or abiotic nutrient sinks within the coastal zone.

2

#### 2.0 A REVIEW OF LITERATURE

Submarine groundwater discharge, SGD, occurs anywhere that an aquifer is connected hydraulically with the sea through permeable bottom sediments, and the head is above sea level ( Johannes, 1980 ). Harr predicted that the rate of discharge of such groundwater decreases rapidly with distance from shore ( Johannes, 1980 ), and Bokuniewicz ( 1980 ) demonstrated that SGD decreased roughly exponentially with distance from shore in Great South Bay, New York, with between 40 and 98 % of the total flow occurring within 100 m of shore. On a global scale, nitrate levels in SGD are reported to be two to three orders of magnitude higher than those typical of coastal waters, and typically are significantly higher than levels of surface runoff. The impact of SGD on marine and estuarine communities is less, on a global scale, than that of surface runoff; however, due to the high dissolved nutrient ( and/or pollutant ) levels and altered salinity attendant to this phenomenon, in some areas, SGD is of greater ecological significance than surface runoff ( Johannes, 1980 ).

Capone (1985) and Lewis (1985, 1987) were the first to directly measure the nitrate concentration in SGD, and thus establish this as an important source of nitrogen to coastal marine environments. Though particulate and dissolved nitrogen and other nutrients can enter coastal waters through several recognised routes (eg. riverine flow, runoff, industrial and domestic sewage discharge), groundwater has most often been ignored, or assumed to be of minor importance in nutrient input budgets to coastal waters, due to the fact that (i) the areal extent and volume of discharge is often minor relative to the other freshwater inputs; and (ii) in the past, submarine transport of nutrient solutes was probably minor, since the extreme concentrations reached in some aquifers is only a recent phenomenon, forcing researchers to reevaluate the potential importance of SGD of nutrient associated with population growth, urbanisation and increased use of coastal areas. Several studies within the last 20 years have shown that groundwater may be an important nutrient source in several lakes ( Capone et. al, 1985), as well as along the coast of the Eastern U.S.A. ( work in Massachusetts by Valiela et. al., 1978; Millham et. al., 1994; Weiskel et. al., 1991 & 1992 ), in estuaries in Western Australia (Sewell, 1982), in tidal areas of Denmark (Pejrup et. al., 1993), and in the coastal zones of islands in the Caribbean and the Pacific (D'Elia et. al, 1981 in Jamaica; Lewis, 1985 in Barbados; Matson, 1993 in Guam; Simmons et. al., 1994 in Bermuda ). Indeed, Weiskel et. al. (1991) state that in general, there is a need to investigate the effect of human settlement on the nutrient budgets of all land margin environments, such as coastal systems.

Lewis (1985, 1987) examined the groundwater flux to the nearshore zone of Barbados, W.I., with emphasis on the spatial and temporal patterns of N loading and groundwater seepage. In 1994, Delcan Ltd. showed that terrestrial water quality in Barbados, has been greatly influenced by terrestrial loadings from upland ( stream ) wells, which are influenced mainly by fertiliser applications ( N:P ratios were found to be in the 200 range, nitrate-N in 7.5 ppm range, phosphate-P in the 0.03 ppm range; while sewage-enriched waters were found to be far more phosphate-rich ( several ppm phosphate-P ), N:P ratios being incredibly low ( in 2:1 range ) ). Nitrogen stable isotope studies on fringing reef food chains off the West Coast, however, indicate that at least for this heavily populated southern half of this coast ( see Figure 1 ), sewage-derived nitrogen versus that of fertiliser, is being heavily assimilated by biota ( Cabana, Ph.D. thesis, McGill, 1996 ).

Over the last decade, there has been increasing concern about the impact of nutrient enrichment on the fringing reefs of Barbados (Tomascik et. al.,1987); and more recently, coral stress has been linked directly to suspended material from run-off and wastewater outfalls, and indirectly to increased algal growth from nutrient enrichment (Faruqui et. al., 1995). The fringe reef off the heavily populated West Coast of Barbados appears in poor health, whilst turf algae appear to be fluorishing. Between 1982 and 1992, cover by macrophytic (benthic turf) algae increased (by 111.9%), percentage cover of substratum by coral decreased (by 37.4%), and the total number of coral species decreased (by 27.1%); and it



Figure 1: BARBADOS - Public water supply wells, nearshore and offshore study sites and population density highlighted (adapted from Harries 1997)

0 5 SCALE

km

is presumed that this trend has continued over the ensuing 5-year period (Allard, 1993; Bellairs Research Institute for Stanley International and the Government of Barbados, 1997). Chlorophyll levels and *Trichodesmium* counts only appear to be modestly enhanced (Rasmussen, 1994). Axelrad also reported a major eutrophication response from the benthic algal community in Port Phillip Bay, Victoria, Australia, with a similar lack of apparent response by the planktonic community, citing that they observed a fivefold increase in epibenthic productivity, but little response in watercolumn productivity when they compared eutrophic and relatively pristine sites(Axelrad et. al., 1981).

Johannes (1980) outlined a theoretical model of submarine groundwater discharge (SGD) from a homogeneous, unconfined aquifer, where freshwater flows out along the coast through a narrow gap between the freshwater-seawater interface (see the 'zone of diffusion', Figure 2) and the watertable outcrop at the beach. In this model, toward the seaward edge of this zone the discharged water will be brackish, due to entrainment of some salt water from the zone of diffusion; and the width of the zone of discharge would be expected to be proportional to the volume of freshwater flow. Along marine coastlines, an underlying salt wedge typically intrudes beneath the freshwater aquifer, impeding the downward mixture of lighter groundwater, magnifying the tendency for groundwater from unconfined aquifers to discharge close to shore ( Johannes, 1980). Indeed, Lewis (1987) showed that groundwater flow rates into the nearshore fell off rapidly with increasing depth of overlying water, such that beyond 1m depth ( a few metres from shore ), submarine groudwater flow approached zero. Hence, one expects fast, shallow, seaward movement of SGD in an unconfined aquifer (Johannes, 1980).

6



Figure 2: Schematic representation of submarine groundwater flow (adapted from Johannes (1980)).

#### 3.0 METHODS

#### 3.1 Mass-balance rationale

It was very difficult to directly analyse and measure the dynamics and hydrology associated with the type of nutrient loading regime which occurs in Barbados.

Figure 2 gives a diagrammatic representation of the exchange of ground and sea waters in the sediments and nearshore coastal zone as might be found in Barbados. There is a general seaward movement of lighter freshwater within the aquifer above a denser, land directed, seawater layer. Within the 'zone of diffusion' there is a mixing of the fresh and sea water; and it is this mixture that arrives at the 'zone of discharge' in the nearshore zone. On limestone platforms, such as Barbados, submarine discharge from the unconfined aquifer ( ie. that which floats on seawater ) is regulated by freshwater head, and occurs through beach seeps, cracks and fissures in the 'zone of diffusion' ( Johannes, 1980; Matson, 1993 ). In turn, freshwater head will be determined primarily by the combined influences of recharge, density differences between the freshwater and underlying seawater, and the steepness of the pycnocline within the 'zone of diffusion', or mixing zone ( Matson, 1993 ).

This complex hydrology presents some problems for the construction of the mass-balance. Groundwater seepage becomes difficult to quantify in the nearshore zone as it mixes with incoming seawater within the beach ('zone of diffusion' in Figure 2), so that water collected in seepage meters is made up mostly of seawater. Further, heterogeneity of the substratum within the 'zone of discharge' in the nearshore sites of study makes groundwater seepage difficult to quantify, both in terms of local rates and spatial extent.

Problems also arose concerning nutrient chemistry. As both nitrate and phosphate are rapidly taken up by biota in the water and sediments, it was necessary to measure total nitrogen ( totalN ) and total phosphorous ( totalP ); otherwise major errors would be introduced to the mass-balance by ignoring organic forms of N and P, which can be both important inputs for, and constituents of, marine plankton. Since water collected in seepage meters does not represent the chemical make-up of incoming groundwater, but is instead predominately seawater, and, in addition, it is exceedingly difficult to obtain clean, uncontaminated nutrient samples from the seepage meter, it was necessary to analyse nearshore wellwater in order to estimate the nutrient concentrations of the incoming freshwater seepage. Quantifying nutrient uptake by coastal biota also proved difficult as there were no observed gradations in nutrient concentration across any reef patches encountered. There was also an absence of recent data for the extent of coastal seagrass beds, which are suspected to absorb much of the coastal nutrient input ( Dr. Wayne Hunte, personal communication ); and there is no physiological data for uptake rates of the primary planktonic and benthic species of marine plant life that might be most frequently encountered in Barbados' coastal waters.

Thus, in order to put together an estimate of the nitrogen and phosphorous mass-balance for the West Coast, Barbados, W.I., where freshwater and entrained nutrients enter the coastal zone primarily by submarine groundwater discharge, SGD, it was necessary to make certain assumptions and approximations.

With regard to hydrology, preliminary studies of salinity gradients suggested that the majority of the seepage enters within 10m from shore ( and this is supported by Lewis, 1987 ). Thus, I established this as the outer limit of the nearshore study zones used in this study. A second assumption made was that the rate at which mixed water seeps into the seepage meter at low tide is a measure of the seepage rate at which fresh groundwater enters the mixing zone or 'zone of diffusion'( see Figure 2 ). It is also assumed that the salinity at the shore-water interface represents the salinity of the groundwater/seawater mixture entering the sea; and marine discharge ( or 'flushing' ) is determined from seepage rates in conjunction with salinity gradients measured nearshore ( as outlined below ).

With regard to nutrient, it was assumed that nutrient concentrations of water taken from taps at the nearshore would be the best indicator of nutrient

levels of groundwater entering the coastal zone. In addition, due to an absence of noticeable nutrient gradients within the zones of study, and the seemingly uniform nutrient concentrations across time, it was decided that nutrient concentrations in the nearshore could be characterised by averaging over the 1200 m<sup>2</sup> study zones along the coast ( see Figure 1 ) for the approximately 10 months of study. This in turn, allowed for an estimate of conditions along the full 30 km length of the West Coast.

Based on this reasoning, then, one can better envision the mathematical basis for the mass-balance.

#### 3.1.1 Components of the mass-balance

If we let M be the total mass of the nutrient under consideration within the water column of the study zone, then :

$$dM/dt = W(t) - Qc - KVc;$$

which is to say that changes in the total mass of the nutrient present (M), depend on the difference between the incoming nutrient load (W(t)) and the losses due to discharge (Qc) and biotic, and perhaps abiotic, uptake (expressed as a proportion of total nutrient present per unit time (K)) multiplied by the volume (V) and concentration (c).

This mass, M, can be converted to concentration, c, by dividing by volume, V. Hence:

$$dc/dt = W(t)/V - (Q/V)c - Kc;$$

and the steady-state solution of this mass-balance equation (valid when dc/dt = 0) is then:

;

$$c = \frac{W(t)}{Q + (Ki).V}$$

where: c = steady state nutrient concentration (mass of nutrient. volume<sup>-1</sup>)W (t) = loading of nutrient (mass of nutrient.time<sup>-1</sup>)

 $K_i = proportional loss term (time<sup>-1</sup>)$ 

- Q = hydraulic discharge = ave. freshwater discharge,  $Q_{SGD}$  + ave. marine discharge,  $Q_M$  (volume time<sup>-1</sup>).
- V = volume of study area (distance<sup>3</sup>).

Thus, nutrient concentration in the nearshore (c) is a function of the quantity of nutrient entering the nearshore (W(t)), which is then diluted by both sea and groundwater (Q), and further diminished by biotic and/or abiotic loss across the zone of study ( $K_{i}$ .V). To gain a better understanding of this mathematical concept, it is necessary to investigate the components of the mass-balance.

As aforementioned, the rate of SGD can be estimated with the seepage meter, allowing one to quantify the term  $Q_{SGD}$ .  $Q_M$  was quantified by employing a combination of seepage rates and observed nearshore gradients. This was achieved mathematically as follows:

$$Q_{\rm M} = \frac{Q_{\rm SGD} * (S_{\rm M} - S_{\rm SGD})}{S_{\rm m} - S_{\rm i}}$$

where

 $Q_{sgp}$  = volume of groundwater entering the study area per unit time.

 $S_{M}$  = mean salinity of the incoming seawater

 $S_i$  = salinity at any given interval within the nearshore zone (see

description of collection of nearshore salinity data below).

 $S_{scd}$  = salinity of the water in the 'zone of diffusion'.

Hence,  $Q_{M}$  and  $Q_{SGD}$  are added to give the total hydraulic discharge, Q, which acts to flush nutrients entering the nearshore zone.

Nutrient loading is calculated mathematically by addition of the relative nutrient contributions of groundwater and incoming seawater to the nearshore zone. Hence:

 $W(t) = Q_{SGD}^{*}(Nutrient)_{SGD} + Q_{M}^{*}(Nutrient)_{o},$ 

where: W(t) = loading of nutrient (mass of nutrient. time<sup>-1</sup>)

 $(Nutrient)_{SGD} = concentration of nutrient in groundwater at the shore (mass$ 

#### of nutrient. volume<sup>-1</sup>

 $(Nutrient)_{o} = concentration of nutrient offshore (mass of nutrient. volume<sup>-1</sup>).$ 

The major source of nutrient in the mass-balance is SGD; but in considering points of nutrient loss in the mass-balance, ie, nutrient sinks, both biotic and abiotic possibilities arise. Uptake by biota in the water and sediment might be expected, but other possible forms of loss for nutrient are: (i) denitrification of nitrogen; and (ii) geochemical adsorption of phosphate to substrate (Pejrup et. al. (1993), Sewell (1982), Simmons et. al., 1994; Weiskel et. al., 1992). Denitrification is unlikely in sandy sediments, since the anoxic conditions required for such activity are rarely realised in such sediments, or in porous limestone for that matter (Walker et. al., 1973). On the West Coast, there is only one site, at the small Holetown lagoon, where substantial rates of denitrification have been reported (Rasmussen, 1994); and so this is not likely to be an important form of nitrogen loss for the West Coast of Barbados as a whole. Phosphate loss to calcium carbonate aquifer substrate has been cited by Simmons et. al. (1994) working in Bermuda. They describe the formation of calcium carbonate-phosphate complexes in aquifers, effectively removing phosphate from water flow. This team also describes denitrification as a very localised occurrence on the largely limestone island. In light of the difficulty of partitioning loss of nutrient, total loss, K<sub>i</sub>, was obtained by rearranging the steadystate equation as shown below:

 $K_i = \frac{Q}{V} * \left[ \left[ \frac{(\text{Theoretical nutrient concentration})}{(\text{Observed nutrient concentration})} - 1 \right] \right]$ 

All of the components have been described thus far, save ' theoretical nutrient concentration ', which represents the nutrient concentration expected if there were no sink (ie. K = 0), and was calculated as:

and 'observed nutrient concentration', which was simply the mean nutrient concentration observed within the nearshore study zone.

It is now possible to achieve the goals of the mass-balance. In a practical sense, salinity was used as a conservative tracer of nearshore water flux at the West Coast of Barbados; and by combining nearshore gradients of salinity with observed and calculated rates of groundwater flux and marine discharge, the hydrological residence times of these nutrients were estimated. Having obtained these residence times, it was then possible to calculate loading rates for the nutrients, and compare observed nutrient levels in the nearshore with those expected if these nutrients were in fact conservative, free from the effects of biological uptake, or any other form of removal. This in turn facilitated an estimation of the location, and relative magnitude, of the major nutrient sources and sinks at the West Coast of Barbados, W.I. The mass-balance application of data gathered was enhanced since all loadings and concentrations were measures of total N and total P.

#### **3.2 Description of Sites Sampled**

In looking for sites, the most desirable characteristic of a prospective locale was an uninterrupted, along-shore stretch of at least 100m of sandy bottom in the nearshore zone (ie. the minimum of rubble outcrops, reef etc.). Efforts were then made to have sites spaced as evenly as possible along the coast. The four (4) West Coast sites sampled over the course of this study ( from July end, 1996, to May, 1997) were ( from South to North ): (i) Brighton/Spring Garden; (ii) Payne's Bay; (iii) Holetown Beach; and (iv) Mullins Beach ( see Figure 1 ).

#### (i) Brighton/Spring Garden:-

is adjacent to an industrial area. Immediately beside this particular stretch of beach is the Barbados Light & Power company, and the West Indies Rum Distillery. The power plant draws water from six deep wells for the purpose of cooling its oil generators. Three of these are close to the seashore and so yield

truly saline seawater; the other three are farther inland, and yield brackish water (Dr. Wayne Hunte, personal communication). Once passed through the plant, this coolant water is put out directly into the nearshore zone (output can range from 40,000 to 440,000 m<sup>3</sup>/day ) (taken from "Marine Environmental Impact Study of the Cooling Water Discharge at Spring Garden ", 1994). This output forms a sizeable warm water plume (approximately 14m wide), known as "The Pot" by locals, as it is thought to be therapeutic to soak in the warm waters. In turn, a shallow sand bar has formed at the mouth of this plume. The area, however, is prone to smelling of hydrogen sulphide, as the inland source wells are often anoxic (Dr. Wayne Hunte, personal communication). The distillery also exports effluent, though at a distance from shore of about 800m at a depth of about 6m, at a rate of 450 m<sup>3</sup>/day ( taken from "Marine Environmental Impact Study of the Cooling Water Discharge at Spring Garden ", 1994). This effluent is sugar-based, and indeed there are small doors cut into the base of the refinery wall abutting the beach, through which some release may occur, as the sand here is consolidated, and the sea grape vegetation is especially lush.

#### (ii) Payne's Bay:-

is a popular beach with locals and tourists alike. This beach is lined by closely spaced private beach front properties and small hotels. There can be considerable water traffic in the form of jetskis and other pleasure craft in the nearshore, though this is heavily contingent on the number of tourists on the beach at any time.

#### (iii) Holetown Beach:-

is a unique area as it is abutted ( as one moves from the northern part of the study area to its southern limit ) by a : (a) a natural, though much constricted, lagoon known as " The Hole "; (b) series of hotels and guest apartments; and ( c ) an old fishing area where locals often haul up and repair not only the traditional wooden boats, but also the fibreglass pleasure craft of the younger generation who make a living giving rides to tourists. The water clarity at this site is extremely poor, and during extreme rain events, the swamp frequently becomes blocked, then gives way, releasing sewage and other organic debris into the nearshore area.

In September, 1996, this site was transformed dramatically, due to (i) exceptionally rough seas; and (ii) an increased frequency in output events from this swamp. The beach gradient increased tremendously, so that when one stepped off the shore, one found oneself immediately in water well over 5 feet deep. The water became dark, and visibility exceedingly poor. The beach substrate at this site became very coarse, and the swells in the nearshore were quite large ( on average 1.5 to 2m high at low tide! ). Indeed it was necessary to suspend sampling for some months.

Over the next six months or so, the beach gradually returned to its original form, the water clearing substantially, and the beach gradient lessening considerably. There was some return of sediment to the nearshore, such that the fall-off into deep water offshore became less dramatic, and swells returned to normal.

#### (iv) Mullins Beach:-

this is a relatively open beach. The eastern limit (ie. inland border ) of this beach is bordered by a coast road. At its northern end are a few guest houses ( though these do not abut the area directly used in this study). There is also a small beach bar placed high above the waterline. There is an extensive coral limestone bedrock which is about six feet below the sand surface at the most inland, highest part of the beach, but downslope at the shore, projects in the form of small outcrops into the nearshore zone. This can be observed primarily at the northern portion of the stretch of beach used directly in this study.

In September, 1996, the seas off the West Coast were exceptionally rough; and since December, 1996, the aforementioned reef outcrops have been exposed, such that at present, there is a large patch of reef stretching well over 25m parallel to shore within the study area. This projects above the water surface with wave drawdown. The beach has increased in gradient, and is of much diminished area. This is hardly surprising since at high tide, the seas often rise high enough to carry sand across the road which runs parallel to this beach.

Sampling was also done at two offshore sites over the bank reef ( approx. 1.5 km from shore ) to characterise sea water entering the nearshore zone from offshore. The first site was off an area of the west coast called Jordan's, which is located approximately midway between Brighton/Spring Garden and Payne's Bay. Farther north, offshore sampling was carried out in a region between Greensleeves and Bellairs, between the Holetown and Mullins beach sites ( see Figure 1; distance from shore of offshore sites not placed to scale ). This latter site is later only referred to as the 'Greensleeves' offshore site.

Also sampled were inland pumping stations of the Barbados Water Authority, so chosen as they supplied those areas directly inland of the beach sites. Codrington station supplies the area adjacent to the Brighton/Spring Garden site, and is located in a moderately populated area, near a government agricultural area. Molyneux pumping station supplies the Payne's Bay area, and is actually located next to the Molyneux/Sandy lane golf course. Trents pumping station supplies Holetown, and sits on an old plantation above the latter. Heyman's pumping station supplies the Mullins area, and it is located far out in the middle of an old cane plantation, its sugar factory having closed in the 1980's. There are no houses in the immediate area, and many acres of land in this area rotate between periods of fallow and cultivation.

In addition, later in the study, water samples were taken from taps on property immediately abutting the beach sites, to get an idea of the nature of the nutrient content of the freshwater immediately before it entered the nearshore zone. At the Brighton/Spring Garden site, nearshore tap samples were obtained from the West Indies Rum Distillery; at Payne's Bay they were obtained from onthe-beach guest houses; at Holetown, they were obtained from the Mango Bay Hotel; and at Mullins, they were obtained from the Mullins Beach Bar.

#### 3.3 Description of Physical Data Collection & Water Sampling

Every effort was made to sample across all sites in the space of one week (maximum), once a month. Therefore for any given month, data collection runs for seepage rates, salinity and temperature, and water sampling for nutrient analyses were carried out daily, at the low tide, over the course of a week in total (weather and sea conditions allowing). Nearshore sites and pumping stations were sampled starting with the southernmost Brighton site, moving north. This pattern of collection was influenced by Bowman et. al. (1994), who describe a south to north flow pattern off of the West Coast; and later supported by the description by Harries (1997) of outfall pollution at the densely populated capital Bridgetown to the south-west, influencing nutrient levels farther north along the west coast. Salinity and temperature data, and water samples for nutrient analyses were taken from over the bank reef at the Jordan's and Greensleeves locations, at the start and end of a week's sampling run, as it is impossible to obtain a boat daily at the Bellairs Research Institute.

A typical run at any site consisted of collection of seepage rates with a seepage meter, collection of salinity, temperature and depth data with the Seabird-SBE 19 CTD ®, and collection of water samples from the nearshore zone and the appropriate pumping station for nutrient analyses.

Data collection runs were carried out across the following dates: July 29 to August 4, 1996; September 21 to 27, 1996; and November 5 to 9, 1996; January 17 to January 24,1997; March 5 to 10, 1997; April 7 to 11, 1997; May 3 to 8, 1997. Data for October was not obtained as this experimenter was out of the island; and sea conditions were simply too rough during the month of December, 1996. A run was attempted in January, 1997, however, sea conditions and the attendant effect on sites made it impossible for data to be obtained from Holetown and Mullins. Indeed, sampling was suspended until March, 1997.

#### 3.3.1 Collection of Seepage Rate Data

In light of the possible effects of wave run-up and tide (Hegge et. al., 1991), seepage rates were taken at low tide in the nearshore zone, using a seepage meter much like that described by Bokuniewicz (1980) and Lewis (1987), pioneered by Lee in 1977 (Bokuniewicz, 1980). A smooth, plastic salt meat pail, 24cm high with diameter 28cm, had a hole approximately 1 cm in diameter bored into its base. Into this hole, a length of rubber tubing was secured, such that it extended from the base of the pail. This apparatus was used as a seepage meter by placing it bottom up and underwater at the sandy bottom in the nearshore zone, the open end of the pail being thrust into the sand until the base, with its protruding tube, was flush to the sand surface. A balloon was then fixed to the free end of the rubber tubing using rubber bands, care being taken to keep air out of the balloon, so that it was completely flaccid once attached, and so allowed free entry of water being displaced from the sediments by groundwater. The time at which the balloon was attached and removed was noted, as was the volume of water collected in the balloon over this time span, yielding a seepage rate in volume of water/ hour/ unit area of sand surface in the nearshore zone. The seepage meter was always placed in the first level spot on the sandy bottom in the nearshore, care being taken to avoid limestone outcrops which might prevent proper implantation of the seepage meter. Depth of water overlying the seepage meter did not exceed 50cm at any site, which usually corresponded to being within 1-2 m of the waterline at low tide. Previous trials with the seepage meter at each site did not reveal any significant heterogeneity of flux within 1-2m of the low tide mark at any single site, corroborating the findings of Lewis (1987). The area covered by the seepage meter was  $0.0616 \text{ m}^2$ .

#### 3.3.2 Collection of Salinity and Temperature Data.

The Seabird-SBE 19 CTD ® was used to facilitate this, data scans being taken by this instrument every 0.5 seconds. Work was always carried out at low tide when the freshwater head was highest relative to the saltwater head, thus

allowing for better detection of freshwater input into the nearshore zone. First, a parallel cast, moving north to south for a 100m stretch of beach, approximately 12m from the water line, was carried out, care being taken to keep the probe as close to the sandy bottom as possible without contact. This process was repeated approximately 9m from shore, moving south to north. All beach sites were been sectioned into 25m intervals, a different landmark denoting the 0m, 25m, 50m, 75m, 100m marks. Perpendicular casts were carried out opposite the aforementioned landmarks, moving inshore from approximately 12m from the waterline, as close in as was physically possible with the CTD. The tapwater at each pumping station was also passed through the CTD.

The salinity data ( in psu) was uploaded from the CTD, each parallel and perpendicular cast being saved as a separate file. The data from each file was plotted against time, then sampled for statistical analysis using SYSTAT  $\circledast$ . For the larger files of the parallel casts, the data of every 10 scans ( 5 seconds) was selected for use in the SYSTAT  $\circledast$  file. For the smaller files of the perpendicular casts, the data of every 2 -3 scans ( 1 -1.5 seconds ) was used. These, along with data from the offshore and pumping station water samples, were used to make up statistical data sets, which in turn were used in the mass balance calculations.

#### 3.3.3 Collection of Water Samples for Nutrient Analyses

All samples were collected in acid-washed Nalgene B bottles. Along the perpendicular paths opposite the 0m, 50m and 100m positions along each 100m stretch of beach at each site, three (3) water samples were taken at equal intervals. The farthest sample was taken from approximately 12m from the shore, the next halfway inshore, and the next as close inshore as could be managed. These samples were labeled p3 (x m), p2 (x m) and p1 (x m) respectively, where 'x m' refers to the 0, 50 or 100m position, according to the perpendicular path along which the samples were collected. Thus on a typical run, nine samples were collected from the nearshore at each site in 500 ml capacity Nalgene B bottles, from about halfway in the water column.

In addition, water was collected from the appropriate pumping station and nearshore taps for any given site, as well as from the areas over the fringing reef, as previously described. All samples were frozen until chemical analyses could be carried out.

#### 3.4 Collection of Chemical Data

Samples were analysed for total nitrogen ( total N ) and total phosphorous ( total P ). For total N, the potassium persulfate oxidation under pressure ( or persulfate digestion ) of organic nitrogen to nitrate, followed by cadmium reduction of the nitrate to nitrite was used, as outlined, <u>in general</u>, by Parsons et. al. ( 1972 ). For total P, organic phosphorous was oxidised to phosphate as described in Standard Methods for the Examination of Water and Wastewater, 18th edition ( 1992 ), then the colorimetric ascorbic acid reactive phosphate test was carried out as described by Parsons et. al. ( 1972 ). In both cases, 100 ml water samples were used.

After several initial trials with the total N procedures, it became clear that certain adjustments had to be made to the methods outlined by Parsons et. al. (1972). After autoclaving samples with persulfate oxidising reagent, the method indicates that you are to add to all samples, that quantity of 1.4M hydrochloric acid required to reduce the pH of a 100ml quantity of distilled water to which the appropriate amount of oxidising reagent has been added, to the range of pH 2.6 to 3.2. After many failed trials, it was finally realised ( with the help of chemists at the Barbados Government Laboratory ) that each seawater sample has a unique pH to start with; and so, it was clear that each sample had to be titrated separately, and carefully, with a pH meter, to bring samples to the correct pH. As a precaution, the volume of acid used, and the end pH was carefully noted for each sample. Further investigation revealed the need for further adjustment, since those samples which had been lowered to a pH of around 3.00 < x < 3.2, did not yield the characteristic fuschia colour at the end of the entire procedure. Another attempt was made, adjusting pH within the range of 2.6 to 2.8, and this appeared

to give more accurate results. Acid additions amounted to approx. 8 to 11ml HCl, depending upon the sample source. Early trials also indicated that total nitrogen levels were very high. Dilution trials indicated that a 1/20 dilution of samples before they were carried through the procedure resulted in the more accurate determination of total N level.

#### **4.0 RESULTS**

#### 4.1 Physical Data

#### 4.1.1 Seepage Rates

As was previously described, the amount of water collected in the balloon of the seepage meter, over time, over the area of sand covered by the seepage meter was noted, and hence the volume of water per unit area of sandy surface, or flux, could be estimated. If one assumes the the study area has dimensions of 100m ( the length of the study area ) by 12m (the farthest distance from shore traversed), then one can estimate the volume of groundwater **entering the study area**; a term which will be from hereon called  $Q_{scp}$ .

Table 1 in the Appendix shows the seepage flux and  $Q_{sGD}$  values calculated. Kruskal-Wallis testing determined that there was no significant difference at the 5% level in flow rates between sites nor over the duration of this study. Further, Wilcoxon paired analysis revealed no difference in magnitude of flux between the wet months (September,1996 to January, 1997; mean flux = 0.065 m/day) and the dry months (July end, 1996, and March to May, 1997; mean flux = 0.058 m/day ). Mean flux over all sites during this study was calculated as 0.061 m/day ( this is equivalent to 73.29 m<sup>3</sup> of groundwater entering the 1200m<sup>2</sup> study area daily ).

#### 4.1.2. Calculation of $Q_M$

With this physical data in hand, it was possible to calculate values for flushing,  $Q_{M}$ ; that is, the volume of seawater coming into the 1200m<sup>2</sup> study area from that area of the ocean beyond the nearshore zone, which is of constant salinity, and exhibits no groundwater influenced salinity gradients. As aforementioned, this value was calculated as follows:-

$$Q_{\rm M} \approx \underline{Q}_{\rm SGD} \ast (\underline{S}_{\rm M} - \underline{S}_{\rm SGD}) \\ S_{\rm m} - S_{\rm I}$$

As was previously stated, each parallel and perpendicular cast made with the CTD was saved as a separate file; and for each, maximum, minimum and mean salinity were noted. Hence  $S_M$  is the mean salinity of the files from the casts taken over the reef for any one month;  $S_i$  is the mean salinity of a particular cast in the nearshore;  $S_{sGD}$  is the minimum salinity of the nearshore perpendicular cast, which invariably occurred at the shore-water interface closest into shore. This was taken as the best indicator of the salinity of the mixed water in the 'zone of diffusion' (Figure 2), since it was impossible to pass water captured from the seepage meter through the chamber of the CTD with the force and volume required to get an accurate reading.

Hence a sample calculation :

For the SYSTAT® file composed by sampling data from a cast at Brighton, mean salinity was found to be 26.784 psu. The minimum salinity inshore was 26.555. Seepage was calculated at a rate of 78.545 m<sup>3</sup> water/day for the area of study. Mean salinity of incoming seawater was 32.695 psu. Thus

$$Q_{M} = \frac{78.545 \text{ m}^{3} \text{ water/day } (32.695 - 26.555) \text{ psu}}{(32.695 - 26.784) \text{ psu}}$$

 $= 81.588 \text{ m}^3$  water/day entering the study area.

This was repeated for all files using the appropriate values. A mean  $Q_M$  value was calculated for each site by averaging the  $Q_M$  values calculated for the files for that site (see Table 2 of Appendix). Kruskal-Wallis testing of the  $Q_M$  values did not reveal any significant differences between sites, nor over the duration of this study. Interestingly, similar testing carried out on the salinity and temperature CTD data revealed that, with few exceptions, all sites exhibited unique hydrological regimes, and so have different degrees of contact with water from offshore. They also had salinity profiles distinct from those taken over the bank reef. The fact that the  $Q_M$  values do not show statistically significant uniqueness between sites, as is reflected by the statistical treatment of the raw CTD data, may be an early indication of an inaccuracy in the calculation of  $Q_M$ . This will be discussed later in this paper.

#### 4.2. Chemical Data

The individual nearshore samples were taken along perpendicular transects opposite the 0m, 50m, and 100m marks (see Methods section), and the three samples taken along a transect were accorded the numbers 1, 2 or 3, going from the most inshore to the most offshore sample. Hence the sample taken most inshore opposite the 0m mark would be labeled ' (Site) p1(0m) '. In an effort to identify any nutrient gradient in the nearshore, the mean nutrient level of those samples equidistant from shore was calculated (ie. the mean of p1(0), p1(50) and p1(100); mean of p2(0), p2(50) and p2(100) etc. ). In addition, the mean nutrient level of the nearshore as a whole was also calculated.

The nutrient data for these nearshore samples are displayed in Tables 3 and 4 in the Appendix. Tables 5 and 6 in the Appendix display the nutrient data of the offshore sites and pumping stations, respectively. The symbols  $N_o$  and  $P_o$  (see Table 5), represent nitrate and phosphate levels over the bank reef, and in theory, in the water entering the nearshore from the open sea from at least 2km off Barbados. In turn the samples from the pumping stations and nearshore taps are used as indicators of the quality of the groundwater; and the symbols  $N_{SGD}$  and  $P_{SGD}$  (Table 6) are used to represent nitrate and phosphate levels in the groundwater, respectively.

Kruskal-Wallis testing and subsequent Dunn's testing of the nearshore nutrient data showed that overall, totalN and totalP levels did not change significantly over the duration of this study. With regard to detection of differences in totalN and totalP between sites, levels appeared similar at all nearshore sites. Mean totalN and totalP nearshore levels were calculated as 238.282  $\mu$ M and 7.3 x 10<sup>-1</sup>  $\mu$ M, respectively. There were no clear gradients within the nearshore study zones; not even within areas, like Mullins, which contained algae-covered reef patches.

Kruskal-Wallis testing of the totalN and totalP data for the offshore data set (Table 5 of Appendix) showed that though there was no change in totalN level detected over the course of this study, there was a significant difference in

24

the total N level between the two offshore sites (P = 0.046). For this reason, separate means were calculated for each offshore site: Jordan's mean totalN = 211.375 µM; Greensleeves mean totalN = 123.881 µM. These tests also detected no differences in totalP during the course of the study nor between offshore sites (overall mean totalP =  $5.86 \times 10^{-1} \mu M$ ). At a glance, comparison of the nutrient levels in the nearshore and offshore suggests there is a nutrient gradient present between the nearshore and offshore zones.

Kruskal-Wallis testing of the nutrient data from the pumping stations and nearshore taps (Table 6 of Appendix) proved quite uneventful. Changes in totalN and totalP level during the course of the study appeared to be statistically insignificant, though somewhat borderline (P = 0.055). Similarly, no differences in totalN and totalP levels were highlighted between the different tap samples. It is suspected that these results may be an artefact of an undersized nearshore tap data set, and reasons for this are discussed later.

#### 4.3. Calculations of Nutrient Loading

With the data acquired thus far, it is possible to derive estimates of nutrient loading within the 1200  $m^2$  study area at each site. The following equation was used:

 $W(t) = Q_{SGD}^{*}(Nutrient)_{SGD} + Q_{M}^{*}(Nutrient)_{o}$ 

where: W(t) = loading of nutrient (g-at nutrient/day)

(Nutrient)<sub>SGD</sub> = concentration of nutrient in groundwater at the shore (  $\mu$ g-at nutrient/L )

(Nutrient)<sub>o</sub> = concentration of nutrient offshore ( $\mu$ g-at nutrient/L). As before,  $Q_{sGD}$  and  $Q_{M}$  represent the averaged volumes of groundwater and marine water entering the study areas, and have units m<sup>3</sup>/day.

Since statistical analysis showed a significant difference in nutrient level between offshore sites, it was decided that different values for  $N_0$  would be used

in the loading calculations, and the results averaged. As there was no difference detected in levels of totalP between offshore locales, one mean value for  $P_0$  was used in the loading calculation.

Despite visual indicators during laboratory analyses, which suggested that the nearshore tap samples were considerably richer in nutrient than those from the pumping stations, this was not borne out in the statistical analysis of the nutrient concentrations calculated. It is suspected, however, that this may be an artefact of the smaller contribution of the nearshore tap data to the data set as a whole, which in turn made the statistical analysis less robust. After the first half of the study, it was realised that the pumping station water, which is invariably located inland from the densely populated coastal areas, was not truly representative of the groundwater entering the nearshore zone. Attempts were made to acquire water from beach wells; however, repeated vandalism of these constructions and sand blockage forced this researcher to use water from taps directly on the beach as representative samples of (Nutrient)<sub>SGD</sub>. Thus, in the second half of the study, one sees the introduction of the nearshore tap samples to the study. The average  $N_{SGD}$ and  $P_{sgp}$  of the nearshore taps ( calculated as 969.83  $\mu$ M and 3.63  $\mu$ M, respectively) were used in the loading calculations for all sites for all study months.

Overall yearly nitrogen load for a 100m stretch of beach was calculated as 486.18 kg NO<sub>3</sub><sup>-</sup>-N/year, while that for phosphorous was 3.93 kg PO<sub>4</sub><sup>3-</sup>-P/year. If one estimates that the length of the West Coast of Barbados is 30 km ( as did Lewis (1987) ), then for the entire coast, 1.46 x 10<sup>5</sup> kg NO<sub>3</sub><sup>-</sup>-N and 1.187 x 10<sup>3</sup> kg PO<sub>4</sub><sup>3-</sup>-P are put into the nearshore yearly.

As was mentioned earlier, Kruskal-Wallis testing of the salinity data revealed that each site was unique in its hydrological regime, even though seepage rates did not reflect this. Out of curiosity, loading calculations were carried out using individual  $Q_{sGD}$  and  $Q_M$  values for each site. The N<sub>o</sub> value of Jordan's was used in the calculation of the two southernmost sites Brighton and Payne's Bay; while that of Greensleeves was used for the Holetown and Mullins calculations. All other parameters remained as previously described. Paired sample t-tests on this loading data ( see Table 7 in Appendix ) did not highlight any differences in loading for the dry ( July- Aug., 1996, and Mar. to May, 1997 ) and the wet ( Sept. to Nov., 1996 ) seasons for either N or P. However, an ANOVA showed that there exists a strong relationship between site and nutrient loading for both N and P ( P=0.000 in both cases ). Mean loading numbers were calculated for each site and nutrient ( Table 8 of Appendix ). Nevertheless, one is seeking an average picture for the entire length of the West Coast of Barbados, and final averaging of these numbers gave a near identical loading rate for the coast as was previously calculated.

#### 4.4 Calculation of the term for Clearance Mechanisms or Loss, K<sub>i</sub>.

As was mentioned earlier, uptake of nutrient ( both biotic and abiotic ) must figure prominently in the mass balance. The fall in nutrient level between the nearshore tap and the nearshore zone, and the absence of a nutrient gradient within the nearshore study areas suggests that biota in the sand ( perhaps bacteria and microalgae ) seems to be acting to lower nutrient levels; or that there is diffusion or mixing with sea water in the sand between the nearshore taps and the nearshore study area. In addition, it was determined that denitrification as an additional pathway for loss of nitrogen seemed unlikely given the coral limestone and sandy sediment features of Barbados, though loss of phosphate via geochemical adsorption to limestone was perhaps viable.  $K_i$ , was obtained by rearranging the steady-state equation so that:

> $K_i = Q * [ [ (Theoretical nutrient concentration) ] - 1 ]$ V (Observed nutrient concentration)

and ' theoretical nutrient concentration' ( expected nutrient concentration in the absence of a sink ) was calculated as:

Volume of the average nearshore study zone, V (m<sup>3</sup>) required knowledge of the

average water depth in this zone, Z (m). This in turn, was obtained by retrieving and sampling the CTD depth profile for each site. This data was statistically analysed by SYSTAT<sup>®</sup> to obtain mean depth, Z across all sites, which was then multiplied by the study zone area of 1200 m<sup>2</sup> to obtain volume of the average study zone, V.

Hence making the appropriate adjustment of units, estimates of  $K_i$  ( day<sup>-1</sup> ) were calculated. The loss term for nitrogen, N( $K_i$ ), was calculated as 0.42 day<sup>-1</sup>, while that for phosphorous, P( $K_i$ ), was 0.60 day<sup>-1</sup>. One would expect that in the event of increased algal or microbial growth, nutrient uptake would increase, and the value of  $K_i$  would become larger ( more positive ). By contrast, in the event of increased mortality of biota, one would expect a smaller  $K_i$ , as nutrient uptake would diminish.

#### 4.5 Assembling a picture of nutrient movement into the coastal zone.

Based on the results shown above, and with careful consideration of the mean salinity data (see Table 9), a schematic of the submarine groundwater movement of nutrient from the land into the coastal zone at the West Coast of Barbados, W.I. was produced, as shown in Figure 3.



FIGURE 3: Proposed schematic representation of the nutrient mass balance for the West Coast of Barbados, W.I.

٤.

#### **5.0 DISCUSSION**

#### 5.1 Technical Discussion

To paraphrase Lee et. al. (1985), the task of predicting the response of marine and estuarine systems to changes in wastewater disposal within their watersheds involves "acknowledging the unknowns, bracketing the uncertainties and by "a reasonable preponderance of evidence", (drawing) responsible conclusions ". This approach then lends itself to one being able to recommend initiatives that reasonably and responsibly address significant problems, though the understanding of the latter may be incomplete ( Lee et. al., 1985 ). Thus, one can attempt to surmise the relative accuracy of this nutrient mass balance model for the West Coast of Barbados, by way of critical assessment of its components, with an eye to pin-pointing weaknesses in the model and formulating improvements for future studies.

#### 5.1.1 Estimates of Rates of Seepage and Coastal Discharge

Lewis (1987), working on the West Coast, estimated total areal groundwater discharge rates along the entire 30 km of the West Coast, by integrating piezometer rates across depths and converting them to units used by Proctor and Redfern Int. Ltd. (1983). For the dry season, he estimated a rate of 128,000 m<sup>3</sup> d<sup>-1</sup>; and this rate more than doubled in the wet season to 296, 000 m<sup>3</sup> d<sup>-1</sup>. A similar estimation was made in this study by assuming that the total coastal discharge area has dimensions of ' 30 km x 12m ' ( the ' 12 m ' representing the farthest distance from shore traversed in this study ), and multiplying this area by the mean flux rate. The resultant estimate of total coastal discharge rate for this study was 21, 960 m<sup>3</sup> d<sup>-1</sup>. Lewis ( 1987 ) cites an estimate by Harris ( 1971 ) of 43, 200 m<sup>3</sup> d<sup>-1</sup>, which is somewhat closer to that of this study. The disparity in calculated total areal discharge appears to be due not only to differences in calculating this parameter, but also to a very real decrease in seepage rates between the time of Lewis' study and this study. Lewis' ( 1987 ) mean seepage

rate was  $393.6 \text{ Lm}^2 \text{ d}^{-1}$ , approximately 6.5 times that of the mean seepage rate measured across sites in this study (which was  $61.1 \text{ Lm}^2 \text{ d}^{-1}$ ). There was no simultaneous dramatic decrease in rainfall between 1985 and 1996 or 1997 (rainfall data from the Caribbean Meteorological Services accessed; not shown), although it has been publicly acknowledged by the Barbados Water Authority (BWA) that well levels have fallen over time. This points at changes in development and land and water use, and attendant increased demand for water, as a suspected cause for the fall in seepage rates.

Though a crude approach was used to estimate total areal discharge in this study, the importance of the spatial distribution of discharge must not be underestimated, as this has implications for the fate of dissolved nutrients, the creation of nutrient budgets, and the application of nutrient loading models. At the land-sea interface, patterns of groundwater discharge have additional complexity due to the added effects of differential hydraulic head and density, tidal regime, and nearshore stratigraphy. Coastal discharge models employed to date tend to concentrate on two spatial dimensions: groundwater flow perpendicular to the shore; and the vertical relationships of hydraulic head and density (Millham et. al., 1994). Patterns of discharge are thus often generalised; though this approach could be considered quite feasible for the highly permeable, undifferentiated limestone aquifer and relatively straight West Coast of Barbados.

#### 5.1.2. Salinity Measurements

In assessing the ranges of salinities measured in this study, the literature seems quite corroborative. Lewis (1987) collected water from the ' zone of diffusion ' as shown in Figure 2, and measured salinities ( equivalent to this study's estimates of  $S_{sGD}$ ) ranging from 26.53 to 35.27 psu, with a mean of 33.79 (+/- 1.19) psu, as compared to a mean salinity of overlying sea water ( $S_i$ ) of 34.93 (+/- 0.53) psu. In this study,  $S_{sGD}$  ranged from 22.32 to 35.84 (mean = 32.97 (+/- 2.843) psu); while mean  $S_i$  was measured at 33.59 (+/- 2.23) psu. The mean salinity measured offshore,  $S_u$ , was 34.31 (+/- 1.25) psu in this study;

and the salinity-depth profiles indicated a subsurface salinity maximum at about 100m depth ( data not shown ). For the most part, offshore salinity,  $S_{M}$ , was greater than that of the nearshore,  $S_i$ , except during the July - August, 1996 run, when mean  $S_M$  was 32.90 psu and mean  $S_i$  was 33.15 psu ( see Table 9 of Appendix ). The subsurface salinity maximum is reported as typical in the literature; and Borstad in 1982 reported salinity ranges of 32.20 to 36.00 psu within 10 km of the island of Barbados, the freshest water most likely to occur in August ( taken from Stansfield et. al., 1995 ). This latter phenomenon is attributed to Amazon River outflow, the effects of which peak at that time of year ( Stansfield et. al., 1995 ).

It is likely that  $S_{sGD}$  estimates in this study were a higher value than in actual fact, since  $S_{sGD}$  was simply taken as the minimum salinity value detected at the immediate shore, since it was impossible to obtain an actual salinity reading from water in the 'zone of diffusion' or mixing. The placement of this inflated parameter value in the nominator of the equation used to calculate  $Q_M$  presents a considerable source of inaccuracy to the mass balance.

#### 5.1.3. Estimates of Q

There were no comparative values of  $Q_M$  to be found in the literature. Comparing the  $Q_M$  and  $Q_{SGD}$  values (Table 10), indicates, the majority of the time, a ratio of these two parameters ranging from about 1:1 (see primarily the Payne's Bay site, and secondarily, Holetown) to around 3:1 (seen primarily at the Brighton site). The larger ratios tended to occur during the dry season, when submarine inputs were low, while the lower ratios were observed largely during the wet season. The mean  $Q_M : Q_{SGD}$  ratios for the sites, however, indicate that on average, at low tide, the volume of seawater entering the study area from offshore is approximately twice that of the groundwater entering from the land. Lewis (1987) discusses the high transmissivity of the Barbados limestone aquifer, which would lend for relatively low  $Q_M : Q_{SGD}$  ratios. Indeed, Johannes (1980) working in Australia describes highly transmissive limestone outcrops in the nearshore, much like those exposed at Mullins during the course of this study. Confidence in  $Q_M$  values calculated however is curtailed, when one considers that it is calculated by an equation which incorporates  $Q_{SGD}$  and  $S_{SGD}$  estimates, which, as discussed in the previous section, are inflated due to the method of used to capture such data from the nearshore rather than from the actual 'zone of diffusion'. This results in an underestimate of  $Q_M$ , and, in effect, the rate at which marine water enters from offshore to diffuse or dissipate nutrient load entering with groundwater into the 'zone of diffusion' and nearshore zone.

#### 5.1.4. Estimating Patterns of Movement of Fresh Groundwater relative to Marine Discharge

As has been outlined in the previous paragraphs, a crude approach was used to estimate  $Q_{SGD}$  in this study, which did not wholly factor in the fact that land-sea interface patterns of groundwater discharge have additional complexity due to the added effects of differential hydraulic head and density, tidal regime, and nearshore stratigraphy (Millham et. al., 1994). Despite the inaccuracies discussed, the estimates of  $S_{\text{sgd}}$  still indicate that there is significant mixing of saline and freshwater beneath the sand, in the 'mixing zone' (see Figure 2). As aforementioned, Q<sub>1</sub> calculations indicate that marine flux is only about twice that of seepage input. If one assumes then that for every part of freshwater, there are two parts of marine water being mixed in the zone of diffusion, and that the freshwater will have a salinity of zero, and the mean S<sub>1</sub> is 34.31 psu as measured in this study, one would expect the mean  $S_{sco}$ , which should reflect the salinity in the mixing zone, to be in the range of 23 psu. This is not the case (see Table 9), as mean  $S_{sgp}$  was observed to be 32.97 psu. This reaffirms suspicions that  $S_{sgp}$  is lower in reality within the 'zone of diffusion', and that it is therefore erroneous to assume that all of the SGD enters the nearshore zone directly. This acts to affect the accuracy of the  $Q_M$  component of the mass balance, and significantly complicate the mass balance approach.

## 5.1.5. Compared Nutrient Levels & Estimation of Nutrient Loading to the Coast

Up to the time of this study, there have been no published totalN or totalP measurements taken for the coastal or groundwaters of Barbados. Nutrient concentrations appear high in the nearshore tap samples relative to those of the oceanic samples: at the nearshore tap, mean totalN = 969.83  $\mu$ M, mean totalP = 3.63  $\mu$ M; at the nearshore, mean totalN = 238.28  $\mu$ M, mean totalP = 7.30 x 10<sup>-1</sup>  $\mu$ M: offshore, mean totalN = 167.63  $\mu$ M, mean totalP = 5.86 x 10<sup>-1</sup>  $\mu$ M. Water from the nearshore taps was taken as the closest representative of SGD at the nearshore, as the Barbados Water Authority publicly announced at the end of 1996 that there was a 60 to 70% leakage rate of their water mains. This, combined with the fact that due to water shortages water pressure was often drastically lowered, or completely turned off at night, made contamination of tap water by surrounding sewage or agricultural effluent quite likely. Indeed, one can see from Table 6 in the Appendix that nutrient levels at the pumping stations (mean totalN = 481.30  $\mu$ M, mean totalP = 1.10  $\mu$ M) are generally lower than at the nearshore tap, and there is a doubling and tripling in totalN and totalP (respectively) as one goes from pumping station to nearshore tap. At Payne's Bay and Holetown, both of which are abutted by hotels and holiday beach residences, phosphorous levels jump by a proportion of ten or more during some months (see Table 6). This indicates heavy nutrient input by the coastal population, probably by way of shallow groundwater contamination with garden fertilisers and sewage effluent. In contrast, when one goes from nearshore tap to the nearshore zone, one sees a fourfold drop in totalN level and a fivefold decrease in totalP. There is also a general decrease in nutrient levels as one moves far offshore from the nearshore zones.

Similar chemical pictures appear in the literature. Johannes (1980) reports from Australia SGD nitrogen levels of 380  $\mu$ M, and states that in general these levels are two to three orders of magnitude higher than coastal levels. Weiskel et. al. (1992) report dissolved nitrogen and phosphorous concentrations

of 3000 µM and 403 µM, respectively, in domestic effluent, which were one hundred to one thousand times higher than concentrations in the receiving water bodies. The increase in nutrient level from the pumping station to the nearshore tap appears to support the view that coastal and suburban development can be an important nutrient source to ground and coastal waters; septic tanks, and perhaps garden fertilisers being the direct root of the problem ( Lee et. al., 1985 ). In densely populated suburban and coastal developments, with several small individual lots, septic tank nitrogen flux ( and by extension P flux ) often becomes the dominant input to ground and coastal waters ( Simmons et. al., 1994; Walker et. al., 1973 ). Although there was a general decrease in nutrient level from nearshore to offshore, the decrease was not extremely dramatic. D'Elia et. al. ( 1981 ) characterise the Atlantic and Caribbean Sea as being naturally low in phosphorous ( relative to the Pacific ), though capable of exhibiting high naturally occurring concentrations of nitrogen; and indeed this description fits what was observed in this study.

This study's figure of  $1.46 \times 10^5$  kg NO<sub>3</sub><sup>--</sup>N/year for annual nitrogen loading at the West Coast is very much in line with that of Harries (1997), who gave a corresponding estimate of  $1.9 \times 10^5$  kg N/year. There are no estimates given for phosphorous loading in Barbados with which to compare this study's figure of  $1.187 \times 10^3$  kg PO<sub>4</sub><sup>3-</sup>-P/year. However, for the largely limestone Caribbean island of Bermuda, Simmons et. al. (1994) describe nitrogen loading rates similar to those seen in Barbados ( up to  $7 \times 10^6$  kg N/year ), though phosphorous loading rates appear lower ( up to 154.87 kg P/year ).

#### 5.1.6. The Mixing Phenomenon and Advection of Nutrient Offshore

The fall in nutrient level between the nearshore tap and the nearshore zone is of such magnitude ( nutrient levels fall four to fivefold ) that one might postulate a sink in the sand, microbial sand biota playing a primary role in nutrient uptake. However, the rest of the evidence makes this unlikely. As aforementioned, it is erroneous to make the assumption that all of the SGD and its

attendant nutrient load ( Q<sub>scp</sub>\*(Nutrient)<sub>scp</sub>) is entering the study zone. It would appear that the mixing which is going on in the sand is advecting much of the nutrient (and freshwater) input further out to sea, beyond the study zone, before it even enters the water column proper. One might expect the mixing of fresh SGD and marine flux to effectively lower the salinity of the latter. As mentioned earlier, a 1:2 mixing of fresh and marine water might be expected to generate a mean S<sub>scp</sub> of about 23 psu. If we carry this crude estimation further, we might say that one would expect about a 30% drop in salinity of marine water once it mixes with fresh water. In this study, we only saw a drop of 3.9% in salinity; and so we might postulate that a little over one tenth of the SGD, and its attendant nutrient load is entering the immediate study zone, based on the mixing model of our Q values. Thus a picture forms that, for the most part, nutrients are probably entering the water column, by diffusion as opposed to seepage, and beyond the immediate shoreline area as well; and it is this offshore nutrient input that is likely impacting the reef as reported (Allard, 1993). Despite the crude approach of this study, it is still likely that the calculated estimate of nutrient loading to the marine environment is good (especially given the close corroboration with that of Harries (1997)), even though only a part of it appears to be entering the immediate nearshore study zone.

#### 5.1.7. Subsurface Behaviour of Nitrate and Phosphate

At this point in the discussion one might make mention of the behaviour of nitrate,  $NO_3^-$ , and phosphate,  $PO_4^{3-}$ , as they move through the aquifer substrate and into the coastal waters. Unreactive solutes, such as  $NO_3^-$ -N, move within aquifers in groundwater via (i) convection due to the mass flow of groundwater and (ii) ionic or molecular diffusion due to concentration gradients (Walker et. al., 1973). Hence net transport of dissolved nitrogen is found to be moderately conservative (Simmons et. al., 1994; Pejrup et. al., 1993; Weiskel et. al., 1992). In contrast, phosphate can be adsorbed by such aquifer materials as limestone (Simmons et. al., 1994). The literature describes occasions of phosphate

36

adsorption onto limestone surfaces and/or the formation of calcium carbonatephosphate surface complexes, acting to remove much phosphate from groundwater, keeping groundwater phosphate concentrations relatively low and constant (Simmons et. al., 1994). However, the similar N:P ratio of the nearshore tap samples and pumping station, and the relatively high phosphorous levels at the former relative to the latter, appears to support conservative movement of phosphorous. In general, where watersheds are groundwater dominated and permeable, and nutrients may be introduced to groundwater primarily by sewage disposal systems, total mass flux and subsurface behaviour of both nitrogen and phosphorous are poorly understood; though they appear to be controlled by chemical and bacterial interactions (Weiskel et. al., 1992). And whilst there have been arguments that these types of mass balance approaches must be totally precluded for phosphorous due to the possibility of its nonconservative transport within the aquifer (Pejrup et. al., 1993), it has been countered that one usually has to make assumptions regarding subsurface behaviour in order to quantify watershed nutrient inputs, (Weiskel et. al., 1992).

#### 5.1.8. Attempts to Calculate Loss Term, Ki

The loss term,  $K_i$ , can be described as the proportion of nutrient at hand either being put in by the source, or taken up or lost by the sink, per unit time. The nitrogen and phosphorous loss terms, N(K<sub>i</sub>) and P (K<sub>i</sub>), were both calculated for this study, by rearrangement of the mass balance equation, as 0.42 and 0.60 d<sup>-1</sup>, respectively, suggesting the presence of a nutrient sink. However, with the absence of a significant nutrient gradient observed in this study, K<sub>i</sub> estimates cannot be calculated with any confidence.

It has been proposed that coastal systems are often N-limited; and as such, 'new' nitrogen from terrestrial sources is a major factor controlling eutrophication in these systems. Further, where there is a greater flux of high N:P groundwater than surface runoff and precipitation as a source of 'new' nitrogen, as appears to occur at the West Coast, the system could conceivably shift from nitrogen to phosphorous limitation (Weiskel et. al., 1992).

#### 5.1.9. Limitations in the Literature and of this Study

In general, there is little in the literature on the biological behaviour of phosphate, apart from its possible hindering effect to calcification processes in reefs (Kinsey et. al., 1979). Biological uptake of nitrate appears to be somewhat slower than that of phosphate. Johannes (1980) states that in general, biological uptake of nitrate is slow relative to the rate of dilution of discharged SGD by incoming seawater; though to know just how much SGD nutrient actually supports coastal productivity requires a knowledge of not only flushing rates by low(er) nutrient offshore waters, but also biota uptake rates, particularly for algae and seagrasses. Thus treating totalN in a conservative way in the mass balance, though a simplification, is justified not only because of its relative unreactive chemical behaviour within the aguifer, but also due to the fact that the amount of nitrate removed biologically from the surrounding water does not change that much over a short time scale. The inorganic nitrogen used by phytoplankton ( or bacteria and other microorganisms ) remains in the water as organic nitrogen due to the negligible amount of organisms grazed or deposited over a short time (Pejrup et. al., 1993). Thus in cases where there is a high total Supply to a coastal system, the primary mechanism for removal of totalN from the system, even on a yearly basis, will be flushing by low nutrient offshore sea water (Peirup et. al., 1993); and this certainly seems to be the case in this study.

#### 5.2 Non-technical Aspects and Summary

Given these observations, the diagrammatic representation of the mass balance at the West Coast of Barbados was composed, as shown in Figure 3. Harries (1997), analyzing well data ranging from the central West Coast to the more rural, northern part of the island, concluded that the main source of nutrient input to groundwater in Barbados is probably agricultural fertiliser applications versus sewage. Using historical data on sugar cane acreage and fertiliser tonnage, Harries suggested that the rise in nitrates in groundwater at West Coast supply wells between 1977 and 1996 is a delay effect, due to leaching of excess agricultural fertiliser with successive wet seasons. However, this present study incorporated sample wells farther south, in a more densely populated, urban part, of the island (see Figure 1); and so the general rise in nutrient level seen at the nearshore tap in this study is probably due also to shallow groundwater contamination by the indiscriminate use of septic tank systems and suckwells so prevalent to the West Coast, and Barbados housing areas in general. Indeed, Hagedorn et. al. (1981) express the view that septic tank soil absorption systems should be confined to rural areas with low population density; and the West Coast of Barbados certainly does not meet this criterion (see Figure 1). Harries (1997) suggests that at about midway along the West Coast, the relative effects of sewage outfall and fertiliser application were about equal for the year 1992, each having a proportionately greater effect south and north respectively. This is consistent with work done by Cabana (Ph.D. thesis, McGill, 1996) using nitrogen stable isotopes, which deduced that from Holetown southward, sewagederived nitrogen is heavily assimilated into fringing reef food-chains on the West Coast (approximately 50% total body nitrogen of the carnivorous bluehead wrasse, Thalassoma bifasciatum, was incorporated from sewage-derived nitrogen ). This effect is not seen farther north.

As was stated previously, the observed nutrient decrease between the nearshore tap and the nearshore study zone, is suspected to be primarily the result of diffusion and convection mixing of freshwater with lower nutrient seawater in the sand. Nutrient uptake in the nearshore study zone does not appear to be significant, as there were no nutrient gradients observed within the latter. A direct result of this mixing phenomenon is the inability to detect either salinity or nutrient gradients within the study zone, which in turn might have provided accurate information on water fluxes. It appears to be a situation where mixing, whether at the sediment-water interface or within the sediment, is simply too strong relative to the SGD input observed; and without detectable gradients, one is unable to complete a mass balance over any defined zone.

Certainly for the last 3 years, Barbadians have been experiencing severe reductions in water availability. Although reduced rainfall levels have been blamed for this, actual annual rainfall data across the period of 1985 to 1997 only show a significant reduction in annual rainfall in 1997. For the January to May period, for example, 267.9 mm of rain fell in 1985 ( average monthly rainfall was 53.58 mm ), while for the same period in 1997, 127.40mm fell ( average monthly rainfall was 25.48mm ) ( data not shown; contributed by Mr. Horace Burton, Caribbean Meteorological Services ).This drastic reduction in rainfall has been attributed to the El Nino phenomenon, and it has acted to reduce flow within the island's aquifers. This in turn could have a very real effect on seepage rate, and hence explain, though only in part, this study's lower estimate of coastal areal discharge relative to those of Lewis ( 1987 ).

However, a more likely explanation, or at least a significant contributor to the reduced groundwater seepage observed in this later study, is a dramatic increase in water use in Barbados. The West Coast has seen an increase in coastal construction, and increased development in water intensive golf courses. Further, the island as a whole has seen an intensification in water use, which is currently being viewed by the Barbadian Government as having reached crisis proportions. Such development along the West Coast has no doubt also brought with it significant increases in nutrient loading, which have been suspected to be at the root of the dramatic deterioration of West Coast reefs (Allard, 1993). General increases in water use further inland in the construction boom ( of roads, residential and business houses ) that has occurred on the island since the 1980's might also mean that water in the aquifer is being drawn before it ever reaches the West Coast; and for purposes that will not encourage good return of used water to the aquifer for percolation. Bringing increased volumes of water for use at the surface also allows for increased evapotranspiration rates. Add to this that this water is taken up into the Barbados Water Authority's extremely leaky piping system which runs just under the ground surface, and the evapotranspiration

problem escalates. The return of used water to the aquifer may be dramatically diminished.

In general, loading models which attempt to quantify nutrient flux are subject to large error because they often involve the examiner making highly conservative assumptions about human activity and population density, initial or background loading rates, and perhaps the transportation behaviour of the nutrient during its journey to the coastal zone. Making such assumptions may lead to substantial over predictions of nutrient flux into the coastal setting (Wieskel et. al., 1996). To combat this, particularly in instances where there is significant residential development within the coastal watershed, one might employ a more site-specific approach, incorporating: (i) land use analysis, with close attention being paid to human activity as well as population density; (ii) water shed runoff studies; (iii) coastal circulation data and hydrological studies; (iv) and spatially intensive groundwater sampling, to better highlight the large number of nutrient sources within the coastal watershed (Monbet et. al., 1981; Wieskel et. al., 1991). The team of Millham et. al. (1994) place emphasis on the fact that there can be changes in the patterns and rates of groundwater discharge due to seasonal variations in water table elevation, or even short-term variations in coastal seawater level. This, they say, " underscores the need to integrate upland water table mapping with hydraulic measurements within the zone of discharge when estimating the input of groundwater and groundwater-borne nutrients to coastal (areas)" (Millham et. al., 1994).

Apart from incorporating the aforementioned approaches into future mass balance studies at the West Coast of Barbados, there is a need for the authorities on the island to set water quality criteria for coastal waters. At the moment, Barbados has no regulated public health criteria for bathing waters, and attempts are being made to set standards for the maintenance of coral reefs, appropriate to the local environment (Farqui et. al., 1995). The decline of the West Coast coral reefs and associated biota (Allard, 1993), and indications of increasing sewage outfall from West Coast development (Cabana, Ph.D. thesis, McGill, 1996) and fertiliser over application (Harries et. al., 1997), have prompted the Barbados Government to launch the West (and South) Coast Sewage Project, and to pay more strict attention to land use above aquifers and around groundwater supply wells. If Barbados is to succeed in diminishing coastal nutrient load for the protection of reefs and bathing areas, treatment levels of sewage must be high, or the outfall long; and in general, effluent standards must be high, so that the sensitive needs of the receiving waters are met (Farqui et. al.; 1995).

### 6.0 Appendix : Tables 1 to 10

RUN	SITE	SEEPAGE METER	$Q_{SGD}$ (m <sup>3</sup> of water/day)
		FLUX (m/day)	
July-Aug,'96	Brighton	0.047	56.104
(dry)	Payne's Bay	0.051	60.779
	Holetown	0.010	11.693
	Mullins	0.082	98.182
Sept.,'96	Brighton	0.065	78.545
(wet)	Payne's Bay	0.056	67.325
	Holetown	0.047	56.104
	Mullins	0.074	89.299
Nov.,'96	Brighton	0.086	103.344
(wet)	Payne's Bay	0.061	73.188
	Holetown	0.058	70.130
L	Mullins	0.088	105.195
Jan.,'97	Brighton	0.078	93.506
(wet)	Payne's Bay	0.037	44.610
Mar.,'97	Brighton	0.064	77.143
(dry)	Payne's Bay	0.047	56.104
	Mullins	0.076	91.169
Apr.,'97	Brighton	0.051	60.974
(dry)	Payne's Bay	0.076	91.169
	Mullins	0.078	93.506
May,'97	Brighton	0.039	46.753
(dry)	Payne's Bay	0.042	50.494
	Holetown	0.047	56.104
	Mullins	0.055	65.922

**Table 1:** Seepage flux (m/day) and  $Q_{SGD}$  estimates. Study area is estimated as 'beach length (100m) x maximum distance from shore investigated (12m) = 1200 m<sup>2</sup> '. Mean flux wet months = 0.065 m/day; mean flux dry months = 0.058 m/day; overall mean flux = 0.061 m/day. The value for the seepage rate taken at Holetown for Jul.-Aug., 1996 was dropped from the statistical data set as it was somewhat low, owing to the extreme coarseness of the substrate during this particular month, preventing placement of the seepage metre such that it was flush with the surface. This affected the hydraulic conductivity of the beach material, which Hegge et. al. (1991) cite as the chief determinant of the rate of SGD. Thus, this value, was omitted from subsequent calculations.

RUN	SITE	AVERAGE $Q_{M}$ (m <sup>3</sup> seawater/day entering the study
		area.)
July-Aug,'96	Brighton	132.418
	Payne's Bay	54.098
	Mullins	62.450
Sept., '96	Brighton	84.450
	Payne's Bay	113.417
	Holetown	80.312
	Mullins	148.212
Nov.,'96	Brighton	149.521
	Payne's Bay	65.965
	Holetown	62.540
	Mullins	81.225
Jan.,'97	Brighton	309.147
	Payne's Bay	46.103
Mar.,'97	Brighton	348.641
	Payne's Bay	51.315
	Mullins	475.554
Apr.,'97	Brighton	264.164
	Payne's Bay	176.779
	Mullins	133.473
May,'97	Brighton	75.913
	Payne's Bay	64.804
	Holetown	183.442
	Mullins	130.807

**Table 2:** Values of  $Q_M$  calculated for each site. Kruskal-Wallis tesing revealed no significant differences with respect to site or time. Average  $Q_M$  calculated as 143.25 m<sup>3</sup>/day.

RUN	SITE	AVERAGE p1 (µM)	AVERAGE p2 (µM)	AVERAGE p3 (µM)	OVERALL NEARSHORE AVERAGE (µM)
July- Aug. '96	BRI PAY HOL MUL	63.36 373.32 86.38 255.62	69.08 396.46 101.66 232.90	78.79 380.57 59.50 248.66	70.41 383.45 82.51 245.73
Sept. '96	BRI PAY HOL MUL	106.61 382.58 159.84 408.53	149.28 442.32 90.62 374.59	120.06 467.71 74.62 255.29	125.32 430.87 108.36 346.14
Nov. '96	BRI PAY HOL MUL	73.61 69.34 196.20 154.56	122.28 131.88 223.20 179.04	528.50 90.96 346.10 119.47	241.46 97.39 255.17 151.02
Jan. ,'97	BRI PAY	345.53 295.94	241.49 266.36	273.77 182.86	286.93 248.39
Mar., '97	BRI PAY HOL MUL	218.38 159.48 N.D. 141.94	191.33 191.35 190.56 150.84	183.48 430.39 N.D. 149.00	197.73 260.41 190.56 147.26
<b>Apr.,</b> '97	BRI PAY HOL MUL	185.09 309.34 N.D. 445.54	198.98 233.18 558.89 491.33	186.02 189.43 N.D. 379.01	190.03 243.98 558.89 438.62
May, '97	BRI PAY HOL MUL	225.58 288.34 N.D. 213.38	416.81 327.98 126.55 193.01	209.14 276.02 N.D. 154.15	283.84 297.45 126.55 186.85

**Table 3:** Average total nitrate values ( $\mu$ M) for samples at all sites. BRI=Brighton/Spring Garden; PAY=Payne's Bay; HOL=Holetown; MUL=Mullins. N.D.- No data. Mean totalN level across sites and months = 238.282  $\mu$ M.

RUN	SITE	AVERAGE p1 ( 10 <sup>-1</sup> µM)	AVERAGE p2 (10 <sup>-1</sup> µM)	AVERAGE p3 (10 <sup>-1</sup> µM)	OVERALL NEARSHORE AVERAGE (10 <sup>-1</sup> µM)
July- Aug. '96	BRI PAY HOL MUL	7.40 4.90 10.80 3.00	7.20 0.60 10.60 1.60	8.00 8.00 9.40 5.30	7.50 4.50 10.30 3.30
Sept. '96	BRI PAY HOL MUL	19.40 10.00 18.10 7.50	13.00 9.80 13.40 14.40	18.00 9.40 15.70 8.50	1.68 9.70 15.70 10.10
Nov. '96	BRI PAY HOL MUL	5.30 19.10 3.00 1.34	3.80 15.90 4.20 18.30	4.30 15.80 3.80 16.00	4.50 16.90 3.70 15.90
Jan. ,'97	BRI PAY	9.00 5.40	8.40 5.40	9.00 5.80	8.80 5.50
Mar., '97	BRI PAY HOL MUL	7.10 4.50 N.D. 5.80	7.00 2.50 7.90 6.10	4.80 3.20 N.D. 6.90	6.30 3.40 7.90 0.63
Apr., '97	BRI PAY HOL MUL	8.80 5.10 N.D. 11.40	7.50 6.10 7.10 11.40	6.60 4.90 N.D. 8.80	7.60 5.40 7.10 10.50
May, '97	BRI PAY HOL MUL	7.30 5.40 N.D. 6.90	5.40 5.40 5.60 5.90	8.00 4.40 N.D. 3.30	6.90 5.10 5.60 5.40

**Table 4:** Averaged total phosphate values  $(10^{-1}\mu M)$  for samples at all sites. BRI=Brighton/Spring Garden; PAY=Payne's Bay; HOL=Holetown; MUL=Mullins. N.D.- No data. Average totalP level across sites and months = 7.30 ( $10^{-1} \mu M$ ).

RUN	OFFSHORE SITE	Ν <sub>ο</sub> (μΜ)	Ρ <sub>o</sub> (10-1 μM)	MEAN N <sub>o</sub> (µM)	MEAN Ρ. (10-1 μΜ)
July-Aug, '96	Jordan's Greensleeves Greensleeves	270.936 223.704 17.28	0 0 3.90	270.936 (Jor) 120.492 (Gr)	1.30
Sept., '96	Jordan's Jordan's Greensleeves Greensleeves	357.264 207.648 50.976 31.896	10.00 10.20 10.00 8.50	282.456 (Jor) 41.436 (Gr)	9.70
Nov., '96	Jordan's Jordan's Greensleeves Greensleeves	40.896 300.96 95.40 63.72	20.40 2.20 19.90 1.60	170.928 (Jor) 79.56 (Gr)	11.00
Jan., '97	Jordan's Jordan's Greensleeves Greensleeves	379.008 203.04 153.864 309.816	3.60 N.D. 5.40 5.40	291.024 (Jor) 231.84 (Gr)	4.80
Mar., '97	Jordan's Jordan's Greensleeves Greensleeves	121.248 132.984 191.232 143.208	5.00 5.60 1.60 3.90	127.116 (Jor) 167.22 (Gr)	4.00
Apr., '97	Jordan's Jordan's Greensleeves Greensleeves	378.144 189.504 188.496 75.60	4.40 N.D. 2.70 4.40	283.824 (Jor) 132.048 (Gr)	3.80
May, '97	Jordan's Jordan's Greensleeves Greensleeves	47.592 118.656 94.68 94.464	5.20 5.20 3.40 4.0	83.124 (Jor) 94.572 (Gr)	4.50

**Table 5:** Nutrient levels over the bank reef ( $\mu$ M). Mean total N (N<sub>o</sub>) calculated for each offshore site monthly ( overall mean N<sub>o</sub> for Jordan's (Jor) = 211.375  $\mu$ M; for Greensleeves (Gr) = 123.881  $\mu$ M), due to statistical differences being detected between sites. Mean total P ( P<sub>o</sub>) was found to be uniform between offshore sites, and so data of both sites was pooled monthly (overall mean P<sub>o</sub> = 0.586  $\mu$ M). N.D. = No data.

RUN	PUMPING STATION	Ν <sub>SGD</sub> (μM)	Р <sub>SGD</sub> (10-1µМ)
July - Aug., '96	Codrington (BRI)	20.40	5.10
	Molyneux (PAY)	543.15	1.10
	Trents (HOL)	142.80	2.10
	Heymans (MUL)	20.40	3.20
Sept., '96 Codrington (BRI) Molyneux (PAY) Trents (HOL) Heymans (MUL)		56.61 271.83 N.D. 633.17	15.30 24.30 23.80 22.00
Nov., '96	Codrington (BRI)	521.73	7.10
	Molyneux (PAY)	339.15	44.00
	Trents (HOL)	1357.62	2.80
	Heymans (MUL)	84.915	33.60
Jan., '97	Codrington (BRI)	495.98	12.00
	Molyneux (PAY)	846.09	16.20
Mar., '97 Codrington (BRI) Molyneux (PAY) Trents (HOL) Heymans (MUL) W.I. Distilleries (BRI) Payne's Bay Residence (PA Mango Bay (HOL) Mulling Beach Bar (MUL)		339.15 594.92 678.30 646.43 883.07 1697.03 877.71 784.89	3.80 5.90 3.20 5.60 6.40 156.65 47.50 7.50
Apr., '97	Codrington (BRI)	289.43	7.90
	Molyneux (PAY)	805.29	10.20
	Trents (HOL)	446.00	5.00
	Heymans (MUL) .	447.78	5.00
	W.I. Distilleries (BRI)	797.39	8.50
	Payne's Bay Residence (PAY)	673.71	62.90
	Mango Bay (HOL)	1073.04	17.50
	Mullins Beach Bar (MUL)	1119.45	7.80
May, '97	Codrington (BRI)	767.55	6.10
	Molyneux (PAY)	673.71	8.60
	Trents (HOL)	588.29	5.80
	Heymans (MUL)	421.77	6.50
	W.I. Distilleries (BRI)	1007.51	8.00
	Payne's Bay Residence (PAY)	960.59	67.00
	Mango Bay (HOL)	924.38	39.10
	Mullins Beach Bar (MUL)	839.21	7.10

 Table 6: Total nutrient levels of pumping stations. Bracketed are the corresponding site areas supplied by the pumping stations or nearshore taps (BRI=Brighton; PAY=Payne's Bay; HOL=Holetown; MUL=Mullins). N.D.- no data.

RUN	SITE	W(t) FOR	NITRATE	W(t) FOR	PHOSPHATE
		in	in	in	in
		kgNO3-N/day	kgNO3-N/year	kgPO <sup>3</sup> <sub>4</sub> -P/day	kgPO <sup>3</sup> ₄-P/year
July-	Brighton	1.155	421.485	0.009	3.141
Aug,	Payne's Bay	0.987	360.202	0.008	2.840
'96	Mullins	1.443	526.675	0.012	4.428
Sept.,	Brighton	1.317	480.815	0.010	3.759
'96	Payne's Bay	1.251	456.506	0.010	3.481
	Holetown	0.902	329.117	0.008	2.811
	Mullins	1.471	536.756	0.013	4.603
Nov.,	Brighton	1.847	674.162	0.014	5.188
'96	Payne's Bay	1.190	434.223	0.009	3.421
	Holetown	1.061	387.418	0.009	3.275
	Mullins	1.570	573.155	0.013	4.832
Jan.,	Brighton	2.187	798.075	0.016	5.793
<b>'</b> 97	Payne's Bay	0.743	271.159	0.006	2.124
Mar.,	Brighton	2.081	759.426	0.015	5.369
<b>'</b> 97	Payne's Bay	0.914	333.706	0.007	2.628
	Mullins	2.064	753.396	0.018	6.747
Apr.,	Brighton	1.611	587.966	0.011	4.172
<b>'</b> 97	Payne's Bay	1.762	643.218	0.013	4.860
	Mullins	1.502	548.288	0.013	4.682
May,	Brighton	0.860	313.919	0.007	2.399
<b>'9</b> 7	Payne's Bay	0.878	320.465	0.007	2.483
	Holetown	1.081	394.448	0.009	3.462
	Mullins	1.123	409.795	0.010	3.533

Table 7: Estimates of nutrient loading into the 1200m<sup>2</sup> study.

SITE	MEAN NITROGEN LOAD	MEAN PHOSPHOROUS
	(kgNO <sub>3</sub> -N/year)	LOAD
		( kgPO <sup>3-</sup> <sub>4</sub> -P/year )
Brighton	576.550	4.260
Payne's Bay	402.783	3.119
Holetown	370.328	3.183
Mullins	558.011	4.804

Table 8: Mean nutrient loadings ( kg of nutrient/year ) for each site

RUN SITE		AVE S <sub>SGD</sub>	AVE S <sub>i</sub>	AVE S <sub>M</sub>
July- Aug., '96	Brighton	30.693	31.213	32.897
	Payne's Bay	33.769	33.878	
	Holetown	33.270	33.416	
	Mullins	33.448	33.695	
Sept., '96	Brighton	27.106	27.455	32.695
	Payne's Bay	32.526	32.604	
	Holetown	32.074	32.249	
	Mullins	32.079	32.399	
Nov., '96	Brighton	29.717	30.531	33.992
	Payne's Bay	34.249	34.276	
	Holetown	34.587	34.660	
	Mullins	34.311	34.462	
Jan., '97	Brighton	30.682	32.683	35.446
	Payne's Bay	35.017	35.030	
Mar., '97	Brighton	28.938	31.151	34.515
	Payne's Bay	34.855	34.887	
	Mullins	33.683	34.662	
Apr., '97	Brighton	29.711	33.610	35.936
	Payne's Bay	35.737	35.830	
	Mullins	34.930	35.359	
May, '97	Brighton	32.266	33.686	35.661
	Payne's Bay	35.344	35.417	
	Holetown	35.437	35.663	
	Mullins	34.819	35.392	

**Table 9:** Averaged salinity values (psu). Mean  $S_{SGD}$  across sites is 32.97 psu; mean  $S_i$  across the sites is 33.59 psu; mean  $S_M$  across sites is 34.31 psu. Note that AVE  $S_M$  will be the same for all sites on any particular run.

SITE	RUN	Q <sub>M</sub> :Q <sub>SGD</sub>	MEAN RATIO
Brighton	July-August, 1996 September, 1996 November, 1996 January, 1997 March, 1997 April, 1997 May, 1997	2.360 1.076 1.447 3.306 4.519 4.332 1.624	2.666
Payne's Bay	July-August, 1996 September, 1996 November, 1996 January, 1997 March, 1997 April, 1997 May, 1997	0.890 1.685 0.901 1.034 0.915 1.939 1.283	1.235
Holetown	September, 1996 November, 1996 May, 1997	1.432 0.892 3.270	1.864
Mullins	July-August, 1996 September, 1996 November, 1996 March, 1997 April, 1997 May, 1997	0.636 1.660 0.772 5.216 1.427 1.984	1.949

**Table 10:**  $Q_M$  to  $Q_{SGD}$  ratios as calculated per run and averaged for each site. Mean ratio across all sites is 1.929.

#### 7.0 REFERENCES

Allard, P. Aug., 1993. Changes in coral community structure in Barbados: effects of eutrophication and reduced grazing pressure. M.Sc. Thesis, McGill University, Montreal, Quebec, Canada. 50 pp.

Axelrad, D.M.; G.C.B. Poore; G.H. Arnott; J. Bauld; V. Brown; R.R.C. Edwards; & N.J. Hickman. "The effects of treated sewerage discharge on the biota of Port Phillip Bay, Victoria, Australia. "*In* <u>Estuaries and Nutrients</u>. B.J. Nielson & L.E. Cronin (eds.), Humana Press, Clifton, N.J., 1981.

Bellairs Research Institute for Stanley International and the Government of Barbados. February, 1997. Environmental deterioration and water quality at fringing reefs on the west coast of Barbados. 27pp.

Bokuniewicz, H. 1980. Groundwater seepage into Great South Bay, New York. Estuarine and Coastal Marine Science 10, 437 -444.

Bowman, M.J.; K.L. Stansfield; S.J. Fauria; & T.C. Wilson. 1994. Coastal ocean circulation near Barbados, West Indies, Spring 1990 and 1991. J. Geophys. Res. 99(C8), 16,131 - 16,142.

Cabana, G. 1996. Comparison of aquatic food chains using nitrogen stable isotopes. Ph.D. Thesis, McGill University, Montreal, Quebec.

Capone, D.G. & M.F. Bautista. 1985. A groundwater source of nitrate in nearshore marine sediments. Nature 313, 214 -216.

Delcan International Corporation. 1994. Nearshore marine water quality of the west and southern coasts of Barbados: present status and management recommendations. Technical Report for the Inter-American Development Bank (Washington, D.C.) and the Government of Barbados. 116 pp.

D'Elia, C.F.; K.L. Webb & J.W. Porter. 1981. Nitrate-rich groundwater inputs to Discovery Bay, Jamaica: a significant source of N to local reefs? Bulletin of Marine Science 31(4), 903 - 910.

D'Elia, C. & W.J. Wiebe. "Biogeochemical nutrient cycles in coral reef ecosystems". In <u>Ecosystems of the World 25: Coral Reefs.</u> Z. Dubinsky (ed.) Elsevier Science Publishers, 1990.

Faruqui, N.; K. Fries; J. Herbert; & B. Humphrey. June 1995. Protecting island treasures. Water Environment and Technology, p 58-63.

Hagedorn, C.; E.L. McCoy; & T.M. Rahe. 1981. The potential for groundwater contamination from septic effluents. J. Environ. Qual. 10(1), 1 - 8.

Harries, K.J. "Relationships between nitrates in groundwater/marine waters and coral reef communities on the west and south-west coasts of Barbados". Discussion paper for

Sir William Halcrow & Partners Ltd., April 1997.

Harris, W.H. 1971. Groundwater-carbonate rock chemical interactions, Barbados, W.I. Ph.D. thesis, Brown University. 384 p.

Johannes, R.E. 1980. The ecological significance of submarine discharge of groundwater. Mar. Ecol. Prog. Ser. 3, 365 -373.

Kinsey, D.W. & P.J. Davies. 1979. Effects of elevated nitrogen and phosphorous on coral reef growth. Limnol. Oceanogr. 24(5), 935 -940.

Lee, V. & S. Olsen. 1985. Eutrophication and management inititatives for the control of nutrient inputs to Rhode Island coastal lagoons. Estuaries 8(2B), 191 - 202.

Lewis, J.B. 1977. Processes of organic Production on Coral Reefs. Biol. Rev. 52: 305 - 347.

Lewis, J. B. 1987. Measurements of groundwater seepage flux onto a coral reef: spatial and temporal variations. Limnol. Oceanogr. 32(5), 1165 - 1169.

Marine Environmental Impact Study of the Barbados Light & Power Cooling Water Discharge at Spring Garden. Prepared by Bellairs Research Institute of McGill. 100pp.

Matson, E. A. 1993. Nutrient flux through soils and aquifers to the coastal zone of Guam (Mariana Islands). Limnol. Oceanogr. 38(2), 361 - 371.

Millham, N.P. & B.L. Howes. 1994. Nutrient balance of a shallow coastal embayment: I. Patterns of groundwater discharge. Mar. Ecol. Prog. Ser. 112, 155 - 167.

Parsons, T.R.; Y. Maita; C.M. Lalli. <u>A Manual of Chemical and Biological Methods for</u> <u>Seawater Analysis</u>. Permagon Press, New York, 1972.

Pejrup, M.; J. Bartholdy; & A. Jensen. 1993. Supply and exchange of water and nutrients in the Grådyb tidal area, Denmark. Estuarine, Coastal and Shelf Science 36, 221 -234.

Rasmussen, J.B. 1994. A review of the Delcan terrestrial water quality report, unpublished.

Sewell, P.L. 1982. Urban groundwater as a possible nutrient source for an estuarine benthic algal bloom. Estuarine, Coastal and Shelf science 15, 569 -576.

Simmons, J.A.K. & W.B. Lyons. 1994. The groundwater flux of nitrogen and phosphorous to Bermuda's coastal waters. Water Resources Bulletin 30(6), 983 - 991.

Standard methods for the Examination of Water and Wastewater. Washington, D.C. 1992.

Stansfield, K.L.; M.J. Bowman; S.J. Fauria & T.C. Wilson. 1995. Water mass and coastal current variability near Barbados, West Indies. J. Geophys. Res. 100 (C12),

24,819 - 244,830.

Tomascik, T & F. Sander. 1987. Effects of eutrophication on reef-building corals, II. Structure of scleractinian coral communities on fringing reefs, Barbados, W.I. Mar. Biol. 94, 53 - 75.

Tomasik, T. & F. Sander. 1987. Effects of eutrophication on reef-building corals, III. Reproduction of the reef-building coral *Porites porites*. Mar. Biol. 94, 77 -94.

Valiela, I.; J.M. Teal; S. Volkmann; D. Shafer & E.J. Carpenter. 1978. Nutrient and particulate fluxes in a salt marsh ecosystem: tidal exchanges and inputs by precipitation and groundwater. Limnol. Oceanogr. 23(4), 798 - 812.

Walker, W.G.; J. Bouma; D.R. Keeney & P.G. Olcott. 1973. Nitrogen transformations during subsurface disposal of septic tank effluent in sands, II. Groundwater quality. J. Environ. Qual. 2, 521 - 525.

Weiskel, P.K. & B.L. Howes. 1992. Differential transport of sewage-derived nitrogen and phosphorous through a coastal watershed. Environ. Sci. Technol. 26, 352 -360.

Weiskel, P.K. & B.L. Howe, 1991. Quantifying dissolved N flux through a coastal watershed. Water Resources Research 27 (11), 2929-2939.