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GEOCHEMICAL EVOLUTION OF GROUNDWATER IN THE PLEISTOCENE LIMESTONE AQUIFER OF BARBADOS

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GEOCHEMICAL EVOLUTION OF GROUNDWATER IN THE PLEISTOCENE LIMESTONE AQUIFER OF BARBADOS

by

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GEOCHEMICAL EVOLUTION OF GROUNDWATER IN THE PLEISTOCENE LIMESTONE AQUIFER OF BARBADOS

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This investigation is a comprehensive study of the hydrology and hydrogeochemistry of the Pleistocene limestone aquifer of Barbados, a tropical karst island aquifer. The purpose of this research is to investigate how groundwater compositions in a tropical karst aquifer vary spatially and temporally, and determine the factors or processes responsible for these variations. These questions are addressed by evaluating spatial and temporal variation of groundwater major and trace element and isotopic compositions, and thus determining relationships between groundwater composition variations and various hydrologic and geochemical factors. These factors include: recharge processes, groundwater flow paths, soil compositions, aquifer and aquitard rock compositions, and

anthropogenic inputs. This research provides insight into natural processes that influence groundwater compositions, allowing us to: 1) better understand geochemical processes taking place in an aquifer; 2) use groundwater constituents as tracers to determine seasonal and interannual variation of recharge and to estimate recharge amounts; and 3) establish relative importance of land use and recharge processes in the susceptibility of a karst aquifer to contamination.

Key results of this study include: 1) development of a method of determining the spatial and seasonal distribution of recharge, and determine interannual variations of recharge using oxygen isotopes; 2) determination that recharge has a greater influence on susceptibility of a karst aquifer to contamination than land use; and 3) spatial ad temporal variations of groundwater major and trace element and isotopic compositions reflect and respond independently to diverse processes, for example, seawater mixing and variations of the aquifer and aquitard rock compositions encountered along flow paths.

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CHAPTER 1: THE STUDY OF GROUNDWATER IN THE PLEISTOCENE LIMESTONE AQUIFER OF BARBADOS

INTRODUCTION

Groundwater major and trace element and isotopic compositions are the products of multiple geochemical processes taking place during infiltration and along flow paths. These factors or processes include: rainwater, soil and aquifer and aquitard rock compositions, groundwater flow paths, sea water mixing, and anthropogenic inputs. In low-temperature settings, groundwater constituents, such as oxygen isotopes, reflect the composition of the initial rainwater. Mixing of fresh groundwater with sea water in coastal areas plays a role in determining groundwater major element compositions. Other groundwater constituents are derived from interaction between vadose water or groundwater and the surrounding rock and reflect the different rock compositions that the water encounters along different flow paths. Inputs from anthropogenic sources contributing to groundwater, such as fertilizers in agricultural areas, and sewage or different industrial wastes in urban areas, are related to land use. This study also investigates how groundwater compositions can be applied to investigations of the groundwater hydrology. This can be achieved because some groundwater constituents, for example, nitrate and oxygen and carbon isotopes, are influenced by hydrologic processes such as recharge.

This research is a study of groundwater hydrology and geochemistry in the Pleistocene limestone aquifer of Barbados. The aim of this study is to investigate the impact of hydrological and geochemical factors on groundwater major and trace element and isotopic compositions. These factors include recharge processes, groundwater flow paths, soil compositions, aquifer and aquitard rock compositions, groundwater mixing and anthropogenic inputs.

The purpose of this research is to address the following questions: 1) how do seasonal and interannual climate variations, land use, and recharge processes influence groundwater compositions; 2) what geochemical process or processes influence groundwater compositions observed in limestone aquifers; 3) how do groundwater compositions vary spatially and temporally, and what factors or processes are responsible for these variations? These questions are addressed by: 1) evaluating spatial and temporal variation of groundwater major and trace element and isotopic compositions; and 2) investigating the relationships between these groundwater composition variations and the factors listed above. Addressing these questions is important because they provide insight into the natural processes that influence groundwater compositions. This allows us to: 1) better understand geochemical processes taking place in an aquifer and thus distinguish between natural and anthropogenic groundwater constituents; 2) use groundwater constituents as tracers to determine the seasonal and interannual variation of recharge and to estimate recharge amounts; and 3) establish the relative importance of land use and recharge processes in determining the susceptibility of a karst aquifer to contamination.

Barbados is well suited for the study of the relationship between oxygen isotopes in groundwater and rainwater because of its relatively low relief (~350 m) and tropical climate characterized by a small mean annual temperature range (2-3 °C). Barbados also has a relatively small land-mass (~430 km^2), a well characterized hydrogeology and hydrogeochemistry (Senn, 1946; Harris, 1971) and relatively long records of rainwater oxygen isotope (1961-1992) and rainfall data (IAEA/WMO, 1998). The small size, low relief, and tropical climate allow us to constrain the factors that influence spatial and seasonal variations of rainwater and groundwater oxygen isotopic compositions. Additionally, short groundwater residence-times of up to a few years make it unlikely that any differences between groundwater and rainwater compositions are due to climate changes that took place after recharge.

PREVIOUS WORK

Early research on limestone aquifer of Barbados was conducted by Senn (1946) and Tullstrom (1964). These studies documented the hydrostratigraphy of Barbados, determining that the Pleistocene-Tertiary contact is the base of the aquifer. These early hydrogeological studies also delineated the groundwater catchments and hydrologic zones in the aquifer. Comprehensive studies of groundwater on Barbados were conducted by Stanley Associates Engineering Ltd. (1978a and 1978b), Proctor and Redfern Int. Ltd. (1983) and DELCAN (1995). These studies investigated water resources, water quality, public health, and socioeconomic aspects of groundwater management on Barbados.

The study of the geochemistry of Barbados groundwater includes investigations by Harris (1971) and Banner et al. (1994) that studied the major and trace element and isotopic compositions of Barbados groundwater with the aim of analyzing fluid-rock interactions. Other studies of Barbados groundwater geochemistry, such as Lewis (1987), Barbados Ministry of Health and others (1991), and Klohn-Crippen Consultants Ltd. (1997) focus on anthropogenic impacts on Barbados groundwater that include nitrate inputs to the aquifer.

Steinen and others (1978) reported the response of the freshwater lens on Barbados to recharge associated with a tropical storm. Investigations of the spatial distribution of karst features, sinkholes and dry valleys, which potentially influence recharge to the limestone aquifer on Barbados, were conducted by Day (1983) and Fermor (1972). These studies are complemented by a dye-tracer study by Mwansa and Barker (1996) and an infiltration test by Smart and Ketterling (1997). These studies indicate that: 1) infiltration rates through the limestone are very high (up to 70,000 mm h^{-1}); and 2) residence times of infiltrating water in the vadose zone can be as short as a few hours. The Global Network of Isotopes in Precipitation

(GNIP) operated by IAEA/WMO (1998) collected the rainwater isotopic data on Barbados (1959-1992) used in this investigation to study recharge to the aquifer.

ORGANIZATION

This dissertation is composed of four separate but related papers covering different aspects of groundwater hydrology and geochemistry on Barbados. In the first paper, groundwater and rainwater oxygen isotopes are used to estimate the spatial and seasonal distribution of recharge on Barbados. The second paper expands on the first by investigating: 1) the hydrology of the Pleistocene limestone aquifer; 2) interannual variations of recharge; and 3) applying some of the findings to other tropical limestone aquifers of northern Puerto Rico and Guam. The third paper is a study of nitrogen fluxes that was conducted to estimate fertilizer inputs to the aquifer and infer the spatial distribution of the nitrogen influxes. The fourth paper investigates the processes contributing to the major and trace element and isotopic compositions of Barbados groundwater.

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CHAPTER 2: ESTIMATING RECHARGE IN A TROPICAL KARST AQUIFER

ABSTRACT

Unique constraints on seasonal and spatial variations in recharge to the Pleistocene limestone aquifer of Barbados are obtained from the analysis of oxygen isotopic compositions of groundwater and rainwater. Conventional methods of estimating recharge are based on groundwater chloride variations, coastal groundwater discharge, and potential evapotranspiration. These methods typically yield estimates of recharge for Barbados that range from 9% to 20% of average annual rainfall, with significant uncertainties that arise from poorly constrained model input parameters.

Due to the low relief and tropical climate of Barbados, variations in rainwater and groundwater $\delta^{18}O$ values are primarily influenced by the amount of rainfall, with negligible temperature or altitude effects. Composite monthly rainwater $\delta^{18}O$ values are inversely related to rainfall amount while groundwater $\delta^{18}O$ values show little seasonal variability. Rainwater $\delta^{18}O$ values are equivalent to groundwater values only at the peak of the wet season. By mass-balance, the difference between groundwater and weighted mean rainwater $\delta^{18}O$ values gives recharge values. These values are in general agreement with estimates by conventional methods (10-20%), and provide unique additional information

including: 1) recharge is restricted to the wettest 1-3 months of the year; and 2) there is less recharge at higher elevations. The effective shift in $\delta^{18}O$ values between contemporaneous rainwater and groundwater via recharge is a useful tool for estimating temporal and spatial variability in recharge, and must be considered in paleoclimatic studies where climate inferences are based on groundwater $\delta^{18}O$ values preserved in the geologic record.

INTRODUCTION

Determining the amount of recharge to an aquifer is a means of constraining its groundwater budget. This aids in estimating groundwater residence times within, and groundwater- and mass-fluxes through the aquifer. Effective groundwater resource management requires knowledge of when and where recharge takes place because land utilization may impact recharge pathways and thus, influence the quality and quantity of groundwater in the aquifer. For example, the construction of drainage wells on Barbados has potentially increased recharge to the aquifer by creating pathways for rapid discrete infiltration to the water table, bypassing diffuse infiltration through the soil. Diffuse infiltration will potentially result in greater losses to evapotranspiration (ET) and more effective removal of potential pollutants than discrete infiltration through karstic or man-made shafts. This research is part of a larger study of groundwater hydrology and geochemistry in the Pleistocene limestone aquifer of Barbados (Banner et al., 1996;

Jones et al., 1998). Estimation of groundwater fluxes through an aquifer together with groundwater geochemical data can allow greater understanding of the impacts of different geochemical processes on groundwater composition.

Comparison of the geochemical constituents of rainwater and groundwater can be used as a tool to estimate recharge by assuming conservative behavior of selected constituents. Oxygen isotopic compositions and dissolved chloride can be used as conservative tracers in order to estimate recharge if they can be demonstrated to be unaffected by interaction between groundwater and aquifer rock or soil.

Barbados is well suited for the study of the relationship between oxygen isotopes in groundwater and rainwater because of its relatively low relief (~350 m) and tropical climate characterized by a small mean annual temperature range (2-3 °C). Barbados also has a relatively small land-mass (~430 km^2), a well characterized hydrogeology and hydrogeochemistry (Senn, 1946; Harris, 1971) and relatively long records of rainwater oxygen isotope (1961-1992) and rainfall data (IAEA/WMO, 1998). The small size, low relief, and tropical climate allow us to constrain the factors that influence spatial and seasonal variations of rainwater and groundwater oxygen isotopic compositions. Additionally, short groundwater residence-times of up to a few years make it unlikely that any differences between groundwater and rainwater compositions are due to climate changes that took place after recharge.

Recharge is typically estimated based on water-balance, and groundwater and rainwater chloride concentrations (Stanley Associates, 1978; Vacher and Ayers, 1980). Oxygen isotopes in groundwater are typically used as tracers to indicate: 1) the elevation at which recharge takes place (Ellins, 1992; Musgrove and Banner, 1993; Scholl et al., 1996); 2) the occurrence of seasonal recharge (Saxena, 1984; Ingraham et al., 1991); 3) modern versus paleo-recharge (Smith et al., 1992; Dutton, 1995); and 4) the relative contribution of recharge waters from different sources, e.g., surface water and inter-aquifer flow (Muir and Coplen, 1981; Guglielmi and Mudry, 1996).

This study uses oxygen isotope and rainfall data to estimate the amount of recharge to the Pleistocene limestone aquifer on Barbados. Using these estimates, we identify and quantify the temporal and spatial distribution of recharge to this karst aquifer. The use of oxygen isotopes in this way is potentially a new tool that can be used to determine groundwater availability in tropical island aquifers.

STUDY AREA

The Pleistocene limestone aquifer of Barbados is composed of Pleistocene-age coral reef limestones and is underlain by Tertiary-age deep-sea sediments that act as an aquitard (Fig. 2-1). Due to continuous uplift, the reef limestone was deposited outwards from the center of the island forming a series of terraces that decrease in age with decreasing elevation. There are three main terraces separated by the First and Second High Cliffs, respectively (Fig. 2-1).

The aquifer is highly permeable with high primary and secondary porosity averaging 44-50% (Tullstrom, 1964). Recharge to the aquifer occurs by diffuse and discrete infiltration to the water table that occurs close to the base of the Pleistocene limestone (Fig. 2-2). Groundwater generally flows from the elevated central portion of the island outward towards the coast following the contours of the top of the aquitard (Fig. 2-2). The aquifer is divided into two hydrogeologic zones, the upland portion of the aquifer characterized by diffuse and conduit flow along the base of the Pleistocene limestone and the freshwater lens that occurs in low-lying parts of the island. Discharge from the aquifer primarily takes the form of groundwater discharge along the coast.

Annual rainfall is greatest at the center of the island but does not coincide with the highest elevations. Dry season rainfall (January – May) is associated with local convection due to moist air flowing over the heated island (Malkus, 1963). During the wet season, in addition to local convection effects, rainfall is associated with tropical weather systems such as tropical waves and tropical storms, and the proximity of the Inter-Tropical Convergence Zone (ITCZ) (Falkland, 1991; Reading et al., 1995).

SAMPLING AND ANALYTICAL PROCEDURES

Groundwater samples were obtained primarily from 29 wells located within groundwater catchments in northwestern and southeastern Barbados (Fig. 2-2). Additional water samples were obtained from a spring and cave drips (Fig. 2-2).

Monthly composite rainwater $\delta^{18}O$ and δD data were collected between 1961 and 1992 at the international airport on Barbados as part of the Global Network of Isotopes in Precipitation (GNIP) project (IAEA/WMO, 1998). Rainwater samples were collected for this study during 1997 to increase the available rainwater isotopic data and to address the question of whether deviation of enriched rainwater from the Global Meteoric Water Line (GMWL) was due to atmospheric evaporation or evaporation in the rainwater collection apparatus. Unlike the GNIP rainwater samples that represent monthly rainfall, these new rainwater data are composite samples from rainfall over periods of 1-7 days and in some cases represent single rainfall events (Table 2-1). Rainwater sampling procedures were designed to avoid evaporation. This was achieved by 1) removing samples from the rainwater collector as soon as possible after rainfall, and 2) storing rainwater samples in air-tight bottles. The rainwater sampling procedure is similar to that used by GNIP except that the rainwater composite samples represent shorter time periods and therefore potentially provide greater resolution, and the rainwater is transferred directly from the rainwater collection apparatus to 20- or 40-ml glass bottles with rubber seals. These are further sealed with Parafilm™ and kept refrigerated until analysis. The results of both methods of rainfall collection are in good agreement (Fig. 2-3b).

Groundwater and rainwater samples were analyzed for their oxygen isotopic compositions at the Colorado School of Mines by a modification of the CO_2 equilibration technique (Epstein and Mayeda, 1953) as described in Socki et al. (1992). Analytical precision, based on analyses of laboratory standards and duplicate samples is ±0.15‰. The hydrogen isotope compositions of the 1997 rainwater samples were determined at Southern Methodist University using a method similar to Bigeleisen et al. (1952). Analytical precision based on standard runs is ±1.4‰.

CONVENTIONAL METHODS OF ESTIMATING RECHARGE

Recharge estimates have previously been made by: 1) hydrologic measurements, such as potential evapotranspiration (PET) or groundwater discharge; 2) indirect methods based on dissolved constituents in both groundwater and rainwater; and 3) groundwater modeling. Accurate determination of recharge based on groundwater models is difficult to achieve because it requires accurate determination of the spatial distribution of input parameters, such as porosity and permeability, to ensure a unique solution. The use of tritium and helium isotopes to estimate recharge (Solomon et al., 1993) is not applicable to Barbados where groundwater flow is not vertical and travel-times are much less than 40 years.

Comparison of mean monthly rainfall and PET data for Barbados from Food and Agriculture Organization (1985) suggests that the potential for recharge only exists when rainfall exceeds PET (Fig. 2-3a). Recharge to an aquifer can also be estimated based on groundwater discharge measurements, assuming steady-state conditions. This is probably a valid assumption in an aquifer where water-level fluctuations are small. Other assumptions used are: 1) all discharge occurs along the coast; 2) recharge is equal to coastal discharge; 3) runoff and net groundwater withdrawal are negligible; and 4) ET accounts for the difference between rainfall and coastal discharge. Using mass-balance, recharge in specific catchments can be estimated by:

$$R = (100 \times Q)/(P \times A) \qquad (2\text{-}1)$$

where:

R = Recharge expressed as a percentage of the volume of rainfall in the catchment;

Q = Average coastal discharge ($m^3\ yr^{-1}$) (From Proctor and Redfern, 1983; and Lewis, 1987);

P = Average annual rainfall in the catchment (m yr^{-1}) (Based on 1992 rainfall data from the Caribbean Meteorological Institute); and

A = Catchment area (m^2).

Comparison of chloride concentrations in rainwater and groundwater can be used to estimate recharge (Vacher and Ayers, 1980). This method assumes that: 1) chloride is conservative; 2) runoff is minimal; 3) ET is responsible for the difference between chloride concentrations in rainwater and groundwater; 4) rainwater is the only source of chloride in the groundwater; and 5) there is no net annual accumulation or depletion of chloride in the soil. The rationale behind this method is that chloride will accumulate in the soil as a result of ET during periods of little or no recharge. The accumulated chloride is then flushed from the soil by infiltrating water during recharge periods. The rainwater chloride concentration used in this method (5.8 mg l^{-1}) is the weighted-average concentration based on 46 rainwater samples collected at Site A and thus takes into account seasonal fluctuations in rainwater composition (Figs. 2-1, 2-4). Recharge can be estimated using the following equation.

$$R = 100 \times C_{Cl_{rainwater}} / C_{Cl_{groundwater}} \qquad (2\text{-}2)$$

where:

R = Recharge (percentage of annual rainfall); and

C_{Cl} = Chloride concentration (mg l^{-1}).

OXYGEN ISOTOPE METHOD OF ESTIMATING RECHARGE

Recharge can be estimated using oxygen isotopic compositions of groundwater and rainwater and associated rainfall data. It is assumed that the groundwater oxygen isotopic composition is the weighted-average of rainwater that actually infiltrates to the water table. The rainwater oxygen isotopic data from the entire GNIP Barbados database (Fig. 2-5a) is used to determine monthly weighted average rainwater $\delta^{18}O$ values over the period of record. These monthly values are used to determine those months that when combined are equivalent to the groundwater $\delta^{18}O$ value, thereby satisfying the above assumption. This is done using the following equation:

$$[\Sigma_n (\delta^{18}O_{rainwater} \times P_{month})] / \Sigma_n P_{month} = \delta^{18}O_{groundwater} \qquad (2\text{-}3)$$

where:

n = Number of individual months taken from the entire 1961-1992 database used in weighted-average;

$\delta^{18}O_{groundwater}$ = Oxygen isotopic composition of groundwater (measured in this study);

$\delta^{18}O_{rainwater}$ = Composite oxygen isotopic composition of rainwater for month n (i.e., individual GNIP analyses); and

P_{month} = Monthly rainfall for month n, (mm).

In Equation 2-3, the term on the left represents the weighted average $\delta^{18}O$ value of the rainwater that contributes to recharge. This equation will not be balanced if all of the GNIP rainwater data are used because Barbados groundwater $\delta^{18}O$ values are not equal to the weighted average rainwater composition (Fig. 2-6b). Therefore, in order for Equation 2-3 to balance, rainwater data associated with months with the least rainfall are removed from the term on the left because they contribute least, if at all, to recharge.

Estimating recharge based on oxygen isotopes is a two-step process. First, Equation 2-3 determines the months that together produce a weighted-average rainwater $\delta^{18}O$ value that is equivalent to the groundwater composition. Because the average groundwater $\delta^{18}O$ value is lower than the weighted average monthly rainwater $\delta^{18}O$ value, months with below average $\delta^{18}O$ values are those that satisfy Equation 2-3 (Fig. 2-6). Second, the rainfall amounts for those months used to balance Equation 2-3 are averaged to determine the amount of annual rainfall that actually contributes to recharge. This method can be applied to estimate: (1) inter-annual variations of recharge; or (2) spatial variations of recharge. For application (1), the average groundwater $\delta^{18}O$ value for the island ($\delta^{18}O$ = -3.0‰; Fig. 2-6) is used in Equation 2-3, and it is assumed that there is a threshold amount of rainfall that must be exceeded before recharge takes place. Application (2) uses local groundwater $\delta^{18}O$ values in Equation 2-3 in order to determine spatial variations in recharge.

ANALYTICAL RESULTS

Barbados Rainwater Compositions

Oxygen and hydrogen isotopic compositions of Barbados rainwater mostly lie along the GMWL (Fig. 2-6a; Table 2-1; Craig, 1961; IAEA/WMO, 1998). The GNIP rainwater isotopic data (1961-1992) and rainwater isotopic data collected during 1997 coincide with each other, although the larger GNIP database (n = 244) exhibits a larger range of compositions than the 1997 data (n = 11; Table 2-1). The deviation of the highest rainwater $\delta^{18}O$ values from the GMWL can be attributed to atmospheric-evaporative effects during the dry season. This pattern has also been observed in rainwater data from other stations in the Caribbean region such as Barranquilla, Colombia; Veracruz, Mexico; and Belem, Brazil (IAEA/WMO, 1998).

Barbados Groundwater Compositions

The $\delta^{18}O$ values of Barbados groundwater and vadose zone water lie within a narrow range compared to those of rainwater (Fig. 2-6b). There is no apparent relationship between Barbados groundwater $\delta^{18}O$ values and land surface elevation, although there is a tendency for groundwater at lower elevations to have higher $\delta^{18}O$ values. The narrow range of groundwater $\delta^{18}O$ values suggests a limited recharge period and little evaporation of infiltrating water prior to recharge. Consequently, it is assumed in this investigation that the effect of evaporation on the rainwater that actually reaches the aquifer during recharge months is very small.

There is potential for groundwater $\delta^{18}O$ values to be altered by water-rock interaction with the surrounding limestone. Modeling of strontium isotope variations indicates that the degree of water-rock interaction experienced by Barbados groundwater is less than 17 mmol aragonite l^{-1} (Banner et al., 1994). This degree of water-rock interaction would produce an insignificant shift (<0.001‰) in the oxygen isotopic composition of the groundwater (Table 2-2).

RECHARGE ESTIMATION RESULTS

Conventional Recharge Estimates

Annual recharge, the difference between monthly rainfall and PET, is approximately 6% of average annual rainfall on Barbados. This recharge estimate also indicates that recharge on Barbados is most likely to occur during September, October and November (Fig. 2-3a). Water-balance recharge estimates based on coastal discharge data from Proctor and Redfern (1983) and Lewis (1987) and water-balance calculations by Stanley Associates (1978) and DELCAN (1995) for the same groundwater catchments vary dramatically in some cases (Table 2-3). On the west coast of Barbados, water-balance recharge estimates lie within the range 6-25% of average annual rainfall, with an average of 14%. Recharge estimates based on chloride concentrations on Barbados vary from 1% to 20% of annual rainfall and increase with elevation (Eq. 2; Fig. 2-7).

Oxygen Isotope Recharge Estimates

Inter-annual Variations in Recharge

Equation 2-3 establishes a relationship between groundwater and rainwater $\delta^{18}O$ values and the rainfall amounts involved in recharge. This equation indicates that the average groundwater $\delta^{18}O$ value is equal to the weighted-average $\delta^{18}O$ value of rainwater when P_{month} >195 mm.

Average recharge on Barbados during a specific year may be estimated using the rainfall data for that year in the following equation where recharge is the ratio of the sum of rainfall occurring during months with more than 195 mm of rainfall to average annual rainfall.

$$R_{year} = 100 \times [\Sigma_n(P_{month} - AET_{month})] / P_{total} \qquad (2\text{-}4)$$

where:

R_{year} = Recharge expressed as a percent of average annual rainfall;

P_{month} = Monthly rainfall for month n (mm);

n = Months of the year when P_{month} >195 mm;

AET_{month} = Actual evapotranspiration for month n (mm); and

P_{total} = Average annual rainfall (mm).

Equation 2-4 assumes that the average Barbados groundwater $\delta^{18}O$ value remains constant over time and that AET_{month} is small. On Barbados, runoff is short-lived and surface water discharge to the sea accounts for <1% of the water budget (Stanley Associates, 1978; DELCAN, 1995) Consequently, losses due to surface runoff during heavy rainfall are probably small.

Using Equation 2-4, overall recharge on Barbados was estimated for each year from 1972 to 1997. Estimated recharge varies from 0 to 69% of average annual rainfall (1,500 mm), generally increasing with annual rainfall. This range of recharge estimates reflects inter-annual variations of rainfall that over the past 40 years has ranged from 700 mm yr^{-1} to 1,800 mm yr^{-1} at Site B.

Spatial Variations in Recharge

Recharge estimates at specific locations within groundwater catchments are based on local groundwater $\delta^{18}O$ values and selected rainwater oxygen isotopic data used in Equation 2-3. Equation 2-5 uses the P_{month} values from Equation 2-3 to estimate the average annual recharge at specific locations.

$$R_{site} = 100 \times [(\Sigma_n (P_{month} - AET_{month}) / n] / P_{total} \qquad (2\text{-}5)$$

where:

R_{site} = Recharge at a groundwater sample site;

P_{month} = Rainfall for months n included in Equation 2-3; and

n = Number of data points used in Equation 2-3.

From Equation 2-5, estimated recharge at most locations was 15-25% of average annual rainfall, although at a few locations recharge apparently exceeds 30%. These recharge estimates reflect a period of average rainfall on Barbados. One would expect higher recharge estimates associated with extremely wet years. There is no apparent relationship between either estimated recharge or groundwater $\delta^{18}O$ values, and annual rainfall at the sample site extrapolated from adjacent rainfall stations. Recharge estimates are 15-20% of average annual rainfall at elevations above 100 m and apparently increase to as much as 45% at lower elevations (Fig. 2-7). This increase in estimated recharge coincides with the location of the Second High Cliff (Fig. 2-1).

Uncertainties in Recharge Estimates

Uncertainties associated with recharge estimates based on Eqs. 2-4 and 2-5 can be attributed to factors, such as AET and surface water discharge to the sea, that potentially affect recharge amounts. Surface water discharge accounts for a very small proportion of the total water budget for Barbados and thus introduces an uncertainty of < 1%. Losses due to AET are difficult to quantify based on available data and it is impossible to quantify uncertainties associated with AET. However, as discussed above it is expected that AET and associated uncertainties are small. In the absence of AET data, recharge estimates based on oxygen isotopes should be considered to maximum estimates.

DISCUSSION

Controls on Rainwater Oxygen Isotope Variations

There is an inverse relationship between $\delta^{18}O$ values of rainwater and the amount of rainfall on tropical islands but unlike temperate climates, there is no apparent relationship with temperature (Dansgaard, 1964; Rozanski et al., 1993; Rozanski and Araguás, 1995). This difference in behavior can be attributed to the small seasonal temperature fluctuations that occur in tropical climates compared to much larger temperature ranges characteristic of temperate climates. The amount effect is a consequence of the extent of the rain-out process of deep convective clouds (Rozanski et al., 1993).

The amount effect is most apparent where seasonal variation of humidity and temperature is minimal, the isotopic composition of water vapor is constant, and there is minimal evaporation of raindrops (Yapp, 1982). This occurs because the other isotope effects (temperature, source water, etc.) are subdued. These three conditions usually occur in tropical marine environments. On Barbados, the effects of evaporation on raindrop $\delta^{18}O$ values is apparent during the dry season and thus weakens any linear correlation that may exist between rainfall amounts and rainwater $\delta^{18}O$ values (Figs. 2-5a; 2-6). The influence of altitude and continental effects on rainwater isotopic compositions is negligible on small islands like Barbados due to their low altitudes (i.e., ~-0.2‰ per 100 m) and small land masses (Gonfiantini, 1985; Rozanski et al., 1993). Consequently, the amount effect is the predominant control on seasonal changes in rainwater composition. The amount effect on Barbados is -2.2‰ to -2.7‰ per 100 mm of monthly rainfall (Dansgaard, 1964; Fig. 2-5b).

The range of Barbados rainwater $\delta^{18}O$ values is related to seasonal compositional fluctuations with higher values associated with dry season rainfall (January to May) and lower values associated with wet season rainfall (June to December) due to the amount effect (Fig. 2-3b). This occurs because rainwater associated with heavy rainfall has lower $\delta^{18}O$ values than rainwater from small rainfall events (Figs. 2-3b; 2-5b). These seasonal fluctuations in rainwater isotopic compositions are a reflection of the different mechanisms responsible for rainfall during the wet and dry seasons. During the wet season, the Inter-Tropical Convergence Zone (ITCZ) is located approximately 8ºN of the Equator, relatively close to Barbados (approximately 13ºN). The proximity of the ITCZ results in increased rainfall and consequently in rainwater with lower $\delta^{18}O$ values due to the amount effect (Rozanski and Araguás, 1995). During the dry season, the ITCZ is located south of the Equator and consequently contributes little to Barbados rainfall.

The Relationship Between Groundwater and Rainwater Oxygen Isotopic Compositions

Research conducted in Israel and Brazil indicate that compositional differences between groundwater and rainwater usually result from: 1) evaporation prior to recharge while the water is on or near land surface; and/or 2) recharge associated with intense rainfall (Levin et al., 1974; Gat, 1987). Gat (1987) showed that groundwater $\delta^{18}O$ values associated with recharge of local runoff has higher $\delta^{18}O$ values than the average rainwater composition while groundwater associated with heavy floods has lower $\delta^{18}O$ values. In both cases, the groundwater deviated from the Meteoric Water Line (MWL) due to evaporation. On Barbados, the relationship between groundwater and rainwater $\delta^{18}O$ values is somewhat similar to the second case, but without the apparent evaporation. This suggests that differences in the average compositions of groundwater and rainwater on Barbados occur because during some periods of the year evaporation is so effective that essentially no rainwater infiltrates to the water table. The result is that rainwater that falls during non-recharge periods will be included in the weighted-average rainwater composition but not in the average groundwater composition. Similar relationships between rainwater and groundwater $\delta^{18}O$ values have been observed on St. Croix and Grand Cayman (Gill, 1994; Jones et al., 1997).

It is unlikely that surface elevation has much of an effect on the $\delta^{18}O$ of rainwater on Barbados because the highest point on the island is approximately 350 m. Different studies of the altitude effect in tropical climates indicate that the $\delta^{18}O$ value of rainwater shifts by approximately -0.2‰ per 100 m (Fontes and Olivry, 1977; Scholl et al., 1996). This would result in a range of groundwater $\delta^{18}O$ values of 0.7‰, which is much smaller than both the range of rainwater (15‰) and groundwater compositions (2.3‰). This suggests that any elevation effect on Barbados would be small compared to the amount effect (Table 2-2).

Factors Affecting Infiltration

The narrow range of groundwater $\delta^{18}O$ values and their position relative to the GMWL indicates negligible evaporation prior to recharge. This suggests that actual recharge takes place by very rapid infiltration that does not allow time for ET to have a major impact on groundwater $\delta^{18}O$ values. It can therefore be concluded that recharge takes place where conditions facilitate rapid infiltration of water through or past the soil zone. These conditions occur where soils are highly permeable or within karst features where water infiltrates directly into the highly permeable limestone and bypasses lower permeability soils.

Variations in soil permeability with elevation may play a role in recharge. The soils that occur above the Second High Cliff have infiltration rates of approximately 250 mm h^{-1} (Tullstrom, 1964). Below the Second High Cliff, at elevations less than 100 m, infiltration rates through the soils range from 12.5 mm h^{-1} to 250 mm h^{-1}, but typically are approximately 50 mm h^{-1} (Tullstrom, 1964). The Pleistocene limestone is much more permeable than the overlying soils with measured infiltration rates of 700-70,000 mm h^{-1} (Tullstrom, 1964; Smart and Ketterling, 1997).

Recharge can potentially take place by diffuse infiltration through the soil or by discrete infiltration through drainage wells, dry valleys and some sinkholes (Fig. 2-8). Diffuse recharge is most likely to occur where soil infiltration rates are highest, such as, above the Second High Cliff. Pleistocene limestone is frequently exposed at the surface in dry valleys, especially where these valleys cut through the Second High Cliff forming deep, narrow channels. Small caves or karstic shafts that frequently along the sides of these dry valleys act as vertical conduits for water to infiltrate directly into the limestone and rapidly recharge the aquifer (Fig. 2-8). This process is only possible when there is sufficient rainfall to generate runoff along these dry valleys. It has been suggested that rainfall of 75-100 mm day^{-1} will generate runoff on Barbados (Tullstrom, 1964). Rainfall rates of this magnitude typically only occur once per year.

The narrow range of groundwater $\delta^{18}O$ values can be explained by two processes either singly or in combination. First, recharge may be limited to large rainfall events that produce runoff to sinkholes and through dry valleys, and result in rapid discrete recharge of large volumes of water. The relatively large volumes of water involved in runoff and the brief flow periods would result in evaporation having little impact on the water volumes and isotopic compositions. Alternatively, recharge can also occur due to rapid diffuse infiltration through permeable soils, especially during the wet season when moist soils have the greatest capacity to transmit water. Studies using dye tracing and discharge measurements suggest that total annual recharge to many karst aquifers is dominated volumetrically by discrete infiltration while diffuse infiltration is a lesser component (Smart and Friederich, 1986). The much higher infiltration rates of limestone relative to soil together with the apparent lack of evaporation prior to recharge suggest that this may be the case on Barbados.

Determining the Seasonal Distribution of Recharge

The average groundwater $\delta^{18}O$ value (-3.0‰) on Barbados is lower than the weighted-average of rainwater (-1.9‰), weighted based on corresponding monthly rainfall amount (Fig. 2-6). Moreover, the range of groundwater $\delta^{18}O$ values does not overlap with the weighted-average of rainwater. This is significant because it indicates that not all rainfall contributes to recharge and recharge primarily occurs during the wettest months of the year, which are usually between August and November. Determining the seasonal distribution of recharge to the aquifer is made possible by the seasonal fluctuation of rainwater $\delta^{18}O$ values due to the amount effect.

The relationship between the average Barbados groundwater $\delta^{18}O$ value and rainwater $\delta^{18}O$ values suggest that significant recharge only takes place during months with more than 195 mm of rainfall, as discussed above. This threshold most likely is a product of the different mechanisms, diffuse and discrete infiltration, by which rainwater infiltrates through the vadose zone and the amounts of water required for each mechanism to take place. Discrete infiltration requires more rainfall in order to generate runoff to sinkholes, dry valleys and drainage wells where actual infiltration and recharge takes place. On Barbados, monthly rainfall exceeding 195 mm typically occurs once per year but may occur during as many as three months per year. These months usually coincide with the peak of the wet season, August through November. During some dry years that have no months with >195 mm of rainfall, such as, 1972, 1974, 1979, and 1993, it appears that very little recharge took place.

Comparison of Recharge Estimates Using Different Methods

Recharge estimation by volumetric comparison of rainfall with either evapotranspiration or measured coastal groundwater discharge potentially encounters problems related to difficulties in accurately determining actual evapotranspiration (AET) and groundwater discharge, respectively. These methods require numerous measurements at several locations over an extended period of time. The recharge estimate based on the comparison of mean monthly rainfall and PET (~6%) is much lower than those obtained using oxygen isotopes (15-45%). This occurs because the use of PET in recharge estimation over-estimates actual losses to evapotranspiration by assuming that AET is limited only by the amount of rainfall, reaching a maximum equivalent to the PET (Rushton and Ward, 1979). However, both methods indicate that recharge takes place during the wettest months of the year. The results of water-balance calculations based on coastal groundwater discharge are influenced by the number and frequency of measurements due to spatial and seasonal variability of discharge rates along the coast and of rainfall within the catchments. Water-balance will give no indication of seasonal fluctuation or spatial distribution of recharge within specific catchments. Coastal discharge rates may be affected by groundwater withdrawal and return-flow in adjacent catchments resulting in artificial redistribution of groundwater discharge along the coast. Consequently, water-balance estimates for individual catchments may under- or over-estimate natural recharge. By estimating recharge in large or combined groundwater catchments where there is no net export of water, the effects of redistributed groundwater discharge are reduced. The results of different water-balance calculations (Lewis, 1987; Proctor and Redfern, 1983; Stanley Assoc., 1978; DELCAN, 1995) for individual west coast catchments are highly variable and do not consistently agree with each other (Table 2-3). However, the results of models A, C, and D, shown in Figure 2-9 and applied to the combined west coast catchments, indicate general agreement with recharge estimates based on chloride concentrations at higher elevations, and oxygen isotopes.

The advantage of chloride recharge estimation is that the results are independent of rainfall measurements that may be influenced by the spatial distribution of rainfall measurement stations, and potentially provide information on the spatial distribution of recharge. With some exceptions, recharge estimates based on chloride concentrations and oxygen isotopic compositions of groundwater and rainwater generally overlap at elevations above 100 m and diverge at lower elevations (Fig. 2-7). This divergence coincides with the landward boundary of the freshwater lens (~50 m) and the Second High Cliff (100 m) and can be explained by mixing of freshwater and seawater in the freshwater lens. Seawater mixing introduces both higher $\delta^{18}O$ values and chloride concentrations into the fresh groundwater. Volumes of seawater involved in the freshwater-seawater mixing are relatively small (<2% based on chloride), but are large enough to dramatically change chloride concentrations from <50 mg l^{-1} to >100 mg l^{-1}. Freshwater-seawater mixing should result in a $\delta^{18}O$ value shift of <0.02‰ that is less than the analytical uncertainty and much smaller than the range of groundwater $\delta^{18}O$ values (~2‰). The shift in oxygen isotope recharge estimates is therefore too large to be attributed to mixing of freshwater and seawater but can be explained by enhanced discrete infiltration from dry valleys adjacent to the Second High Cliff. Elevated chloride concentrations due to freshwater-seawater mixing would result in over-estimation of evaporation and would therefore under-estimate recharge.

Divergence between recharge estimates based on oxygen isotopes and chloride concentrations also occurs at some sample sites located outside the freshwater lens. These sites fall into one of three categories: 1) abandoned, low-yield, large-diameter dug wells located at the highest elevations; 2) where the water table is close to land surface; and 3) a slow cave drip. All of these sites are susceptible to the effects of ET. This could cause differences in oxygen isotope- and chloride-based recharge estimates by elevating the chloride concentrations and $\delta^{18}O$ values. However, groundwater $\delta^{18}O$ values show no apparent effects of fractionation due to evaporation (see Barbados Groundwater Compositions section). Consequently, it is concluded that recharge estimates based on chloride data are only useful if collected at elevations above 100 m on Barbados. Data indicating high chloride due to seawater mixing or ET under-estimate recharge and are excluded from Figure 2-7b. Figure 2-7b therefore indicates that recharge is typically between 15% and 20% of average annual rainfall at higher elevations on Barbados, rising to as much as 45% at lower elevations.

For similar amounts of annual rainfall, overall recharge estimates based on Equation 2-4 vary widely because the result is dependent on the proportion of annual rainfall occurring during the wettest 1-3 months of the year. Recharge estimates for years with typical rainfall (~1150 mm yr^{-1} in southern Barbados) vary widely from 0 to 30% of average annual rainfall with an average of 25%. These aquifer-wide recharge estimates coincide approximately with recharge estimates based on groundwater compositions at individual sites.

Implications to Hydrogeologic and Paleoclimatic Studies

The use of oxygen isotopes to constrain the amount and seasonal and spatial distribution of recharge is most applicable to small aquifers in tropical climates. Under these conditions, the amount of rainfall is the primary factor controlling variations in rainwater $\delta^{18}O$ values. In temperate climates, seasonal temperature fluctuations may play a greater role in controlling rainwater compositional fluctuations than the amount of rainfall. This complication may allow for qualitative interpretation of the seasonal distribution of recharge without providing any clear information on the amount of recharge. Small aquifers are typically characterized by short groundwater residence times, which allow the use of present-day rainfall patterns and rainwater isotopic compositions to constrain recharge patterns. On the other hand, large aquifers may contain older groundwater recharged when climatic conditions and rainwater isotopic compositions differed from the present.

Average recharge estimates from hydrogeological studies of other tropical limestone island-aquifers using water-balance, PET, and rainwater and groundwater chloride methods, typically lie within the range of 20-30% of annual rainfall (Vacher and Quinn, 1997). These recharge estimates are very similar despite different aquifer configurations. However, this similarity may be explained by similar tropical climates and aquifer lithology composed of coral reef limestone.

Paleoclimatic studies use groundwater or vadose water oxygen isotopic compositions preserved in fossils, cements, sediments or rocks in order to constrain changes in climatic conditions over geologic time (e.g., Winograd et al., 1992; Dettman et al., 1993). Interpretation of paleoclimate data requires an understanding of how different climatic factors, such as temperature, rainfall, altitude, etc., affect the $\delta^{18}O$ values of rainwater and groundwater, and the relationships between $\delta^{18}O$ values of contemporaneous rainwater and groundwater. Understanding rainwater-groundwater relationships in modern aquifers will allow us to better estimate ancient rainwater compositions based on isotopic signatures preserved in the geologic record, thereby allowing the interpretation of paleoclimatic variations.

CONCLUSIONS

Seasonal fluctuations of Barbados rainwater $\delta^{18}O$ values are related to the amount of rainfall, with lower $\delta^{18}O$ values associated with wet season months (June to December) and higher $\delta^{18}O$ values associated with the dry season. These seasonal fluctuations make it possible to infer recharge seasonality by comparing the isotopic compositions of groundwater and rainwater. Groundwater $\delta^{18}O$ values on Barbados indicate that most recharge is rapid and takes place only during the wettest 1-3 months of the year.

Based on evaluation of different potential sites for infiltration, the potential for recharge is greatest by a combination of rapid diffuse infiltration through permeable soils, primarily above the Second High Cliff, and discrete infiltration through the sides of dry valleys within and immediately below the Second High Cliff. Recharge to the aquifer is 15-20% of average annual rainfall above the Second High Cliff, increasing to 25-30% at lower elevations in response to discrete infiltration of large volumes of water through the highly permeable limestone.

Recharge estimates based on groundwater constituents, such as oxygen isotopes and dissolved chloride: 1) have fewer uncertainties than recharge estimates based on direct measurement of hydrologic parameters; 2) have the advantage of providing some insight into the spatial and seasonal distribution of recharge to the aquifer; 3) are less affected by groundwater withdrawal; and 4) require fewer field measurements. Additionally, unlike the chloride recharge estimation method that is restricted to inland areas, oxygen isotope recharge estimation is a more robust method that can be used in both coastal and inland portions of the aquifer.

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Table 2-1. Stable isotope data for rainwater samples collected in this study. The dates indicate the periods of time over which the rainwater samples were collected. For groundwater stable isotope data from this study see Table A-2 in the appendix.

Dates	$\delta^{18}O$ (‰)	δD (‰)
3/23-24/97	-0.34	-3.8
3/24-26/97	0.45	9.3
3/24-26/97	0.38	11.2
3/30-31/97	-0.16	0.7
4/13-30/97	-0.27	7.1
4/23-24/97	-0.36	4.9
5/12-15/97	0.02	-0.4
6/10-12/97	-2.25	-2.3
6/22-23/97	-2.52	-16.7
6/27-29/97	-1.26	0.3
7/14/97	-1.89	-10.9

Table 2-2. Factors affecting oxygen isotope variations in Barbados groundwater.

Isotope effect	Variation on Barbados	Corresponding $\delta^{18}O$ shift
Temperature effect on rainwater	Mean annual temperature range (2-3°C)	0.7 to 1.0‰ [Dansgaard, 1964]
Altitude effect on rainwater	0 – 350 m above sea level	0 to -0.7‰ [Fontes and Olivry, 1977; Scholl et al., 1996]
Amount effect on rainwater	40 - 160 mm/month	-2 to -3‰ [Dansgaard, 1964; Gonfiantini, 1985]
Mixing with seawater	<3%, based on chloride	<+0.1‰
Fluid-rock interaction	<17 mmol $CaCO_3$/L, based on $^{87}Sr/^{86}Sr$	<+0.001‰ [Banner et al., 1994]

Table 2-3. The results of different water-balance calculations of recharge relative to annual rainfall on Barbados (expressed as percent of annual rainfall in the respective catchments). Catchments are shown on Figure 2-2.

Catchment	FAO [1985] Data*	Lewis [1987] Data†	Proctor & Redfern [1983] Data‡	Stanley Associates [1978] (Dry Year)§	Stanley Associates [1978] (Av. Year)§	DELCAN [1995]**
Carlton	6	14.1	15.4	10.0	16.1	20.5
Haymans	6	5.7	6.3	8.6	17.4	19.2
The Whim	6	12.3	25.0	9.7	18.3	20.4
Ashton Hall	6	7.6	15.0	12.1	16.5	20.1
Alleynedale	6	6.6	13.1	12.4	14.1	16.9
Bourbon	6	12.6	16.2	9.3	13.0	15.0
Entire west coast	6	9.3	14.5	10.8	15.2	18.1
St. Philip North	6	--	--	5.8	15.1	--

Note:

* Based on mean monthly potential evapotranspiration and rainfall data for Barbados from the Food and Agriculture Organization [1985].

† Water-balance calculations based on measured coastal discharge rates from Lewis [1987].

‡ Water-balance calculations based on measured coastal discharge rates from Proctor and Redfern [1983].

§ Water-balance calculations by Stanley Associates [1978]. In dry and average years it is assumed that Barbados receives average annual rainfall of 1000 mm/yr and 1,500 mm/yr, respectively.

** Water-balance calculations by DELCAN [1995].

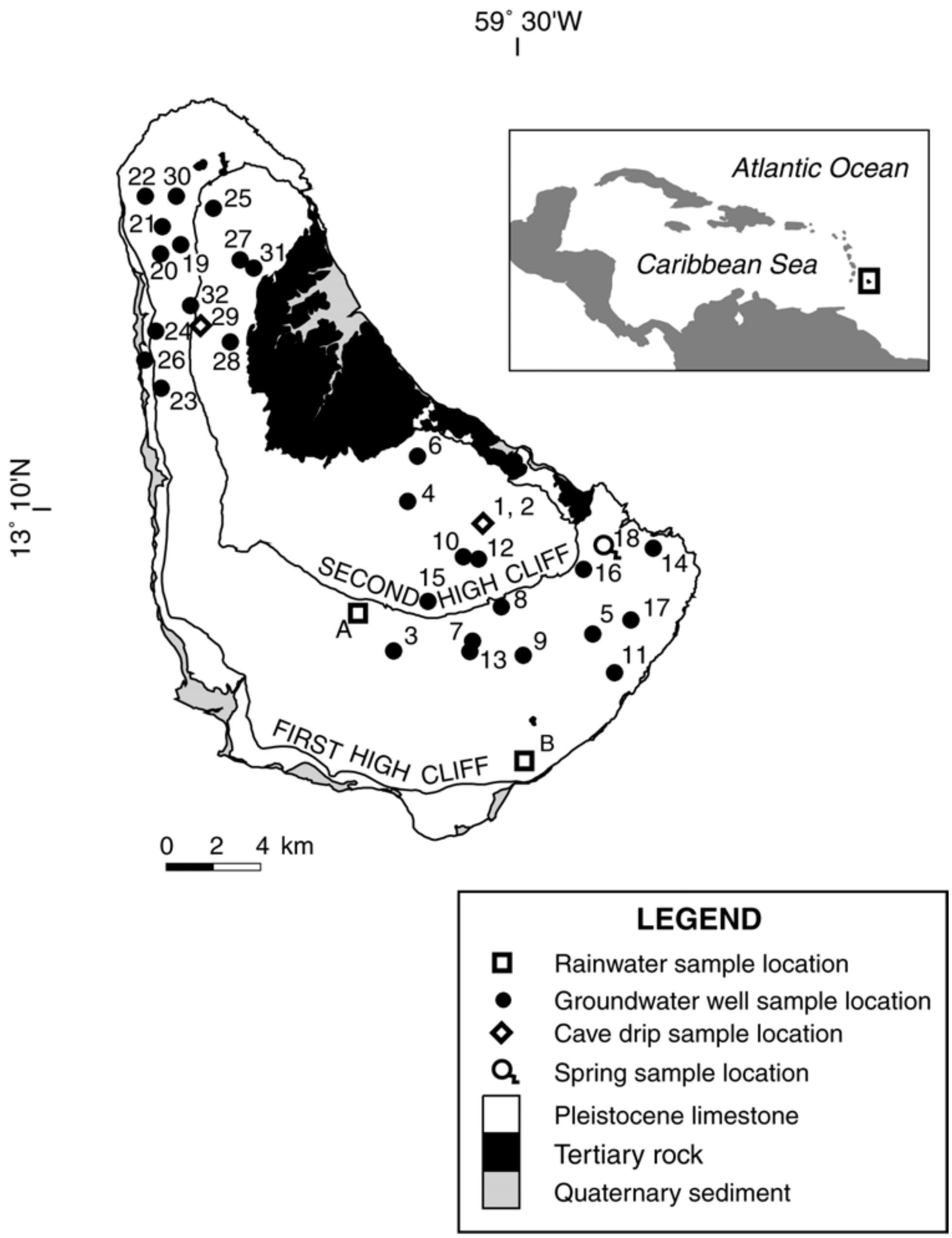

Figure 2-1. Location and geologic map of Barbados. The Pleistocene limestone that comprises the aquifer occurs in the northern, western and southern portions of Barbados. Adapted from 1:50,000 geologic map (Directorate of Overseas Surveys, 1983).

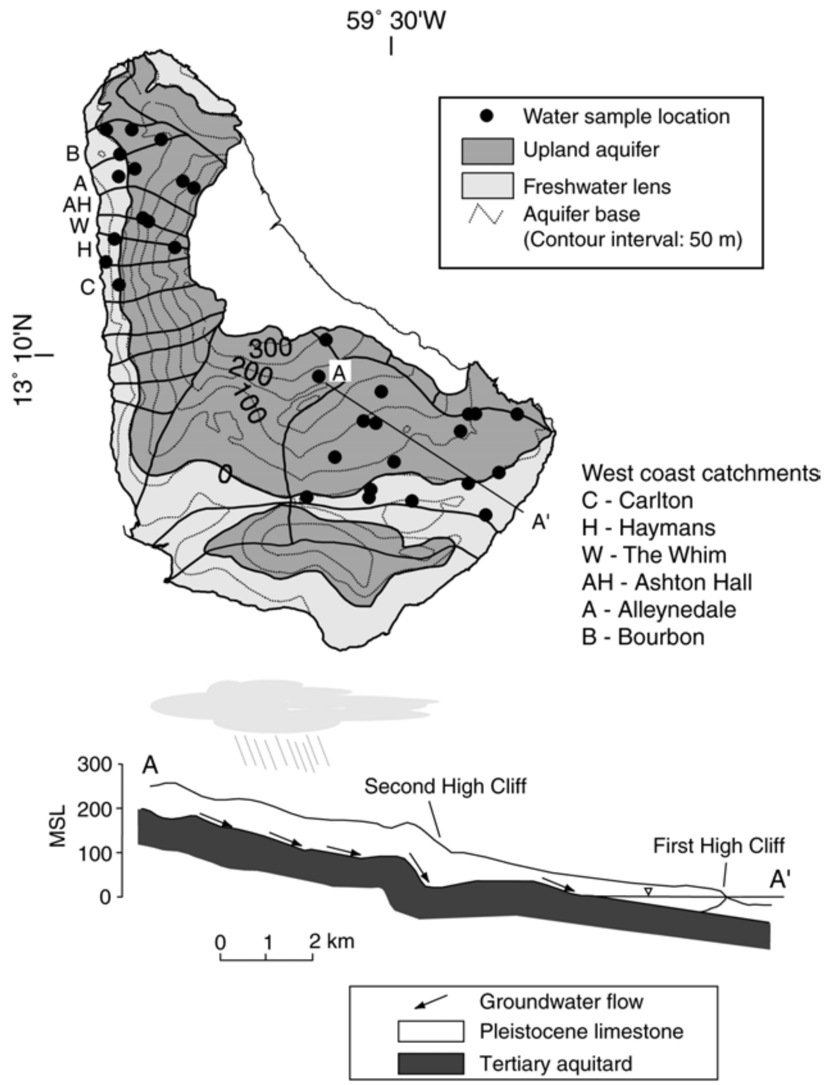

Figure 2-2. Hydrogeologic map of Barbados. The Pleistocene limestone aquifer is divided into several groundwater catchments due to the topography of the Pleistocene-Tertiary contact. Adapted from hydrogeologic map by Stanley Associates (1978) and cross-section by Barbados Ministry of Health et al. (1991).

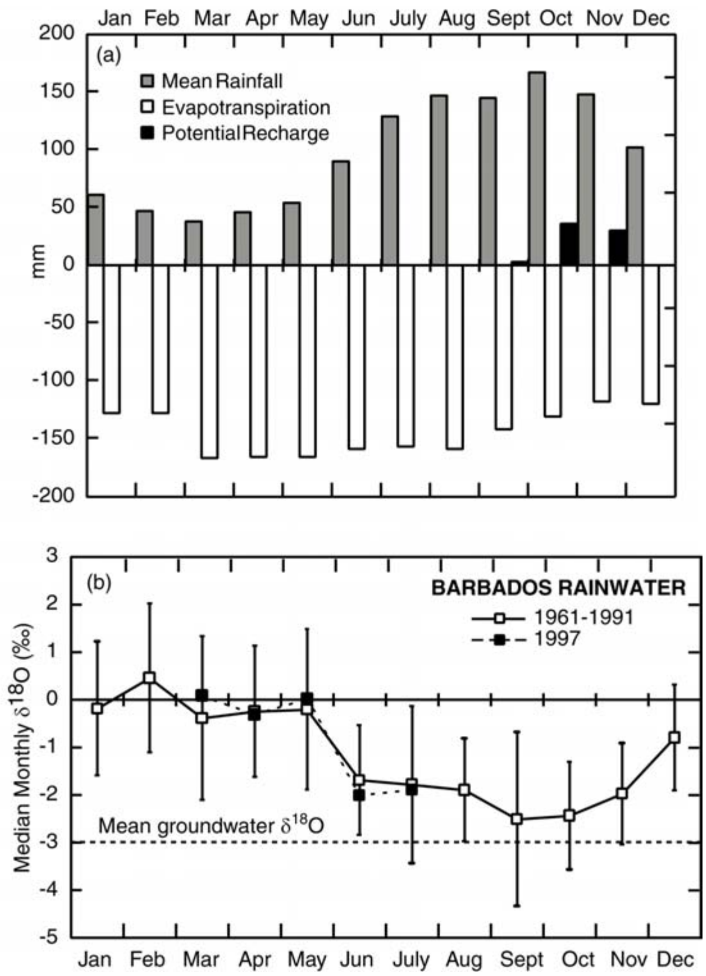

Figure 2-3. (a) Mean monthly rainfall and potential evapotranspiration for Barbados (1951-1980) from Food and Agriculture Organization (1985). Recharge is assumed to be the difference between mean monthly rainfall and evapotranspiration when rainfall exceeds potential evapotranspiration. This recharge estimate is conservative, indicating that recharge only occurs during the peak of the wet season. (b) Seasonal fluctuation of Barbados rainwater $\delta^{18}O$ values. The open symbols represent median monthly $\delta^{18}O$ values based on 1961-1992 rainwater data from the GNIP database (IAEA/WMO, 1998) and the closed symbols represent median monthly d18O values from this study (1997). The bars represent the standard deviation (1σ) for the GNIP data.

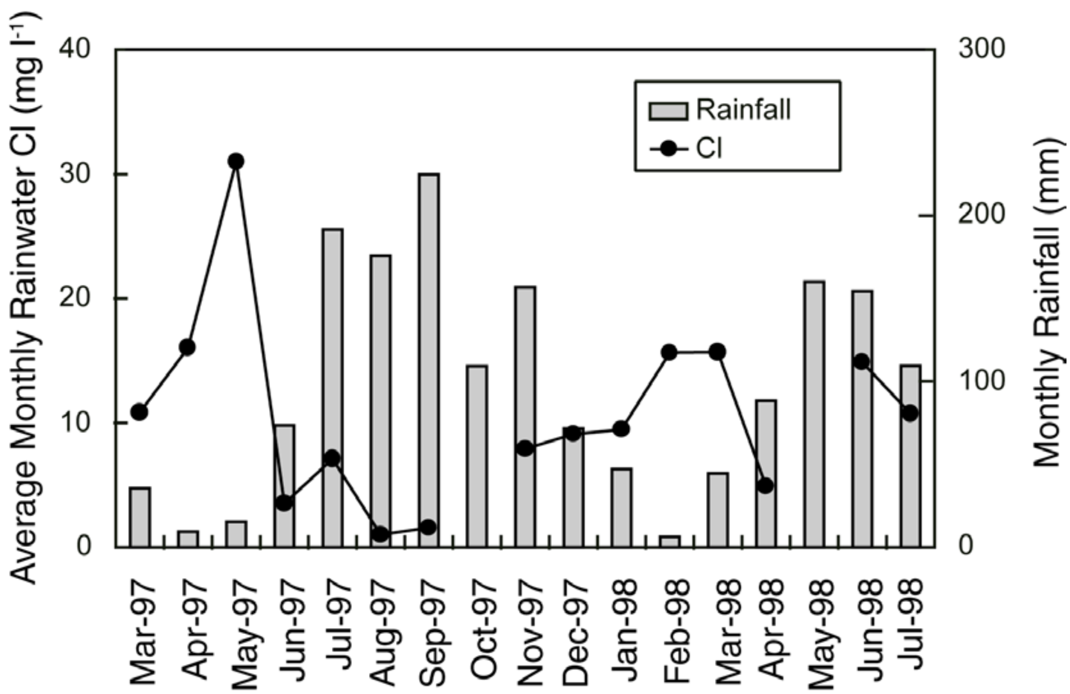

Figure 2-4. Seasonal fluctuation of Barbados rainwater chloride. These rainwater chloride data represent average monthly concentrations weighted based on associated rainfall amounts. The apparent inverse relationship between chloride concentrations and rainfall is due to dilution, especially during the wet season. For additional rainwater data see Table A-1 in the appendix).

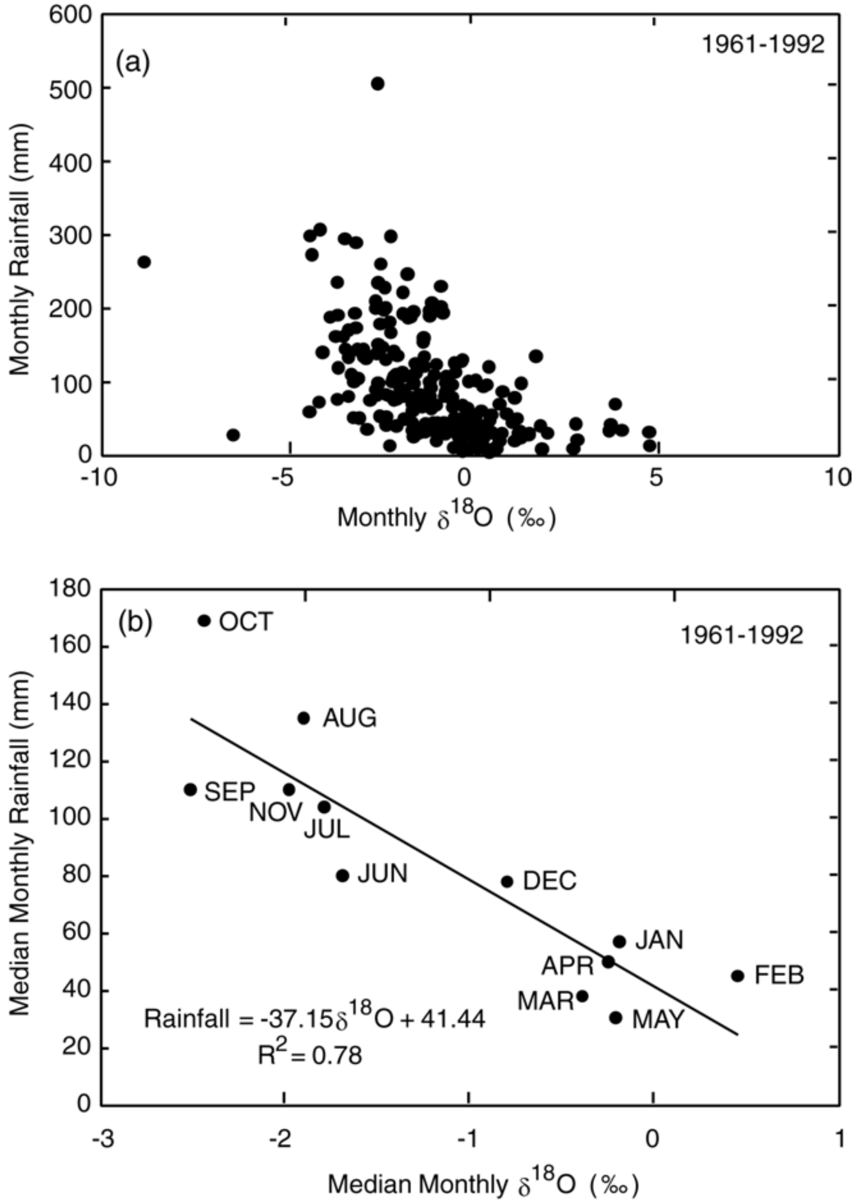

Figure 2-5. (a) Relationship between monthly $\delta^{18}O$ values of Barbados rainwater and monthly rainfall. (b) Relationship between median monthly $\delta^{18}O$ values of Barbados rainwater and median monthly rainfall for1961-1997. Based on data from GNIP database (IAEA/WMO, 1998).

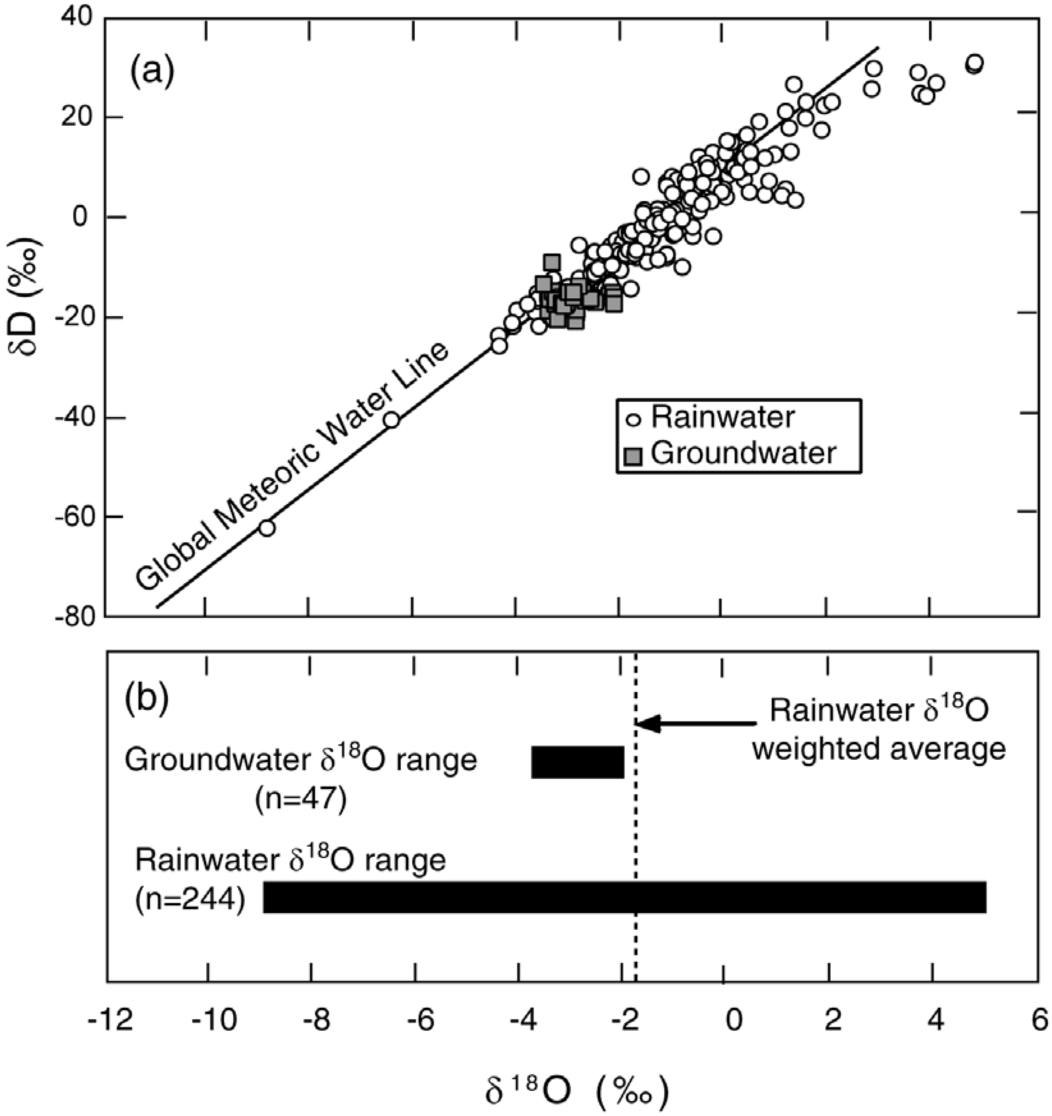

Figure 2-6. (a) The $\delta^{18}O$-δD compositions of rainwater and groundwater on Barbados. The rainwater data are from this study and the GNIP database (IAEA/WMO, 1998) and the groundwater data are from this study and Banner et al. (1991). (b) The ranges of $\delta^{18}O$ values for Barbados groundwater and rainwater.

$$\delta^{18}O_{\text{rainwater (weighted av.)}} = \Sigma n\,(\delta^{18}{}_{\text{Orainwater}} \text{ x } P_{\text{month}}) / \Sigma_n P_{\text{month}}$$

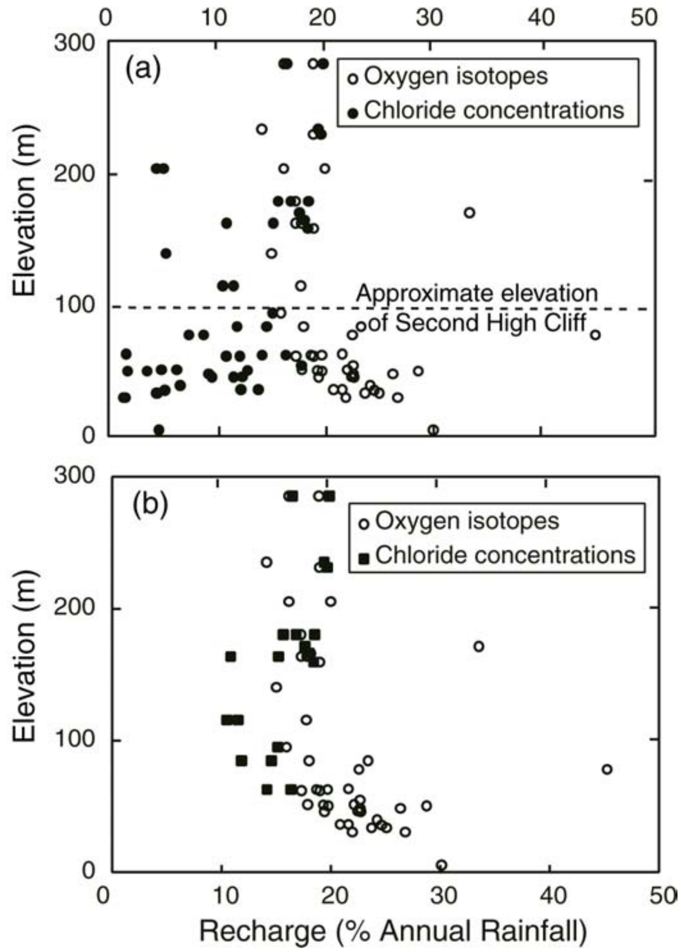

Figure 2-7. The variation of estimated recharge based on oxygen isotopes(Equation 1-5) and chloride concentrations of groundwater and rainwater, with surface elevation. These data are tabulated in Tables A-3 and A-4 in the appendix. Figure 2-7(b) is similar to (a) except for the omission of low chloride-based recharge estimates that under-estimate recharge as a result of elevated chloride concentrations due to freshwater-sea water mixing in coastal areas or evapotranspiration.

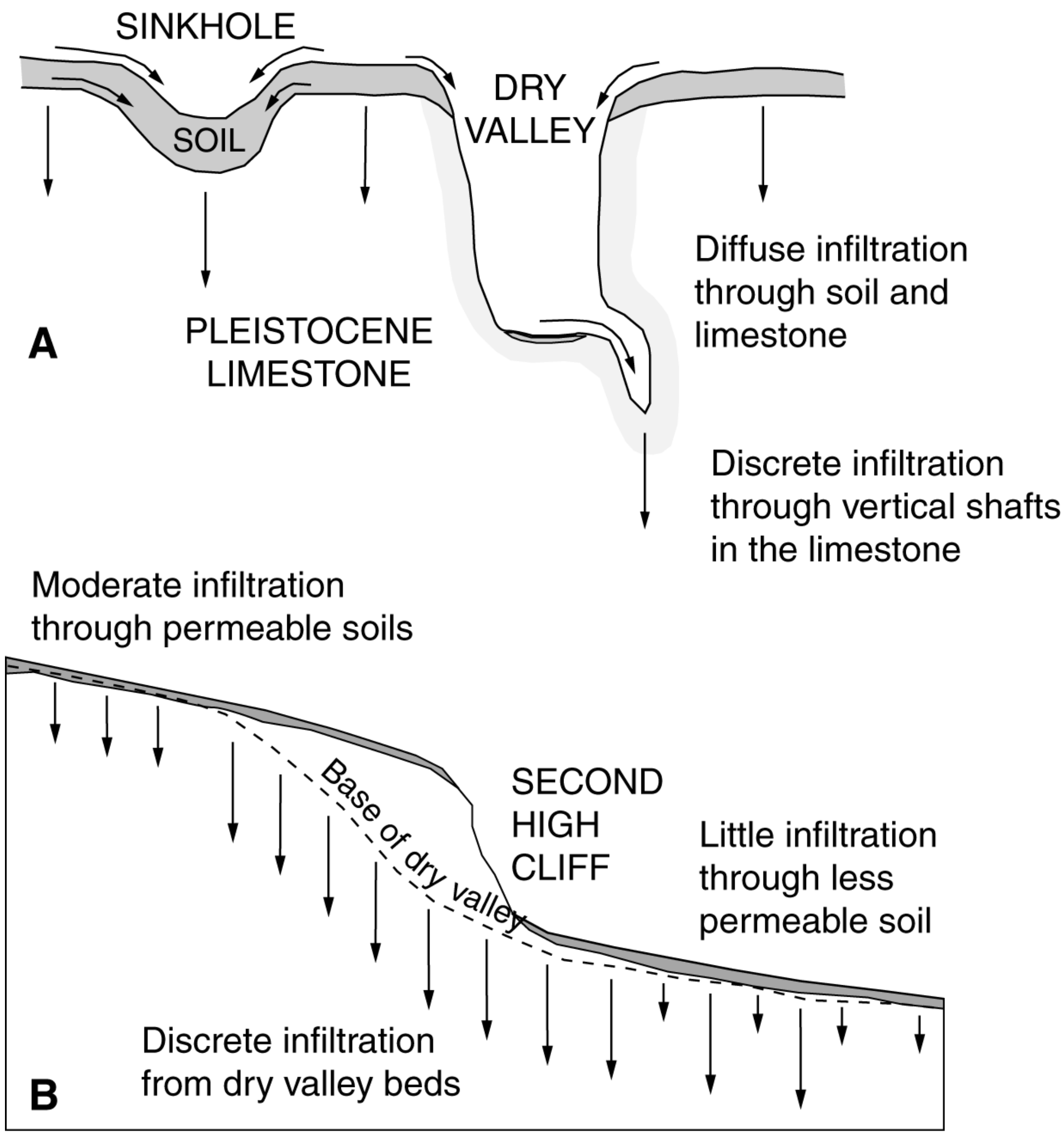

Figure 2-8. Schematic diagrams showing different pathways by which infiltrating water recharges the limestone aquifer of Barbados. Diagrams A and B are oriented perpendicular and parallel to a hypothetical dry valley, respectively.

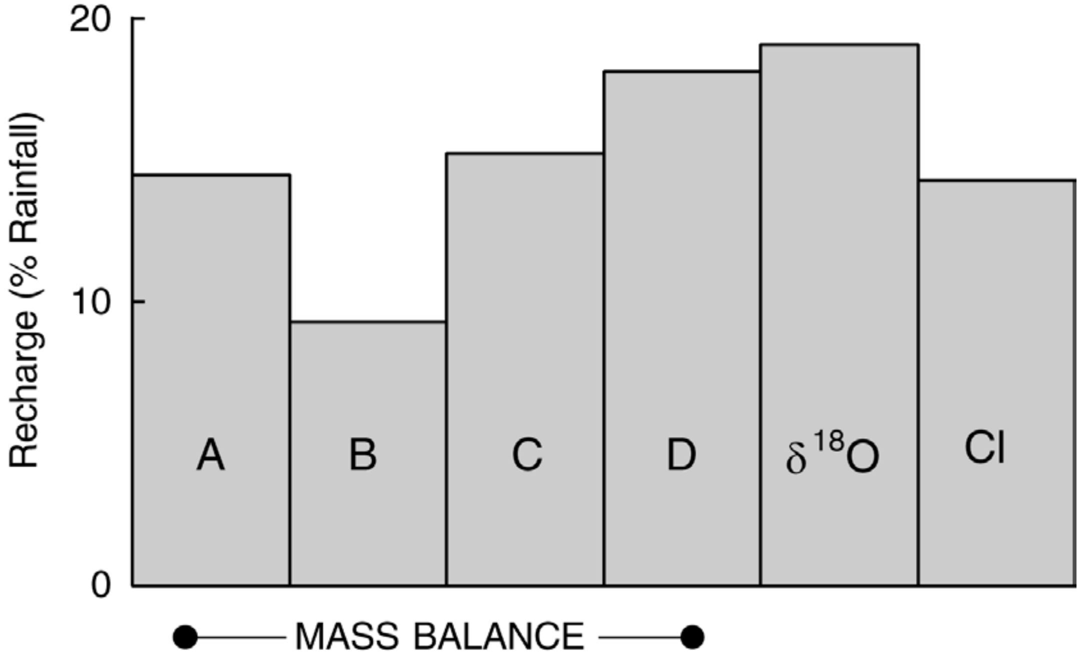

Figure 2-9. Recharge estimates for combined west coast catchments obtained by using different water-balance calculations, oxygen isotopes, and chloride concentrations. Water-balance calculations A and B are based on coastal discharge data from Proctor and Redfern (1983) and Lewis (1987), respectively, while C and D are water-balance calculations by Stanley Associates (1978) and DELCAN (1995), respectively.

CHAPTER 3: RECHARGE PROCESSES IN KARST ISLAND AQUIFERS ON BARBADOS, PUERTO RICO AND GUAM

ABSTRACT

The hydrology and geochemistry of groundwater in tropical island aquifers, such as Barbados, Guam and Puerto Rico, are significantly influenced by tropical climatic conditions. Recharge to these aquifers is the product of regional and local climate patterns that control rainfall. Oxygen isotopes can be used to estimate the amount and timing of recharge on these islands because seasonal fluctuations of rainwater oxygen isotopic compositions are related to the amount of rainfall. This study shows that average annual recharge to the limestone aquifer on Barbados varies widely, displaying a more direct relationship to the distribution of rainfall throughout each year than to total annual rainfall. Recharge is higher during years when rainfall is concentrated in the peak wet season months than during years when rainfall is more evenly distributed throughout the year. El Niño-Southern Oscillation may be partially responsible for these rainfall and recharge fluctuations.

The karst aquifers on Barbados, Guam and Puerto Rico have similar rainwater and groundwater oxygen isotopic compositions. Comparison of groundwater and rainwater oxygen isotopic compositions in all three aquifers indicates that recharge: 1) occurs by rapid infiltration with little evaporation prior to recharge; and 2) is associated with similar monthly rainfall thresholds of 190 - 200 mm. These are remarkably similar rainfall threshold results for three aquifers

from different geographic locations. Differences between the spatial variations of groundwater oxygen isotopic compositions on Barbados and Puerto Rico can be attributed to the more complex groundwater flow system on Puerto Rico. The surprising similarities of hydrologic conditions under which recharge will take place can be attributed to similarities in climate and geologic conditions, such as, soils, limestone bedrock, etc., that exist on all three islands. One could therefore speculate that similar recharge rainfall thresholds may be observed in other tropical karst aquifers.

INTRODUCTION

Island aquifers, especially limestone aquifers, are the primary sources of potable water for the islands' inhabitants. These aquifers are usually relatively small, unconfined and characterized by groundwater residence times of years to tens of years. Consequently, they are fragile systems that respond rapidly to impacts of natural and anthropogenic processes. Groundwater quantities in these aquifers usually respond to short- and long-term climatic fluctuations that influence the amount of recharge and therefore the amount of groundwater available for use. Consequently, it is vital that we understand recharge processes and interannual variations of recharge amounts. Groundwater quality in island aquifers is susceptible to: 1) the effects of seawater intrusion related to fluctuations in recharge or groundwater consumption for growing domestic, industrial (especially tourism), and agricultural needs; and 2) contamination by wastewater and fertilizer. The susceptibility of these aquifers to contamination is a direct function of shallow water tables and dense populations.

Limestone island aquifers are generally characterized by: 1) fresh meteoric water, seawater or a mixture of the two; 2) hydraulic heads affected by sea-level fluctuations, such as tides; and 3) aquifer rock that is more permeable than the underlying basement rock (Vacher, 1997). Limestone island aquifers have been classified based on the characteristics of limestone islands. These categories include coral reef islands which are subdivided into atolls, modern reefs, Quaternary reef islands, uplifted atolls, composite islands, and eolianite islands (Vacher, 1997). Large islands like Puerto Rico are not included in this classification system. Composite islands like Barbados and Guam are limestone islands composed of permeable limestone overlying relatively impermeable non-carbonate rocks that form an aquitard (Vacher, 1997). This aquitard is comprised of deep-sea sedimentary rocks in the case of Barbados and volcanic rocks on Guam. On composite limestone islands, freshwater lenses occur where the base of the limestone dips below sea level. Consequently, these limestone aquifers can be subdivided into two hydrologic zones with the intersection of the limestone base and sea level forming the boundary between zones. Composite aquifers display characteristics that are similar to unconfined aquifers on larger islands or continents, such as Puerto Rico. Similar to unconfined coastal continental aquifers, groundwater flow in composite island aquifers is primarily influenced by stratigraphy and sea-level fluctuations only near the coast. In other words, composite island aquifers and unconfined coastal continental aquifers only meet the first and third of the three characteristics of limestone island aquifers discussed above.

The primary aim of this research is to investigate: 1) the processes by which recharge occurs in a composite limestone aquifer, the Pleistocene limestone aquifer on Barbados; and 2) interannual variation of recharge over the past 30 years. It has been shown that recharge to the limestone aquifer on Barbados is primarily influenced by the occurrence of runoff (Jones et al., 2000). Runoff along dry valleys produces discrete recharge by rapid infiltration through karst shafts or sinkholes that occur along the sides of the dry valleys. Comparison of oxygen isotopic compositions of groundwater and rainwater on Barbados indicates the rainfall threshold that must be exceeded before recharge takes place (Jones et al., 2000). One would therefore expect that this threshold is the minimum rainfall required for the generation of runoff on Barbados. Interannual variations of rainfall on Barbados may be influenced by phenomena such as the El Niño-Southern Oscillation (ENSO) and this must be considered as a factor influencing interannual variations of both rainfall and recharge amounts on Barbados.

In this study, the same methods used on Barbados are used on Guam and Puerto Rico with the aim of determining whether the rainfall thresholds vary from island to island. The three islands are characterized by similar tropical climates and limestone geology. The much higher rainfall on Guam, however may produce a different rainfall threshold for recharge and higher recharge rates than on the other two islands. The similarity between the climate of Puerto Rico and Barbados suggests that rainfall thresholds may be similar.

PLEISTOCENE LIMESTONE AQUIFER OF BARBADOS

Climate

Average annual rainfall on Barbados varies from about 1,000 mm yr^{-1} at the extreme northern and southeastern margins of the island to more than 2,000 mm yr^{-1} at the center of the island (Fig. 3-1). On Barbados, the wet season extends from June to December and reaches a peak in August through October. Wet season rainfall accounts for approximately 60% of average annual rainfall. Dry season rainfall is associated with local convection due to moist air flowing over the heated island (Malkus, 1963). During the wet season, in addition to local convection effects, rainfall occurs due to the combined effects of moisture associated with: 1) tropical weather systems, such as tropical depressions and hurricanes; and 2) the proximity of the Intertropical Convergence Zone (Falkland, 1991; Reading et al., 1995). Rainfall distribution varies seasonally with highest rainfall occurring at the center of the island during dry season months and the western, leeward side of the island during the wet season (Fig. 3-2). Orographic effects that normally produce enhanced rainfall on windward slopes do not apparently play a major role in influencing the rainfall distribution on Barbados (Reading et al., 1995).

Geology

Pleistocene Limestone

The Pleistocene limestone aquifer of Barbados is composed of the Pleistocene coral reef limestone that covers about 85% of the island (Fig. 3-3). The coral reefs developed outwards from the center of the island forming terraces in response to continuous uplift. There are three main groups of terraces separated by the First and Second High Cliffs. The Second High Cliff is about 30 m high and occurs at an elevation of approximately 100 m. The Second High Cliff is highly karstified with the frequent occurrence of dry valleys and caves, and consequently is the site of a large amount of discrete recharge to the aquifer. This spatial distribution of recharge has been confirmed by comparison of oxygen isotopic compositions of rainwater and groundwater (Jones et al., 2000). The Pleistocene limestone is up to 100 m thick and is characterized by porosity of 20 – 60%, averaging 45%, and a specific yield of 12.5 – 15% (Senn, 1946; Tullstrom, 1964). The Pleistocene limestone overlies Tertiary-age rocks of the upper Scotland

Formation and Oceanics Group. Recharge to this aquifer takes the form of diffuse and discrete infiltration through the soil and underlying limestone. Groundwater flows outward from the elevated parts of the aquifer and discharges primarily along the coast. This coastal discharge varies both spatially and seasonally with higher discharge rates during the wet season (Lewis, 1985; 1987).

Upper Scotland Formation

The upper Scotland Formation is composed of sand with inter-bedded clay. These rocks potentially form an aquifer that directly underlies the Pleistocene limestone in parts of northern and eastern Barbados (Senn, 1946). Little is known of the potential for the upper Scotland Formation as an aquifer because few, if any, wells penetrate it. This is due to the adequate groundwater supply from the overlying Pleistocene aquifer and the well construction methods used on the island. Most wells on Barbados are dug wells, constructed more than one hundred years ago. These wells are typically vertical shafts about 2 – 3 m in diameter dug until the water table is encountered. In some cases, horizontal shafts are constructed perpendicular to the hydraulic gradient to increase well yields. Well depths are limited by the base of Pleistocene limestone in upland areas and the thickness of the freshwater lens in coastal areas.

Oceanics Group

The Oceanics Group in most areas separates the Pleistocene limestone from the upper Scotland Formation. This group is composed of low permeability clay and marl. The Oceanics Group forms an aquitard at the base of the Pleistocene limestone aquifer (Senn, 1946). In upland areas of Barbados, most wells are dug to top of Oceanics Group to maximize saturated thickness. Historically, at the highest elevations where the saturated zone is very thin, a few wells have been dug into underlying Oceanics Group rock. These wells take advantage of the very low permeability of the Oceanics rock in order to collect water flowing along Pleistocene-Oceanics contact and therefore act as a cistern. On Barbados, there is only one well known to obtain water from the Oceanics Group. This well is located in an area in southern Barbados where the Oceanics Group crops out and is highly jointed (Senn, 1946).

Hydrologic Zones

The Pleistocene limestone aquifer is divided into two hydrologic zones referred to as the Stream- and Sheet-water zones, depending on whether the top of the Oceanics Group aquitard occurs above or below sea level, respectively (Fig. 3-4). The Stream-water zone constitutes the bulk of the areal extent of the Pleistocene limestone aquifer with the freshwater lenses of the Sheet-water zone primarily occurring within 1 – 2 km of the coast. In addition to hydrologic zones, the Pleistocene limestone aquifer of Barbados is subdivided into groundwater catchments (Stanley Associates Engineering Ltd., 1978a). These groundwater catchments are defined based on our knowledge of the topography of the aquifer base. It is assumed that ridges in the topography of the top of the Oceanics Group form hydrologic divides and thus control groundwater flow paths in the aquifer.

Stream-Water Zone

The term ‘Stream water’ refers to the occurrence of underground streams in this portion of the aquifer. This zone forms the upland portions of Pleistocene limestone aquifer. In the Stream-water zone, groundwater forms a thin layer, a few meters thick, at the base of the Pleistocene limestone (Senn, 1946). Groundwater flows along the top of the underlying aquitard. At some locations, groundwater flows through underground streams that incise into the aquitard (Harris, 1971). The topography of this surface controls the groundwater flow paths and hydraulic gradients.

Water-level variations in wells in the Stream-water zone have been reported at several locations in the aquifer (Senn, 1946). These water-level fluctuations are typically seasonal fluctuations of less than one meter, but may be as much as 7 m (Senn, 1946). The relatively large water-level fluctuations are associated with: 1) sinkhole depressions (Sites 8, 10, 19; Fig. 3-3); 2) depressions in the topography of the aquitard (Site 3); and 3) known underground streams (Site 2; Senn, 1946). One can infer that these relatively large water-level fluctuations are due to mounding of the water table during periods of recharge: 1) adjacent to points of discrete recharge; 2) where groundwater flow paths converge; and 3) due to water from underground streams infiltrating into the surrounding aquifer rock.

Sheet-Water Zone

The Sheet-water zone occurs where the top of the basal aquitard occurs below sea level, consequently, groundwater occurs in freshwater lenses. In this part of the aquifer, the water table lies close to sea level (Senn, 1946). Water-levels variations in the Sheet-water zone are typically due to tidal effects, especially near the coast. Water-level fluctuations that have been observed near the landward margin of this zone are attributed to large influxes of groundwater from the Stream-water zone (Senn, 1946; Stanley Associates Engineering Ltd., 1978b). Water-level data for the period 1965 – 1971 from the southwestern parts of island show that minimum water-levels generally coincide with the dry season (Fig. 3-5). Water-levels may rise up to 0.75 m above the average water level in response to above average monthly rainfall during the wet season (Stanley Associates Engineering Ltd., 1978b). Water levels may rise gradually in response to the cumulative effects of a long wet season (e.g., 1966) or rapidly in response to exceptionally wet months (e.g., October 1970). Generally, the water table will gradually return to average water-levels over a period of 6 – 12 months (Stanley Associates Engineering Ltd., 1978b). There is little apparent response of water levels to rainfall during years with average or below average rainfall.

The Ghyben-Herzberg Principle (Baydon-Ghyben, 1888; Herzberg, 1901) suggests that fluctuations in Sheet-water zone water-levels would be accompanied by fluctuations in the thickness of the freshwater lens. The freshwater lens on Barbados is 10 – 25 m thick (Stanley Associates Engineering Ltd., 1978a). Seasonal fluctuation in water-levels would be accompanied by fluctuations in freshwater lens thickness. The freshwater lens and the mixing zone separating the freshwater from seawater are thickest towards the end of the wet season in response to recharge and thinnest by the end of the dry season (Steinen et al., 1978; Stanley Associates Engineering Ltd., 1978a).

Infiltration Rates: Diffuse Recharge

Variations in soil permeability may play a role in recharge to the Pleistocene limestone aquifer (Fig. 3-6). Barbados soils are typically less than 2 m thick and become less permeable with depth (Vernon and Carroll, 1965). Soils occurring above the Second High Cliff tend to have the highest permeabilities with measured infiltration rates greater than 250 mm h^{-1} (Tullstrom, 1964). Soils that occur below the Second High Cliff, at elevations below 100 m, tend to be less permeable with measured infiltration rates that range from 12.5 mm h^{-1} to 250 mm

h^{-1}, but are mostly about 50 mm h^{-1} (Tullstrom, 1964). These infiltration rates most likely represent infiltration through sugar cane fields that are only plowed at four to five year intervals (Tullstrom, 1964). The lowest soil permeabilities occur along topographic valley axes and in some sinkholes. Barbados soils are typically composed of 60 – 70% clay (Vernon and Carroll, 1965). Differences in soil infiltration rates can be attributed to differences in age and clay mineralogy. Smectitic clays are converted over time to kaolinite in soil environments. The soils that occur at lower elevations on Barbados are younger and have undergone less alteration than older soils (Vernon and Carroll, 1965). Consequently, the predominant clay mineral present in these soils is smectite and their lower permeabilities are likely the result of the shrink-swell properties of smectite. Older soils occurring at higher elevations contain increasing amounts of kaolinite (Vernon and Carroll, 1965; Beaven and Dumbleton, 1966). The Pleistocene limestone is much more permeable than the overlying soils with measured infiltration rates of 700 to 70,000 mm h^{-1} (Tullstrom, 1964; Smart and Ketterling, 1997).

Karst Features: Discrete Recharge

Dry valleys and sinkholes are the most obvious karst features that occur on Barbados (Fig. 3-7). In addition to the less obvious karst features, such as caves, these are potential sites of discrete recharge to the underlying aquifer.

Dry valleys on Barbados take the form of relatively narrow gullies that seem to be more numerous in areas characterized by moderate to steep slopes (Day, 1983). These valleys are usually dry except along the west coast where they intersect the water table (Fermor, 1972). Runoff through the dry valleys only occurs for brief periods of time and is associated with heavy rainfall. It has been suggested that runoff is generated by rainfall rates exceeding 75 – 100 mm d^{-1} (Tullstrom, 1964). Surface runoff to the sea is only possible along the western and northern coasts of Barbados. Elsewhere, dry valleys peter out at lower elevations. Consequently, runoff generally either recharges the aquifer or is taken up by evapotranspiration. Surface water discharge on Barbados is very low and has been estimated to be less than 1 % of average annual rainfall (Stanley Associates Engineering Ltd., 1978a).

The mean sinkhole density in western Barbados is 9.47 km^{-2} and the sinkhole density is highest at elevations of 100 - 150 m (Day, 1983; Fig. 3-8). This elevation range coincides with the Second High Cliff. There is little evidence of structural controls on the orientations of sinkhole depressions axes (Day, 1983). On Barbados, sinkhole and dry valley development seem to be competitive (Day, 1983). This is most apparent in western Barbados where some areas are characterized by the frequent occurrence of dry valleys and absence of sinkholes. High sinkhole densities tend to occur in areas where dry valleys are not well developed. These areas tend to be characterized by low relief. Similarly, dry valleys tend to be more numerous in areas characterized by relatively high relief. This can be explained by the effects of runoff and infiltration, factors that control the development of dry valleys and sinkholes, respectively (Day, 1983). Infiltration dominates over runoff in areas characterized by low relief, and vice versa in high relief areas. Consequently, sinkholes and dry valleys preferentially form in areas characterized by low relief and steeper slopes, respectively.

Sinkholes on Barbados can be divided into two sub-populations. These sub-populations are: 1) relatively large interfluvial sinkholes that occur between dry valleys; and 2) relatively small karst shafts occurring within the dry valleys (Day, 1983). The karst shafts have greater potential as conduits for recharge to the aquifer than the larger interfluvial sinkholes. This is the case because interfluvial sinkholes are frequently filled with very low permeability soils that reduce their ability to transmit infiltrating water without ponding and extensive losses to evapotranspiration. On the other hand, the karst shafts that occur on the sides of dry valleys can potentially transmit large volumes of water to the aquifer during the brief periods of runoff (Jones et al., 2000).

Recharge Processes

Recharge to the Pleistocene limestone aquifer can take place by diffuse infiltration through the soil or by discrete infiltration through drainage wells, dry valleys and some sinkholes. Infiltration tests and field observations on Barbados indicate that water residence-times in the vadose zone ranges from several minutes to a few days for water infiltrating through sinkholes or drainage wells (Mwansa and Barker, 1996; Smart and Ketterling, 1997). Residence times associated with diffuse infiltration are believed to be much longer, ranging from days to several months (Senn, 1946). This conclusion was reached based on observed responses to rainfall in caves where a flow rate response is observed within hours of a large rainfall event followed by a second smaller responses weeks or months later (Senn, 1946). The first flow response is the associated with rapid discrete infiltration while the second response is related to slower diffuse infiltration. Diffuse recharge is most likely to occur where soil infiltration rates are highest (e.g., above the Second High Cliff). Pleistocene limestone is frequently exposed at the surface in dry valleys, especially where these valleys cut through the Second High Cliff forming narrow, deep channels. Small caves or karstic shafts along the sides of these dry valleys potentially act as vertical conduits for water to infiltrate directly into the limestone and rapidly recharge the aquifer. This process is only possible when there is sufficient rainfall to generate runoff along these dry valleys. Drainage wells constructed with the aim of preventing flooding of agricultural fields provide man-made conduits for recharge during periods of heavy rainfall, and are also potential sources of groundwater contamination (Smart and Ketterling, 1997; Jones, 2000).

Estimated Recharge Rates

Seasonal fluctuations in rainwater $\delta^{18}O$ values has made it possible for the first time to infer recharge seasonality and estimate the amounts of recharge on Barbados by comparing the isotopic compositions of groundwater and rainwater (Jones et al., 2000). The unique results of this study indicate that most recharge: 1) is rapid; 2) takes place only during the wettest 1 – 3 months of each year; and 3) is 15 – 20% of average annual rainfall above the Second High Cliff, increasing to 25 – 30% at lower elevations. The higher recharge rates at lower elevations likely occur in response to discrete infiltration of large volumes of water through the highly permeable limestone (Jones et al., 2000). Recharge estimates based on groundwater constituents such as oxygen isotopes and dissolved chloride: 1) have fewer uncertainties; 2) have the advantage of providing insight into the spatial and seasonal distribution of recharge to the aquifer; 3) are less affected by groundwater withdrawal; and 4) require fewer field measurements than recharge estimates based on direct measurement of hydrologic parameters (Jones et al., 2000). An advantage of the application of oxygen isotopes over chloride is that oxygen isotopes can be used to estimate recharge in both coastal and inland portions of the aquifer (Jones et al., 2000).

Interannual Recharge Variations

Interannual variations of recharge have been estimated based on the relationship between the average groundwater $\delta^{18}O$ value on Barbados and rainwater $\delta^{18}O$ values (Jones et al., 2000). This method of estimating recharge on Barbados infers that recharge only occurs during months with more than 195 mm of rainfall. This method is based on mass balance and assumes that the groundwater oxygen isotopic composition is the weighted average of the rainwater that actually recharges the water table. The average groundwater oxygen isotopic composition on Barbados (-3.0‰) is equivalent to an average rainwater composition comprised only of rainwater associated with monthly rainfall exceeding 195 mm. Recharge estimates for 1960 – 1998 fall within the range 0 – 99% of average annual rainfall with an average of 30% (Fig. 3-9). These recharge estimates, therefore, are a measure of the proportion of rainfall during each year that occurs during months with more than 195 mm of rainfall. The variation of recharge over time is therefore related more to the distribution of rainfall throughout a given year than variations in total annual rainfall. For example, there is apparently much more recharge during 1994 (30%) than 1993 (0%) despite approximately equal amounts of rainfall during the respective years. This occurs because the amount of recharge is apparently higher when rainfall is concentrated in a few months of the year, usually the peak wet season months of August, September, and October. The conditions conducive to recharge usually occur during one month per year but may occur during as many as three months (Jones et al., 2000).

Relationship Between Recharge and ENSO

The phenomena of ENSO is known to affect climatic conditions throughout the world. El Niño occurs when the cold Peruvian Current along the west coast of South America is periodically replaced by a weak warm ocean current (Bigg, 1990). This phenomenon is closely associated with changes in upper atmospheric circulation that occur due to fluctuations of barometric pressures between the eastern and western South Pacific, known as the Southern Oscillation. The Southern Oscillation is caused by interannual sea surface temperature variations in the tropical Pacific Ocean (Philander, 1990; Quinn et al., 1987). These climatic fluctuations occur every 2 – 7 years (Bigg, 1990).

ENSO potentially has an impact on hydrogeology by influencing variations of the spatial and temporal distribution of rainfall. In the western Atlantic, the onset of ENSO typically results in the development of fewer tropical weather systems, such as hurricanes, tropical depressions, and other tropical disturbances (Gray, 1984). These weather systems are partially responsible for rainfall on islands like Barbados, especially during the peak wet season months (August-October), which coincide with the peak of the hurricane season. ENSO therefore results in less rainfall and reduces the likelihood that recharge will occur. Tropical weather systems are less frequent during moderate to strong ENSO episodes because increased upper tropospheric westerly winds over the Caribbean basin and equatorial Atlantic enhance vertical shear and consequently inhibit their development (Gray, 1984; Reading, 1990). The development of tropical weather systems, however, is also influenced by other factors such as sea-surface temperature and equatorial stratospheric winds (Gray, 1984; Reading, 1990). This complicates the relationship between the development of tropical weather systems and ENSO (Reading, 1990). Consequently, the correlation between the frequency of Atlantic tropical weather systems and El Niño-La Niña episodes is weak (Reading, 1990). The onset of La Niña episodes has the opposite climatic effect to El Niño and results in more frequent development of tropical weather systems. Consequently, La Niña episodes result in more rainfall and a greater probability of recharge on Barbados.

The Multivariate ENSO Index (MEI) is a means of measuring the strength of ENSO episodes based on six variables: 1) sea-level pressure; 2) zonal component of surface wind; 3) meridional component of surface wind; 4) sea surface temperature; 5) surface air temperature; and 6) total cloudiness fraction of the sky (Wolter and Timlin, 1993). Positive MEI values represent El Niño episodes while negative values represent La Niña episodes (Wolter and Timlin, 1993). Annual MEI values fluctuate in response to cycles of El Niño-La Niña episodes (Fig. 3-10). Generally, estimated annual recharge increases as the MEI values decrease, such that annual MEI minima coincide approximately with highest recharge estimates. This relationship can be attributed to the effects of ENSO on the frequency of tropical weather systems. Little recharge takes place during El Niño years when wet season rainfall is suppressed, while much more recharge takes place associated with La Niña episodes when peak wet season rainfall is enhanced. There are periods, for example the early 1960s and late 1970s, when the relationship between average annual MEI and recharge estimates is not apparent. The apparent relationship between average annual MEI and annual recharge can only be used qualitatively to predict periods of relatively high or low recharge because the correlation between annual MEI values and the magnitude of recharge is not statistically significant. This can be attributed to the weak correlation between tropical weather system development and ENSO episodes.

Monthly MEI values have been compared to the frequency at which the monthly rainfall threshold of 195 mm is exceeded for recharge to occur. These data suggest that on Barbados potential recharge episodes occur most frequently, 2 – 4 months per year, when monthly MEI values are at or near minimum values. The number of months per year with rainfall exceeding 195 mm plays a role in determining the amount of recharge. Consequently, years with higher recharge episode frequencies will potentially have more recharge.

THE LIMESTONE AQUIFER OF NORTHERN PUERTO RICO

Comparison of oxygen isotopes in rainwater and groundwater has previously been used to establish a relationship between monthly rainfall amounts and recharge on Barbados (Jones et al., 2000). As part of this study, similar methods are used in other karst aquifers to investigate how the rainfall thresholds that must be exceeded before recharge occurs vary in different aquifers.

Puerto Rico is a relatively large tropical island composed of limestone flanking a volcanic core (Fig. 3-11). In this paper, discussion of the hydrogeology of Puerto Rico is restricted to: 1) the north coast of Puerto Rico where limestone aquifers are better developed; and 2) the unconfined aquifer within the limestone aquifer of north Puerto Rico. The unconfined limestone aquifer of north Puerto Rico, a relatively large island, was selected for comparison with the Barbados aquifer because it potentially displays more similarities to limestone aquifers that occur on small limestone islands than the underlying confined aquifers.

Climate

Puerto Rico has a humid tropical climate. Average annual rainfall along the north coast varies from about 1,500 mm yr^{-1} along the coast to about 2,500 mm yr^{-1} inland. There is less rainfall on the leeward southern coast. The dry season occurs from December to March or April while the wet season generally occurs from June through November reaching a peak from August through November. The wettest months are usually September and October. About 60% of annual rainfall occurs during the wet season. Unlike Barbados, Puerto Rico is a mountainous island with elevations in excess of 1,000 meters. The spatial distribution of rainfall on the island is indicative of orographic effects (Reading et al., 1995).

Geology and Hydrogeology

The limestone aquifers of Puerto Rico are composed of Oligocene to Miocene limestone (Fig. 3-11; Giusti, 1978). This limestone forms wedges that thicken seaward and overly Cretaceous and Tertiary volcanic rocks (Fig. 3-12). The limestone is subdivided into seven formations, the San Sebastián Formation, Lares Limestone, Mucarabones Sand, Cibao Formation, Aguada Limestone, Aymamón Limestone, and Camuy Limestone. The limestones of northern Puerto Rico are highly karstified (Giusti, 1978). Karstification takes the form of sinkholes and other solution features in the east and karst hills and rivers that partly flow underground in the west. The karst hill topography that occur on Puerto Rico does not occur on Barbados.

There are two limestone aquifers in northern Puerto Rico, an unconfined aquifer that occurs in the Miocene limestones of the Aymamón and Aguada Formations, and a confined aquifer in the underlying Oligocene limestones of the Cibao and Lares Formations (Giusti, 1978). The two aquifers are separated by lower permeability units that occur at the top of the Cibao Formation (Rodríguez-Martínez, 1995). Recharge to the aquifer takes the form of infiltration from perennial and intermittent streams and rivers, as well as through sinkholes that may be more than 30 meters deep. The streams and rivers often have channels that disappear underground and reappear a few kilometers downstream. In northern Puerto Rico groundwater generally flows downdip to the north (Fig. 3-12). The saturated thickness of the unconfined aquifer is 100 – 300 m (Rodríguez-Martínez, 1995). Freshwater lenses occur along the coast and may extend several kilometers inland (Rodríguez-Martínez, 1995). Groundwater discharge primarily takes place along the coast in the form of seepage into the sea or coastal swamps and lagoons (Giusti, 1978). Groundwater residence times in the aquifer are unknown. Groundwater flow through the aquifer is highly controlled by fractures, especially in the outcrop areas (Rodríguez-Martínez, 1997).

Recharge Processes

The available $\delta^{18}O$ and δD data for northern Puerto Rico indicate spatial and temporal variations in rainwater and groundwater compositions. The monthly $\delta^{18}O$ values of rainwater collected at several locations in northern Puerto Rico have a relatively large range of –5‰ to +1‰ (Fig. 3-13; Rodríguez-Martínez, 1997; IAEA/WMO, 1998). These data represent monthly composite samples collected from 1968 through 1973 in San Juan (IAEA/WMO, 1998) and at different stations located in north-central and northwestern Puerto Rico from 1993 through 1995 (Rodríguez-Martínez, 1997). This range represents seasonal fluctuations similar to those observed on Barbados (Jones et al., 2000). During the wet season, rainwater compositions have lower $\delta^{18}O$ values than the dry season (Fig. 3-14). This seasonal fluctuation of rainwater $\delta^{18}O$ values is related to the amount of rainfall (Fig. 3-15). Groundwater $\delta^{18}O$ values in the unconfined limestone aquifer of northern Puerto Rico display a relatively narrow range of compositions of –3‰ to –2‰. Both groundwater and rainwater compositions lie along the Global Meteoric Water Line (GMWL). Groundwater $\delta^{18}O$ values tend to be more negative towards the north and display no apparent temporal trends (Rodríguez-Martínez, 1997).

As part of this study, groundwater oxygen isotopic data from Rodríguez-Martínez (1997) and rainwater data from the Global Network for Isotopes in Precipitation (GNIP) database for San Juan, Puerto Rico (IAEA/WMO, 1998) were compared using methods similar to Jones et al. (2000). This determines the weighted average $\delta^{18}O$ value of the rainwater that contributes to recharge. The average groundwater composition in northern Puerto Rico is equivalent to the weighted average of monthly rainfall exceeding 190 mm. This suggests that on Puerto Rico, recharge to the limestone aquifer is associated with monthly rainfall exceeding 190 mm. This rainfall threshold value is essentially the same as the rainfall threshold value of 195 mm calculated for Barbados. The coincidence of groundwater compositions with the GMWL suggests that losses due to evaporation prior to recharge are small.

THE LIMESTONE AQUIFER OF NORTHERN GUAM

Guam is an island characterized by size, climate and geology similar to Barbados. The limestone aquifer of northern Guam shares similar characteristics to the Pleistocene limestone of Barbados because, like Barbados, Guam is the subaerially exposed portion of a submarine ridge. In both aquifers, the limestone aquifer rock is underlain by low permeability Tertiary rocks that form an aquitard.

Climate

The climate of northern Guam is similar to Barbados. However, Guam is more humid with annual rainfall of 2,200 to 2,500 mm. Like Barbados, about 60 – 70% of annual rainfall occurs during the wet season that extends from July through November (Ward et al., 1965; Mink and Vacher, 1997).

Geology and Hydrogeology

The Miocene to Pleistocene coral reef limestone occurs on northern half of island forming a plateau with elevations ranging from 180 m in the north to 30 m in the south (Fig. 3-16). The limestone overlies Tertiary-age volcanic rock. In most areas, the contact between coral reef limestone and the volcanic rock lies below sea level (Ward et al., 1965). Limestone deposition starting during the Miocene initially centered around volcanic highs and like Barbados has been uplifted over geologic time (Mink and Vacher, 1997).

The hydrology of northern Guam is dominated by subsurface flow. There are no perennial streams and any surface runoff that occurs is short-lived and quickly infiltrates through sinkholes or dry valleys (Ward, 1961; Ward et al., 1965; Mink and Vacher, 1997). The limestone aquifer is primarily composed of freshwater lenses that occur where the base of the limestone lies below sea level (Mink and Vacher, 1997). Little groundwater occurs where base of limestone lies above sea level. The aquifer rock has an average porosity 10 – 25% (Mink and Vacher, 1997). The freshwater lens on Guam is up to 30 m thick. Groundwater flow generally takes the form of diffuse flow. Groundwater flow rates have been measured at 6 – 15 m day^{-1} (Barner, 1997; Mink and Vacher, 1997). Estimated groundwater residence time for this aquifer are 5 years or less (Barner, 1997). Numerous dry valleys and sinkholes in limestone act as conduits for recharge to the aquifer (Ward, 1961; Ward et al., 1965; Mink and Vacher, 1997). Groundwater discharge from the freshwater lens is characterized by diffuse flow and discrete flow in the form of perennial springs and seeps along the coast (Ward et al., 1965; Jenson et al., 1997). Recharge estimation based on water-balance and groundwater and rainwater chloride concentrations indicate recharge to the limestone aquifer of 35 – 40% of rainfall on Guam (Mink and Vacher, 1997).

Recharge Processes

The $\delta^{18}O$ values of rainwater collected in northern Guam as part of the GNIP project have a relatively large range of –9‰ to +2‰ (Fig. 3-17; IAEA/WMO, 1998). These data represent monthly composite samples collected from 1962 through 1966 and 1973 through 1977 (IAEA/WMO, 1998). This range represents seasonal fluctuations similar to those observed on Barbados (Jones et al., 2000). During the wet season, rainwater compositions have lower $\delta^{18}O$ values than the dry season (Fig. 3-17). This seasonal fluctuation of rainwater $\delta^{18}O$ values is related to the amount of rainfall (Fig. 3-18). As part of this study three groundwater samples were collected on Guam (Fig. 3-16). These groundwater samples display a relatively narrow range of $\delta^{18}O$ values of –6.7 ‰, –6.1 ‰, and –5.1 ‰, respectively. Both groundwater and rainwater compositions lie along the GMWL (Fig. 3-19). This indicated negligible effects of evaporation of rainwater prior to recharge.

Comparison of groundwater and rainwater $\delta^{18}O$ values can be used to estimate recharge at specific sites or for the overall aquifer (Jones et al., 2000). This determines the weighted average $\delta^{18}O$ value of the rainwater that contributes to recharge. By applying this method to the Guam groundwater samples, recharge estimates for the three sample locations in northern Guam fall within the range of 70-100 % of average annual rainfall. This method also indicates that recharge will take place associated with monthly rainfall exceeding 200 mm, a rainfall threshold remarkably similar to those of Puerto Rico (190 mm) and Barbados (195 mm). The rainfall threshold of Guam normally occurs during the wet season months of July through November (Fig. 3-17). This indicates that the recharge period on Guam is about five months, much longer than on Barbados (one month) and would explain the high estimated recharge rates.

DISCUSSION

It has been demonstrated on Barbados that oxygen isotopes in groundwater and rainwater can be used to estimate recharge and indicate recharge seasonality and spatial distribution (Jones et al., 2000). This can be achieved because on Barbados the oxygen isotopic composition of rainwater is primarily influenced by the amount of rainfall. This results in seasonal fluctuations of rainwater composition that allow us to infer the recharge seasonality. Similar relationships between rainfall amounts and rainwater oxygen isotopic compositions are observed on Puerto Rico and Guam (Fig. 3-20). This relationship does not exist on subtropical or temperate islands, such as Bermuda (Fig. 3-20). Barbados, Puerto Rico and Guam are all characterized by tropical climates with distinct wet and dry seasons. These conditions produce a relatively wide range of rainwater $\delta^{18}O$ values that represent seasonal fluctuations. On the other hand, the temperate climate and almost uniform distribution of rainfall on Bermuda produce no apparent relationship between rainfall and rainwater oxygen isotopic compositions. Consequently, it may not be possible to use groundwater and rainwater oxygen isotopes to estimate recharge in temperate climates. It may still be possible use oxygen isotopes to constrain the seasonal distribution of recharge in temperate climates if there is a relationship between rainwater oxygen isotopic compositions and either temperature or rainfall. Due to the complex climate of Bermuda, rainwater $\delta^{18}O$ values neither display seasonal fluctuations nor statistically significant relationships with either temperature or rainfall. Consequently, oxygen isotopes can neither be used to estimate the amount of recharge nor constrain the seasonality of recharge on Bermuda.

The unconfined limestone aquifer of northern Puerto Rico displays some similarities to much smaller composite island aquifers, such as the limestone aquifers of Barbados and Guam. The most obvious similarity is the restriction of freshwater lenses to coastal areas due to the presence of an underlying aquitard. There are major differences, however, between the unconfined aquifer on Puerto Rico and composite island aquifers because the Puerto Rican aquifer is: 1) much larger and thicker than most island aquifers and will consequently have much longer groundwater flow-paths and residence-times; and 2) a more complex flow system displaying significant lateral and vertical flow components, as well as interaction with the underlying confined aquifer. Comparison of the limestone aquifers on Barbados, Guam and Puerto Rico show many similarities. They are karst aquifers characterized by diffuse recharge through soil and limestone and discrete recharge through karst features. Recharge on Barbados and Puerto Rico is associated with the peak of the wet season, while on Guam conditions conducive for recharge typically occur throughout the wet season (Jones et al., 2000). However, the limestone aquifer on Puerto Rico is much larger and has a more complex flow system characterized by multiple permeable layers and recharge and discharge zones.

Oxygen isotopic compositions of rainwater collected on Barbados, Guam and at low elevations on Puerto Rico display similar $\delta^{18}O$ values that lie within ranges of –9 to +5‰, -9 to +2‰ and –6 to +3‰ on Barbados, Guam and Puerto Rico, respectively. The slightly wider ranges of values on Barbados and Guam can be attributed to the much longer period of record of approximately 30 and 16 years, respectively, compared to 6 years on Puerto Rico. Rainwater $\delta^{18}O$ values are generally lower on Guam than on the other two islands because of higher rainfall (Fig.3-20). By the amount effect, higher rainfall produces lower $\delta^{18}O$ values (Dansgaard, 1964). This produces lower groundwater $\delta^{18}O$ values on Guam (-7 to –5‰) than on Puerto Rico and Barbados. The apparently similar rainwater oxygen isotopic compositions on Barbados and Puerto Rico produce similar groundwater compositions in the respective aquifers. These groundwater oxygen isotopic compositions lie within ranges of –3 to –2‰ and –4.5 to –2‰ on Puerto Rico and

Barbados, respectively. Despite the similarities in groundwater and rainwater compositions on Barbados and Puerto Rico, the two aquifers display differences in spatial variations of groundwater oxygen isotopic compositions. In northern Puerto Rico, groundwaters are characterized by lower $\delta^{18}O$ values at lower elevations while the opposite trend occurs on Barbados. On Barbados, higher groundwater $\delta^{18}O$ values can be explained by enhanced recharge at lower elevations. The limestone aquifer of northern Puerto Rico is more complex. The spatial variations of groundwater oxygen isotopic compositions on Puerto Rico do not reflect the spatial distribution of recharge. The spatial variations of groundwater $\delta^{18}O$ values may be explained by interaquifer flow (Rodríguez-Martínez, 1997). This interaquifer flow may reflect the upward flow of groundwater characterized by low $\delta^{18}O$ values from the underlying confined aquifer. These low groundwater $\delta^{18}O$ values may reflect: 1) recharge when climatic conditions and rainwater isotopic compositions differed from the present; or 2) groundwater recharge taking place at high elevations, where rainwater is characterized by lower $\delta^{18}O$ values. Further research is required to explain the spatial distribution of groundwater oxygen isotopic compositions on Puerto Rico using rainfall and rainwater data from stations that are close to the groundwater sample sites and therefore representative of actual recharge water compositions.

Conditions for the occurrence of recharge inferred from comparison of rainwater and groundwater oxygen isotopic compositions in the respective aquifers are surprisingly similar on all three islands. The relationship between average groundwater $\delta^{18}O$ values and rainwater oxygen isotopic compositions indicate that in all three aquifers: 1) recharge requires monthly rainfall in excess of 190-200 mm; and 2) there is little evaporation of infiltrating water prior to recharge. The similarity among the rainfall thresholds that must be exceeded before recharge occurs suggests similarities in the factors, such as soil permeability, that influence the occurrence of runoff. The narrow range of rainfall thresholds is unexpected because one would expect significant variability from island to island. However, when one considers that all three islands studied in this investigation are characterized by similar tropical climates and parent rocks, it should not be surprising to find similar soil types with similar properties (Buol et al., 1989; Fitzpatrick, 1995). One can speculate that the rainfall thresholds observed on Barbados, Guam and Puerto Rico may occur in many tropical karst aquifers. To test this hypothesis, further study may be conducted on other tropical islands. These studies should not only include comparisons of groundwater and rainwater oxygen isotopic compositions but also investigate relationships between rainfall and surface runoff.

CONCLUSIONS

The Pleistocene limestone aquifer of Barbados is a composite limestone island aquifer composed of Pleistocene coral reef limestone underlain by a deep-sea sedimentary aquitard. Groundwater flow paths in this aquifer are controlled by the topography of the top of the aquitard. Interannual variation of recharge to the Pleistocene limestone aquifer generally fluctuates in response to ENSO. This interannual variation shows how recharge to the aquifer has fluctuated over time and is therefore a general indicator of how climatic conditions may influence recharge in the future. However, the relationship between recharge and ENSO on Barbados is complicated by other factors that also influence interannual variations of rainfall and therefore recharge.

The limestone aquifers of northern Puerto Rico and Guam display some similarities to the aquifer on Barbados. However, the limestone aquifer of northern Puerto Rico displays significant differences due to its much larger size and more complex flow system. The similar climatic and geologic conditions that exist on Barbados, Guam and Puerto Rico produce similar relationships between rainwater and groundwater oxygen isotopic compositions that allow us to determine the seasonal distribution of recharge and rainfall thresholds that must be exceeded before recharge occurs. These rainfall thresholds indicate that recharge on Barbados and Puerto Rico is only associated with the peak wet season months while the more humid climate of Guam results in recharge throughout the wet season, as well as during some dry season months. Consequently, estimated recharge rates on Guam are much higher (70 – 100% of average annual rainfall) than recharge estimates on Barbados (15-25 %). The narrow range of rainfall thresholds of 190-200 mm per month found for all three limestone aquifers studied is surprising. These results indicate that similar conditions are required in order for runoff, the prerequisite for discrete recharge, to occur. This narrow range may be attributable to the similar climate and geology that produce soils with similar hydraulic properties in all of these settings.

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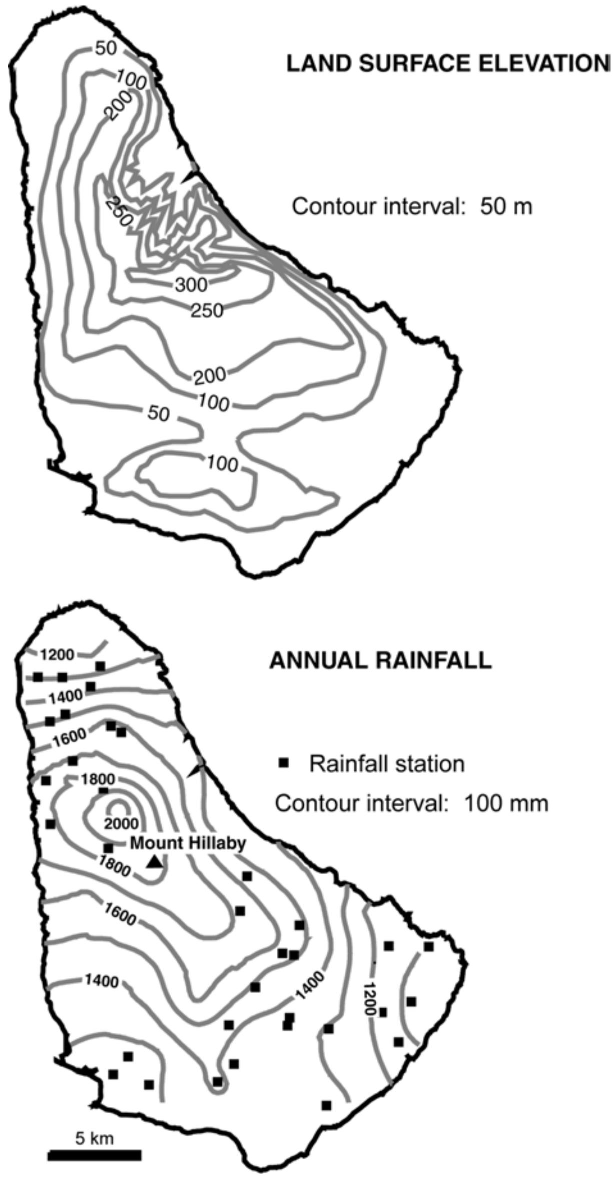

Figure 3-1. The distribution of annual rainfall (1992) on Barbados. Total annual rainfall is highest at the center of the island. Rainfall data obtained from the Caribbean Institute of Meteorology and Hydrology.

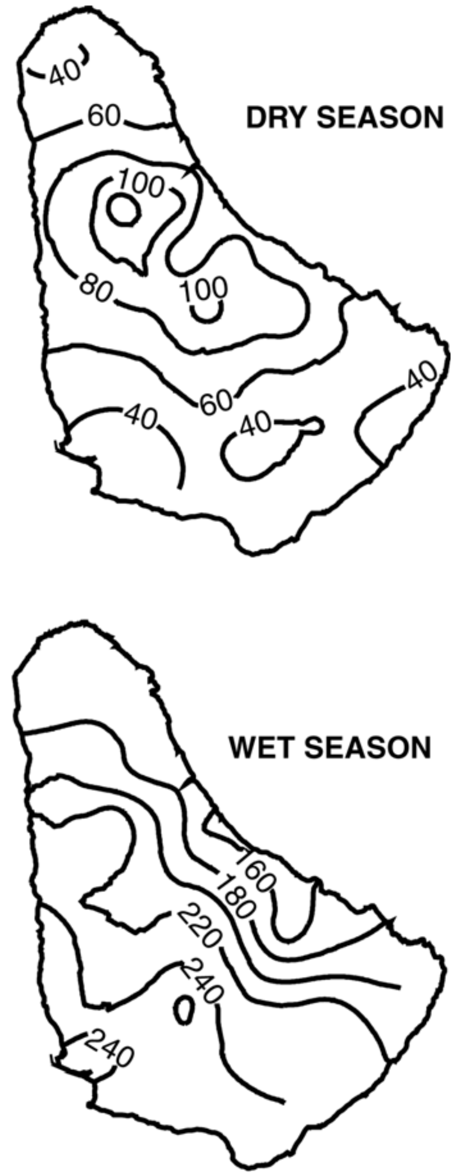

Figure 3-2. Wet season rainfall is highest on the western, leeward side of Barbados, especially at the peak of the wet season. Dry season rainfall is heaviest at the center of the island. Rainfall data obtained from the Caribbean Institute of Meteorology and Hydrology.

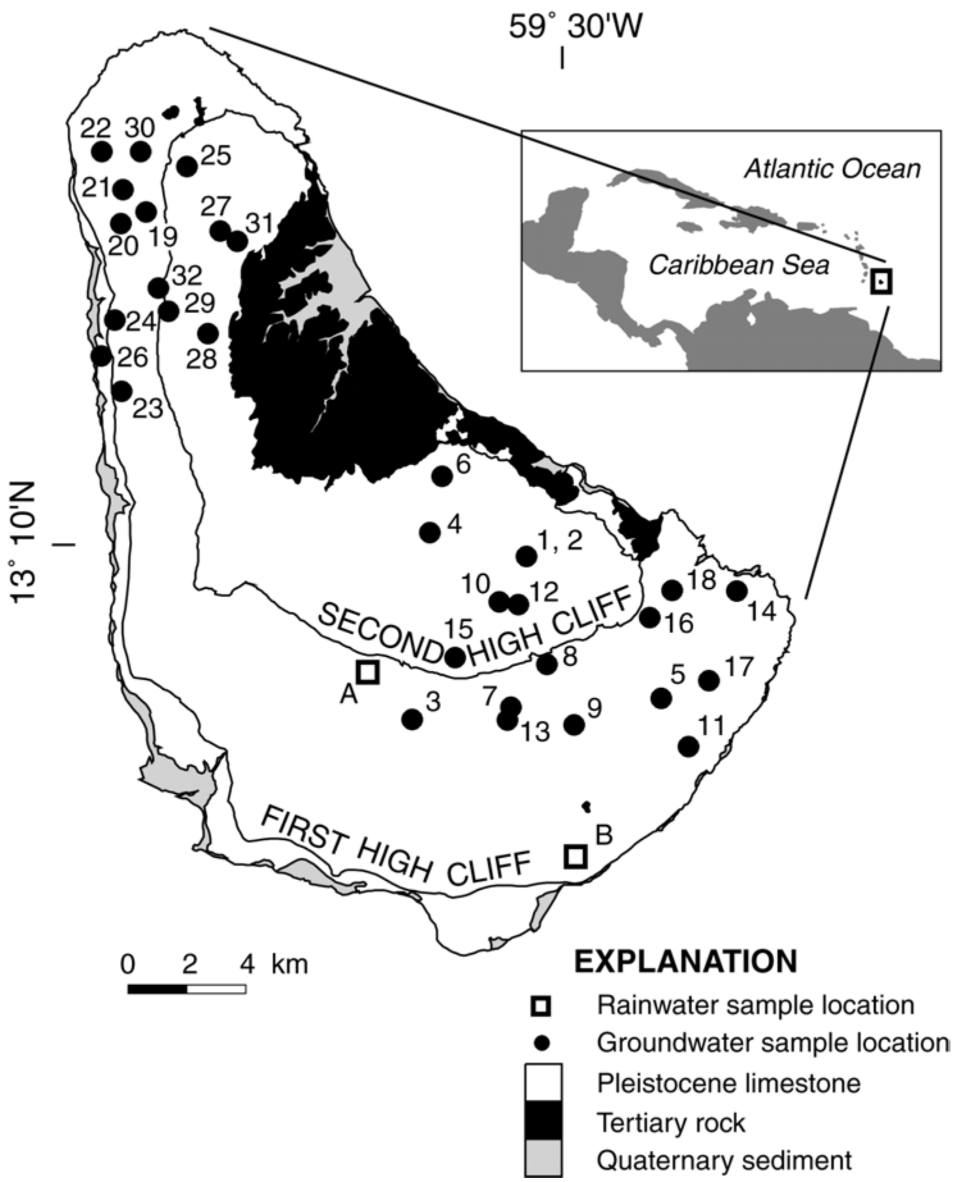

Figure 3-3. Geologic map of Barbados. The Pleistocene limestone that comprises the aquifer occurs in the northern, western and southern portions of the island. The Second High Cliff is approximately 30 m high and has been identified as a major site for discrete recharge to the underlying aquifer. Adapted from Directorate of Overseas Surveys 1:50,000 geologic map (1983).

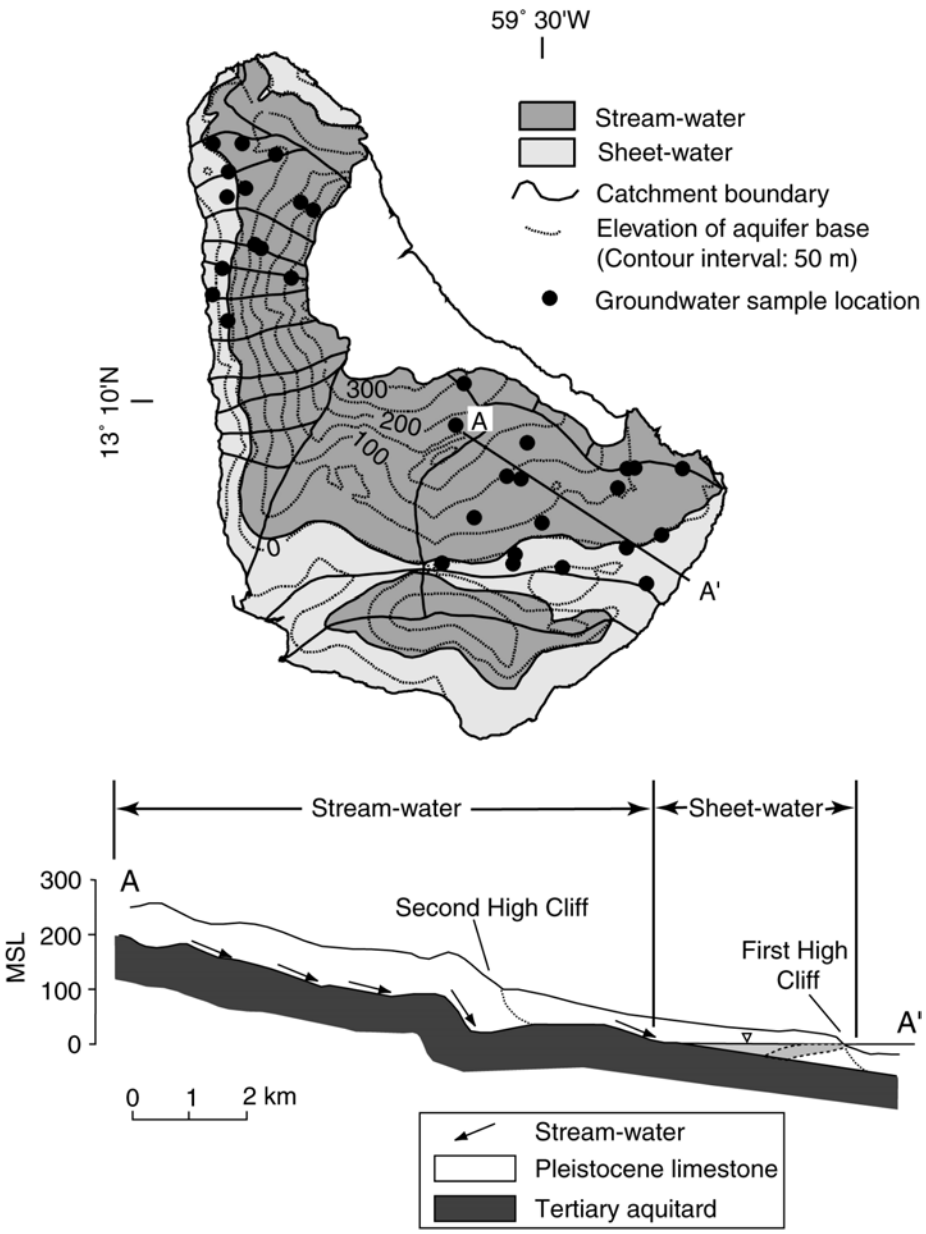

Figure 3-4. Hydrogeologic map of Barbados. The Pleistocene limestone aquifer is divided into several groundwater catchments due to the topography of the Pleistocene-Tertiary contact. The contours shown indicate the elevation of the base of the Pleistocene limestone (Adapted from Stanley Associates, 1978; Barbados Ministry of Health et al., 1991).

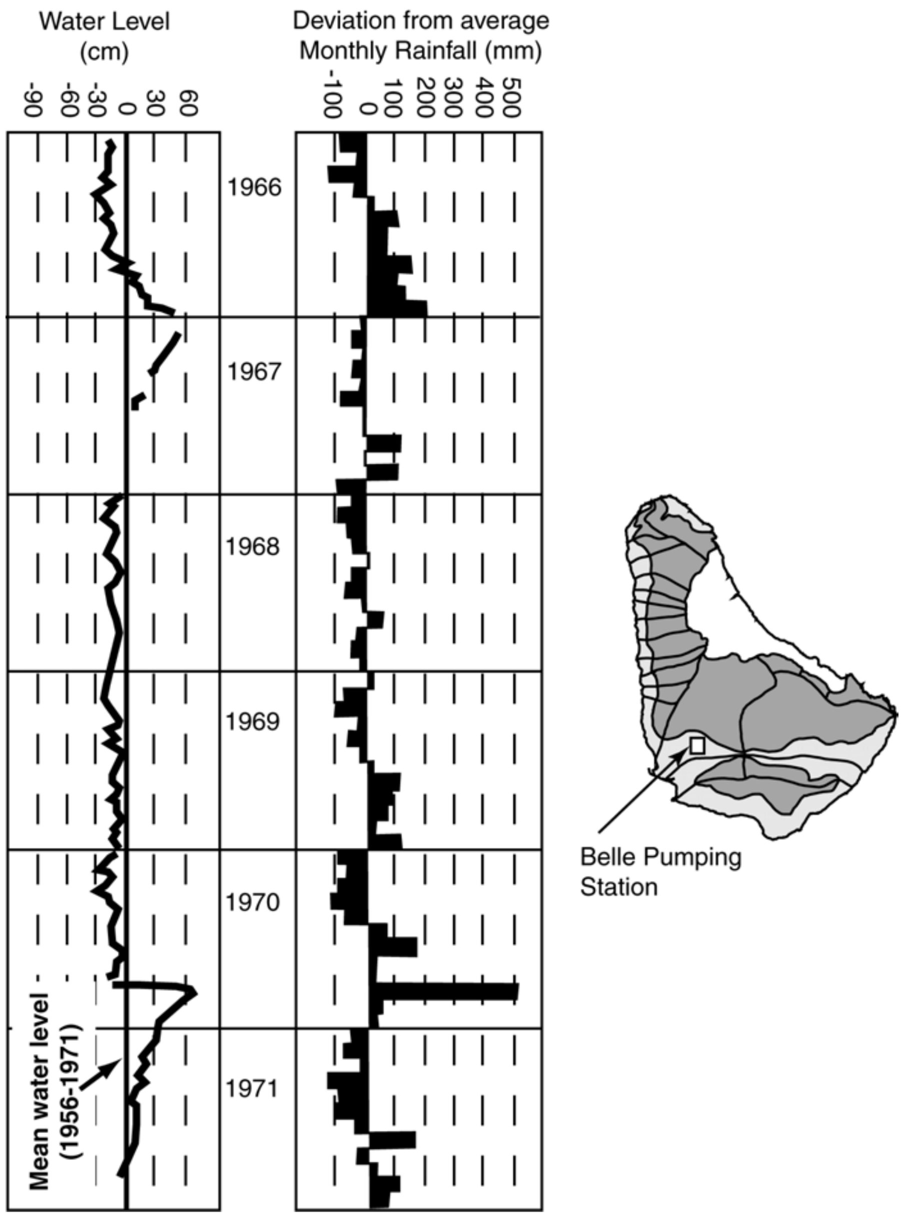

Figure 3-5. Water-level fluctuations in the Sheet-water zone in response to rainfall observed at the Belle Pumping station during the period 1966-1971 (Adapted from Stanley Associates Engineering Ltd., 1978b). The average monthly rainfall is the average rainfall for January, February, etc. for the period 1956-1971.

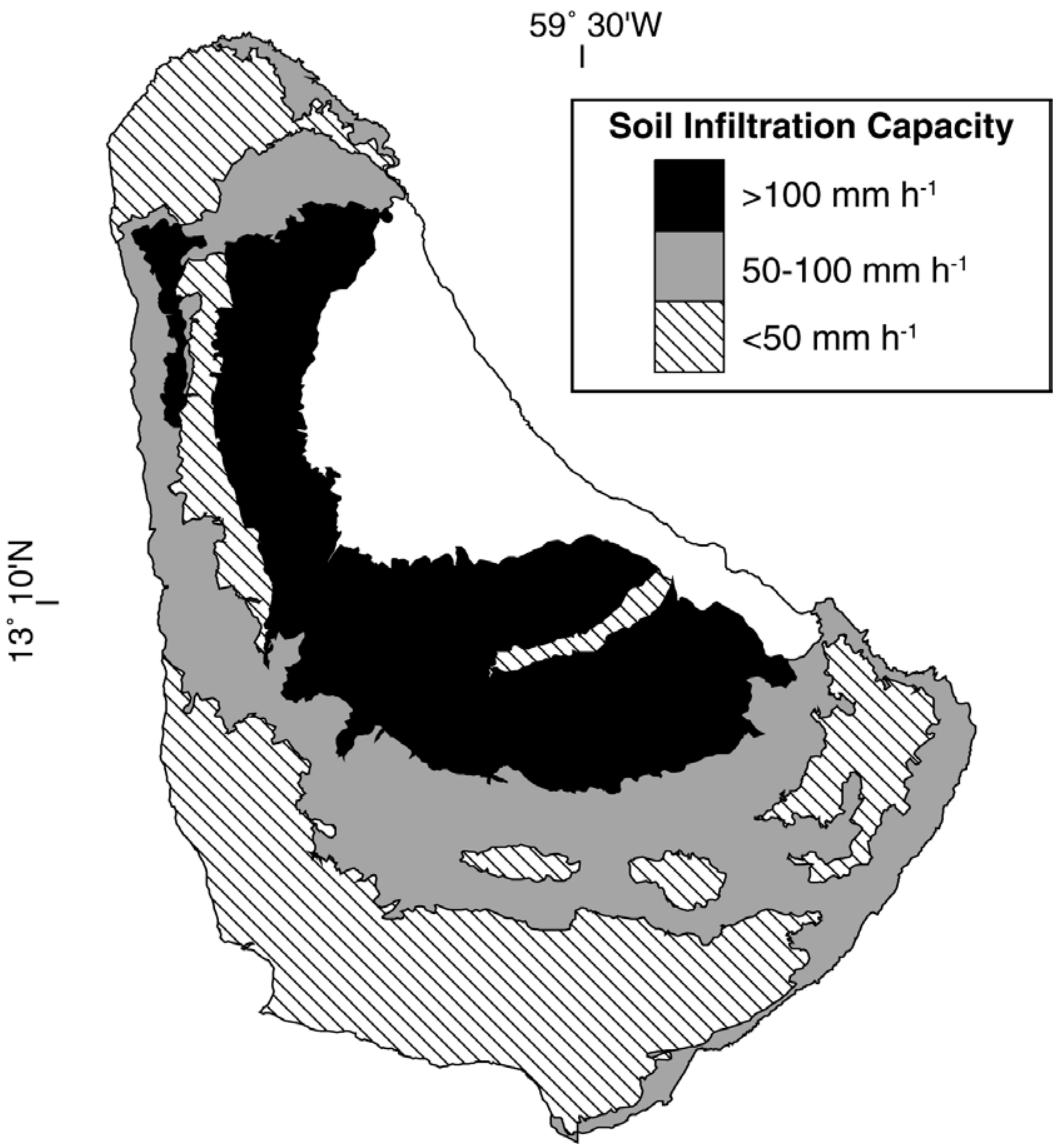

Figure 3-6. The infiltration capacities of soils developed over the Pleistocene limestone aquifer. Barbados soil permeabilities tend to increase with elevation. The most permeable soils occur above the Second High Cliff (Adapted from Vernon and Carroll, 1965; Tullstrom, 1964).

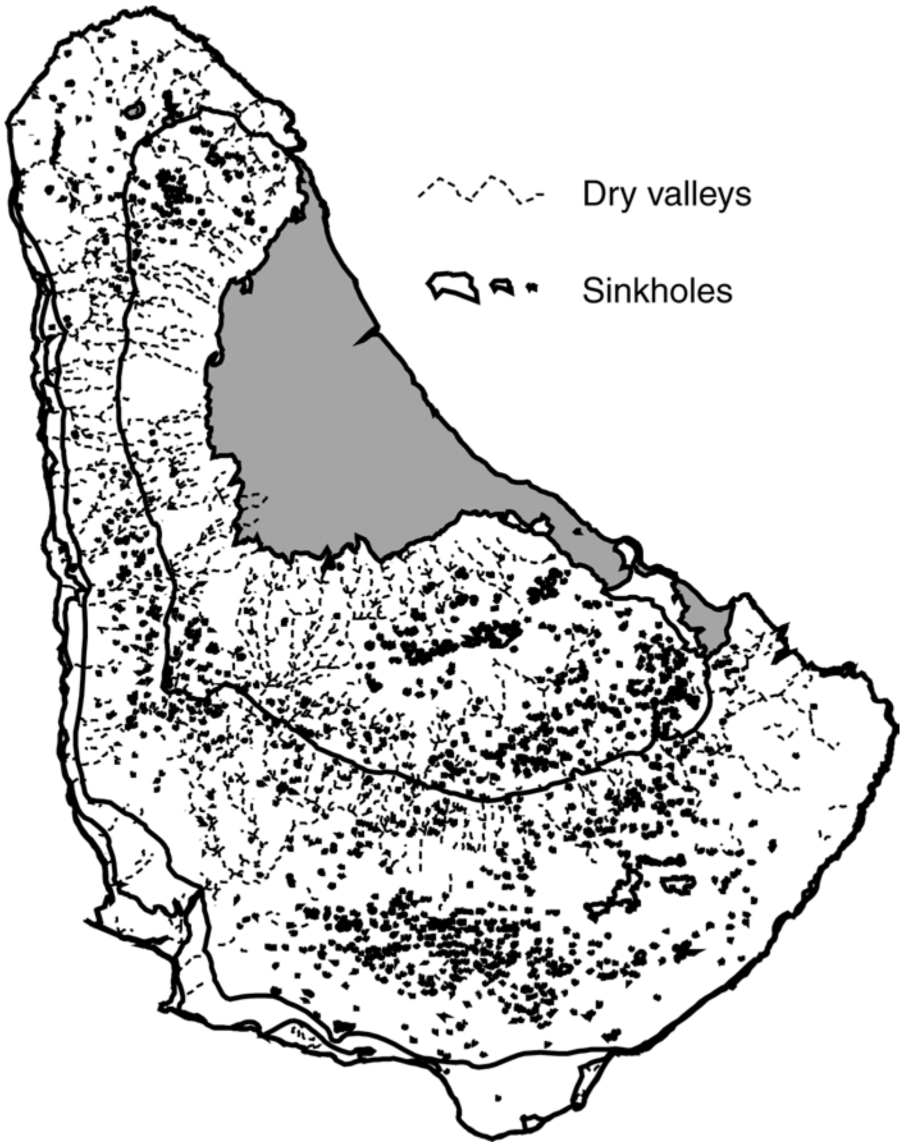

Figure 3-7. The major karst features on Barbados take the form of dry valleys on moderate to steep slopes and sinkhole depressions in flat areas, especially adjacent to the Second High Cliff (Adapted from Directorate of Overseas Surveys 1:10,000 topographic map series).

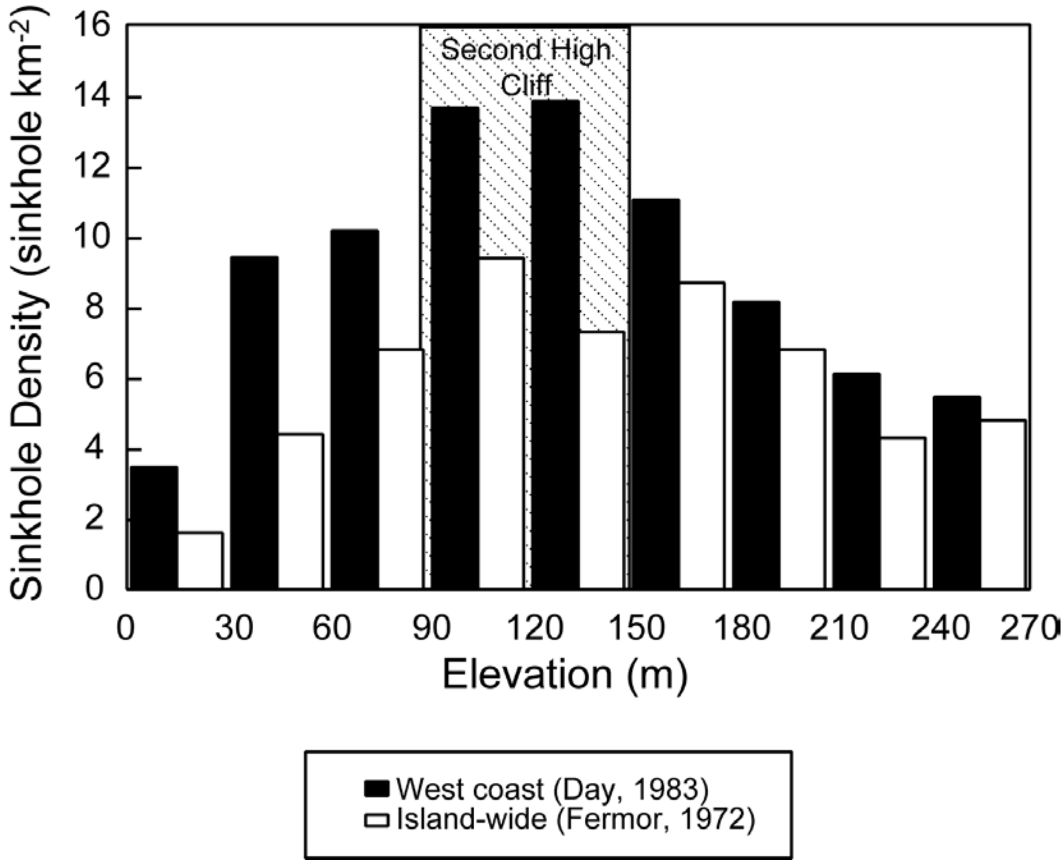

Figure 3-8. Studies by Fermor (1972) and Day (1983) indicate that the sinkhole density on Barbados reaches a maximum at elevations adjacent to the Second High Cliff. These elevations coincide with the low relief areas at top and base of the Second High Cliff.

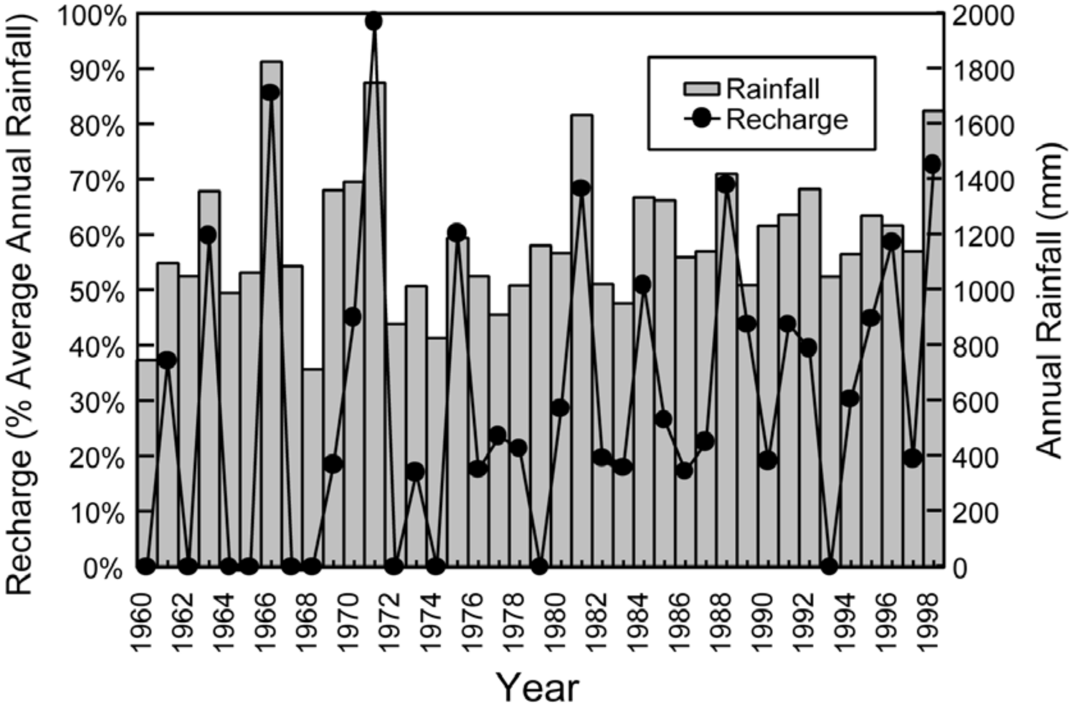

Figure 3-9. Inter-annual variation of recharge on Barbados responds more to the distribution of rainfall throughout the year than total annual rainfall. Consequently, years with very similar amounts of rainfall, for example, 1961 and 1962, may have significantly different recharge estimates.

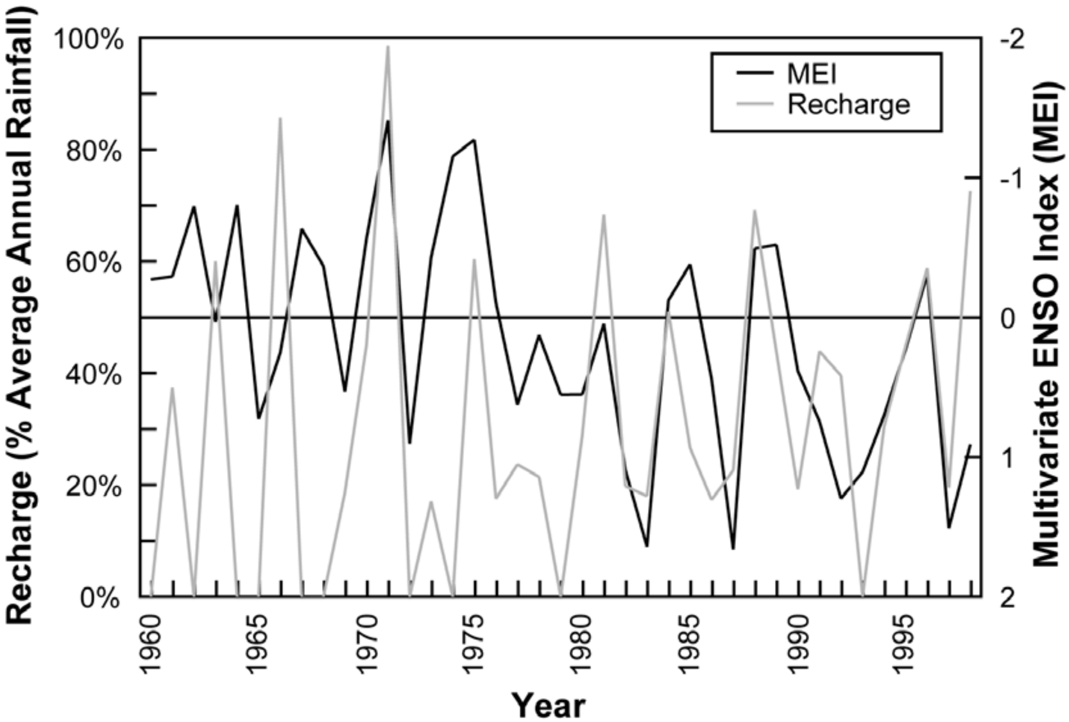

Figure 3-10. Interannual variations of recharge on Barbados display a general inverse relationship with ENSO. This apparent relationship is not statistically significant. This is likely due to the multiple conflicting factors, such as sea surface temperature and wind patterns at different altitudes. These factors influence the interannual variations in the frequency of tropical weather systems and thus indirectly influence the amount of rainfall and recharge on Barbados.

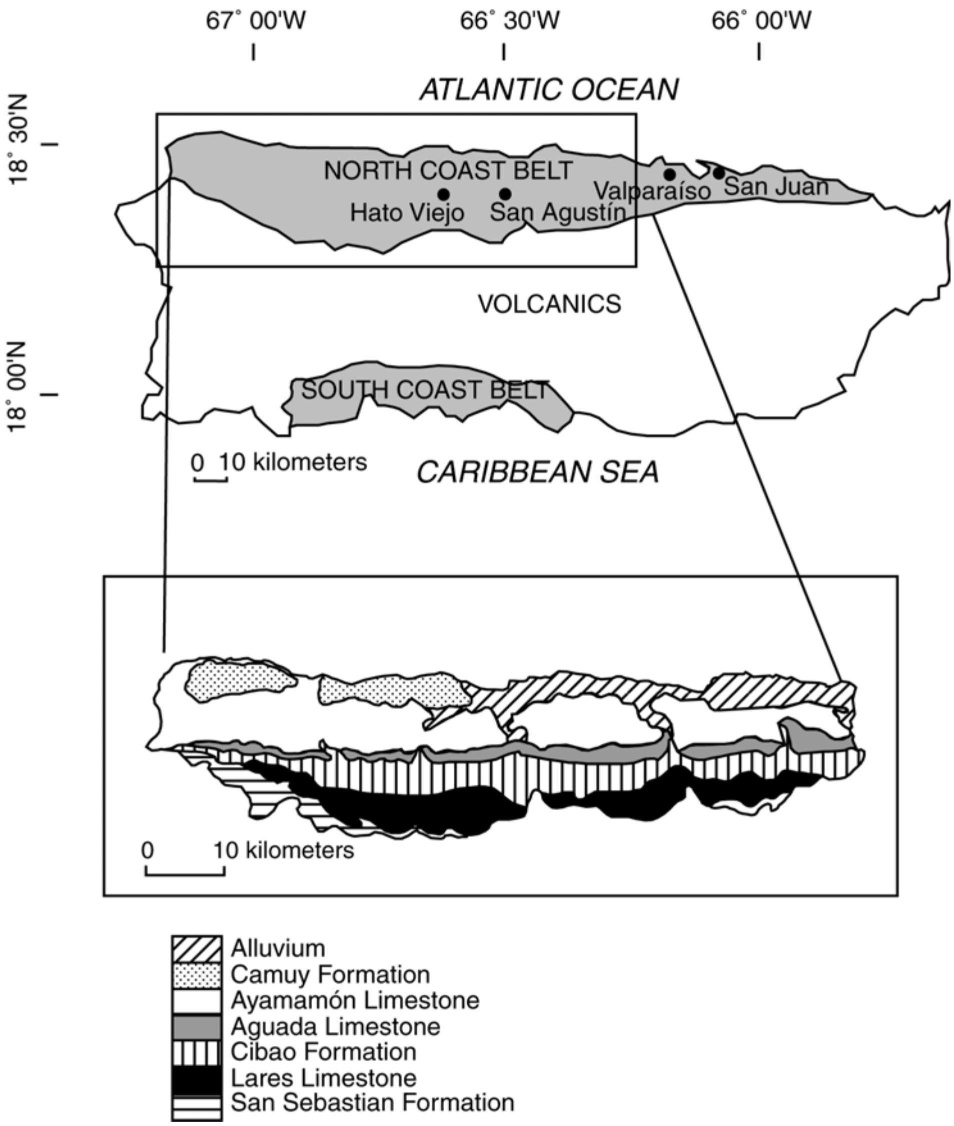

Figure 3-11. Limestone on Puerto Rico primarily occur in belts along the northern and southern coasts of the island flanking the volcanic core of the island. Adapted from Giusti (1978). Rainwater data used in this study was collected at San Juan (IAEA/WMO,1998), and at San Agustín and Valparaíso (Rodríguez-Martínez,1997). Groundwater samples were throughout the North Coast Belt west of Valparaíso.

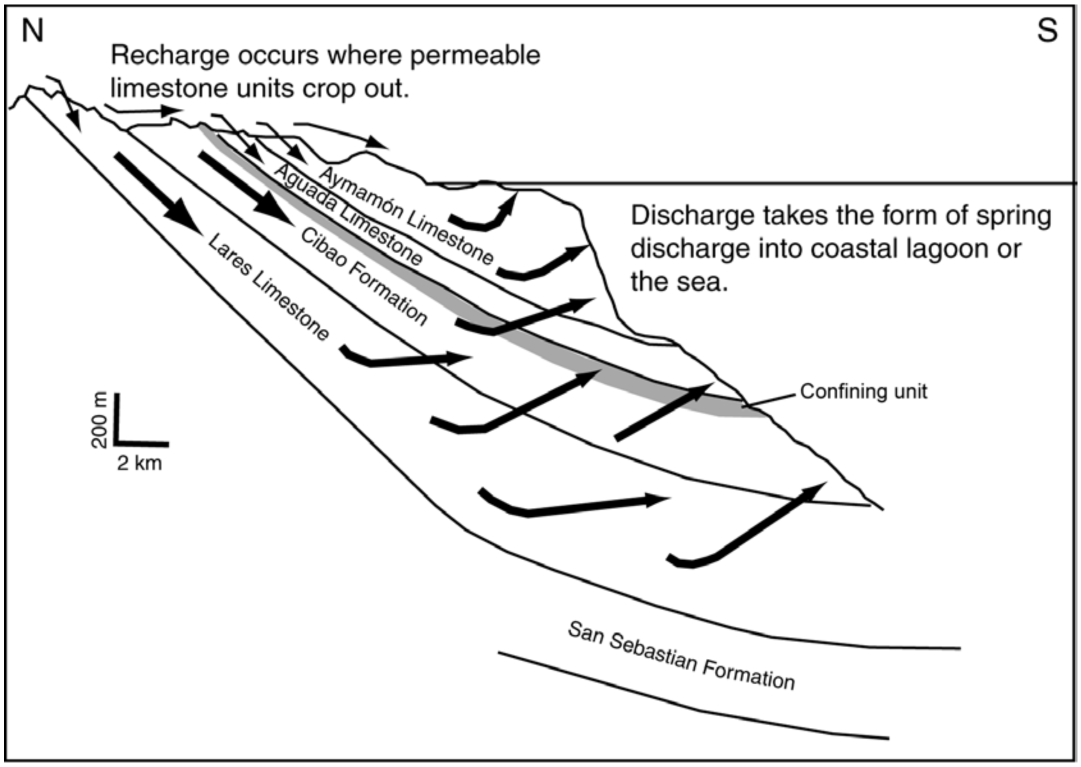

Figure 3-12. Cross-section of limestone aquifers of northern Puerto Rico. The aquifer system of northern Puerto Rico is composed of two aquifers, an unconfined aquifer composed of the Aymamón Limestone and Aguada Limestone, and an underlying confined aquifer composed of part of the Cibao Formation and the Lares Limestone. The confining unit separating the two aquifers occurs in the upper part of the Cibao Formation. Adapted from Giusti (1978).

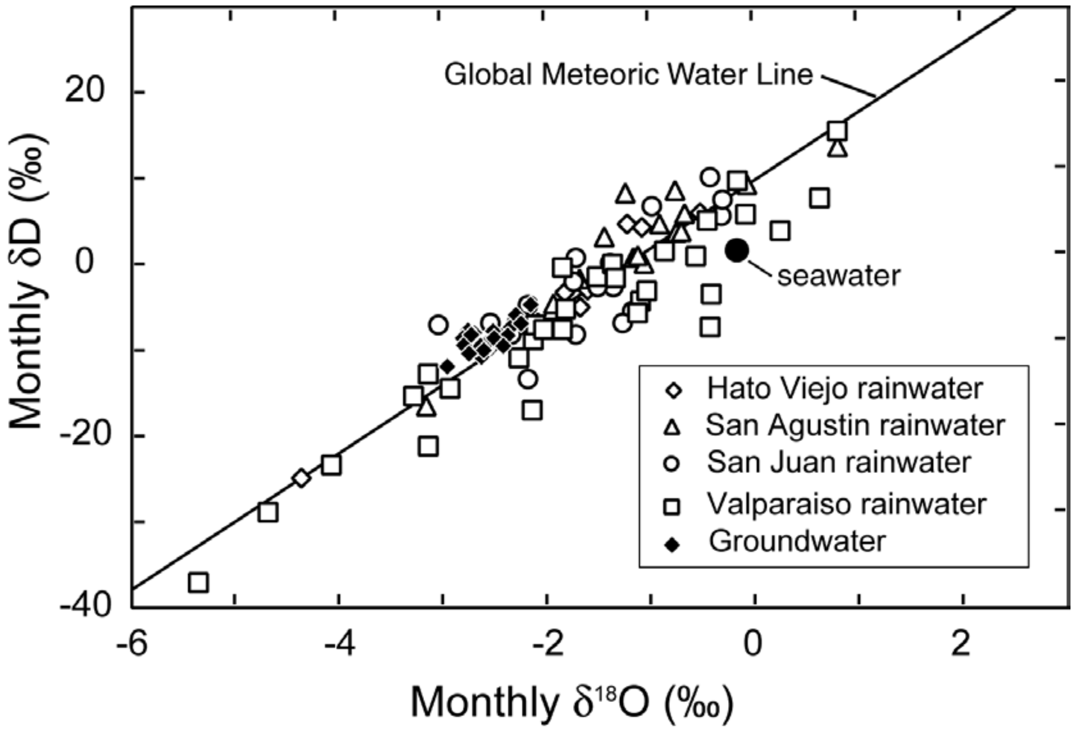

Figure 3-13. The $\delta^{18}O$-δD compositions of rainwater and groundwater associated with the limestone aquifer of northern Puerto Rico. Data from Rodríguez-Martínez (1997) and IAEA/WMO (1998).

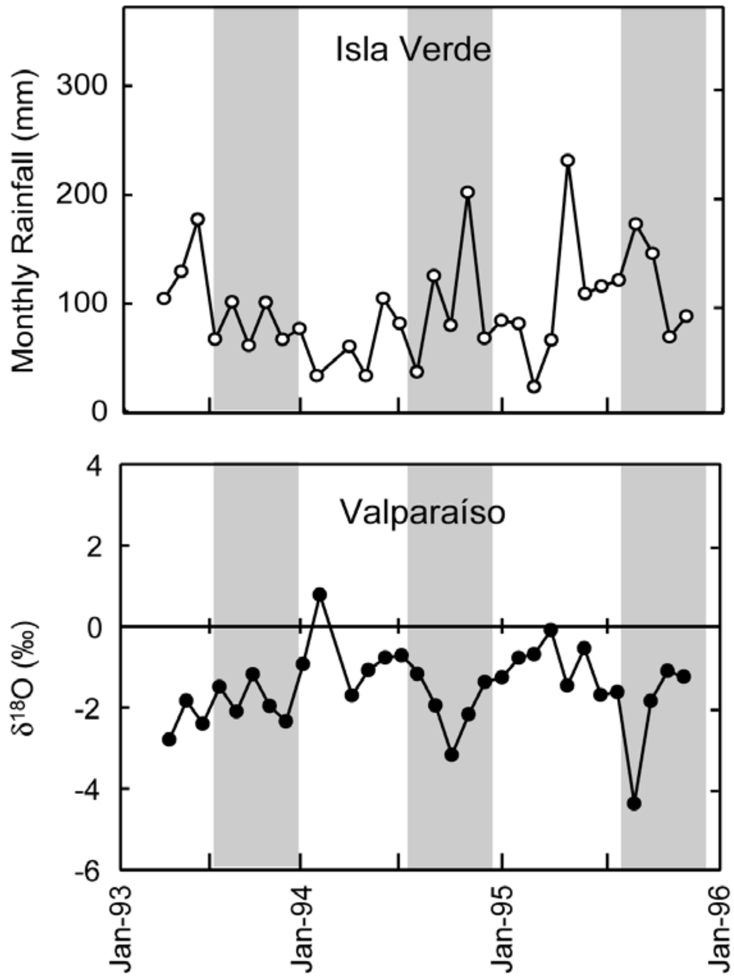

Figure 3-14. Seasonal variations of rainwater oxygen isotopic compositions on Puerto Rico (1993-94). Rainwater $\delta^{18}O$ values are lower during peak wet season months (August to October). The grey shading indicates the peak wet season months. Based on data from Rodríguez-Martínez (1997).

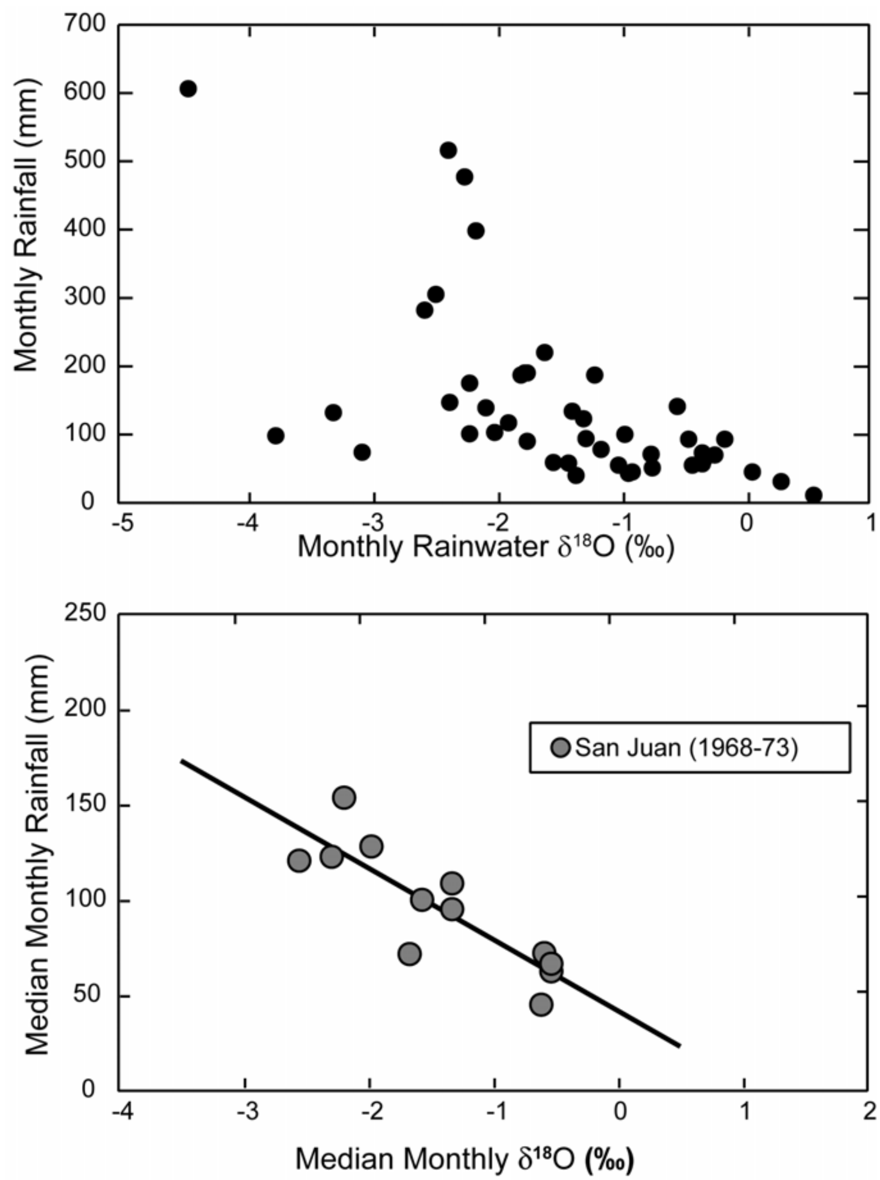

Figure 3-15. The relationship between median monthly rainwater $\delta^{18}O$ values and median monthly rainfall for San Juan, Puerto Rico. Based on 1968-1973 data from GNIP (IAEA/WMO, 1998).

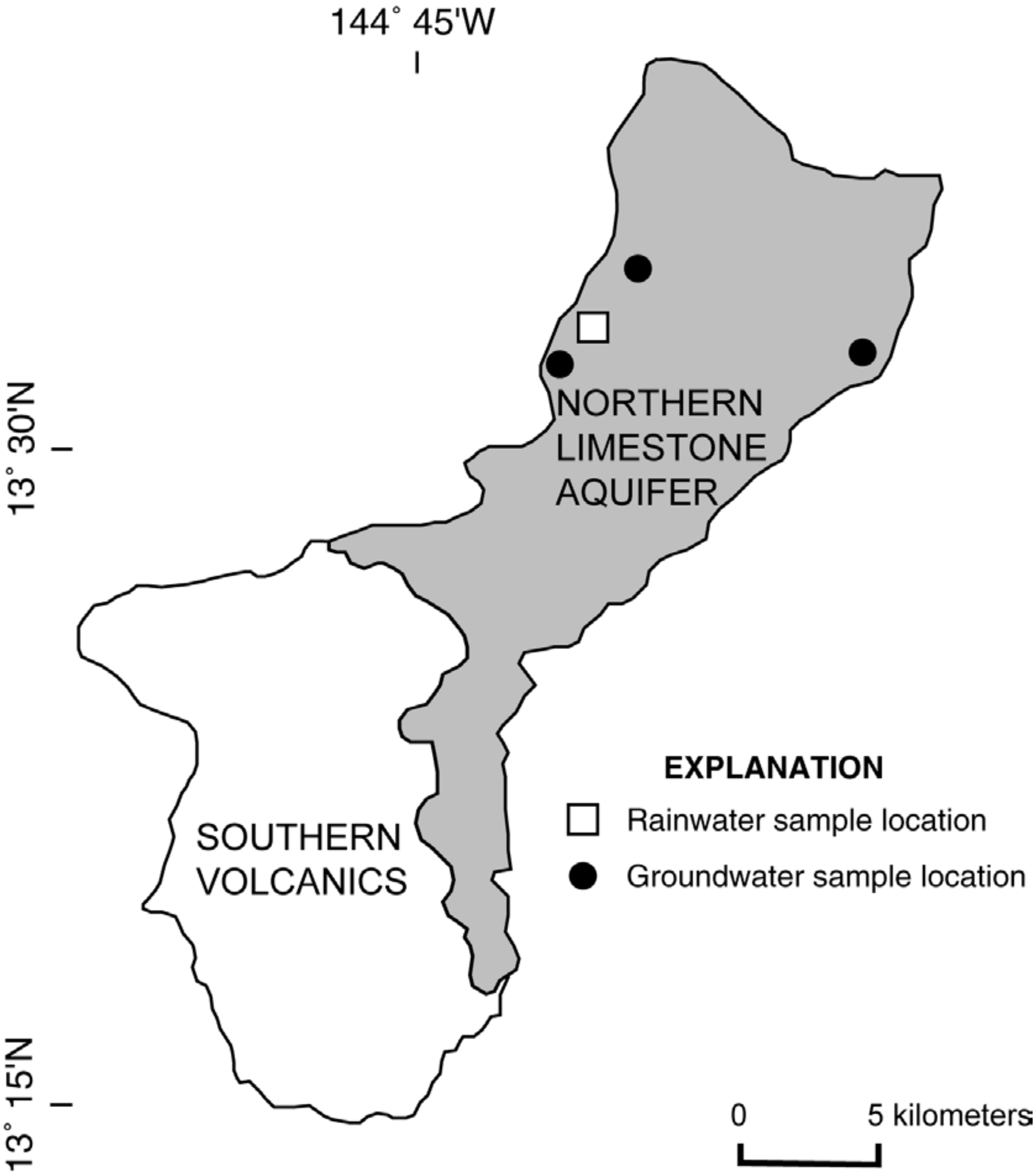

Figure 3-16. Limestone on Guam primarily occurs on the northern portion of the island. For this study groundwater samples were collected at three locations on the island. The rainwater data used in this study was collected as part of the GNIP project during the period 1961-1977 (IAEA/WMO, 1998). Adapted from Ward (1965).

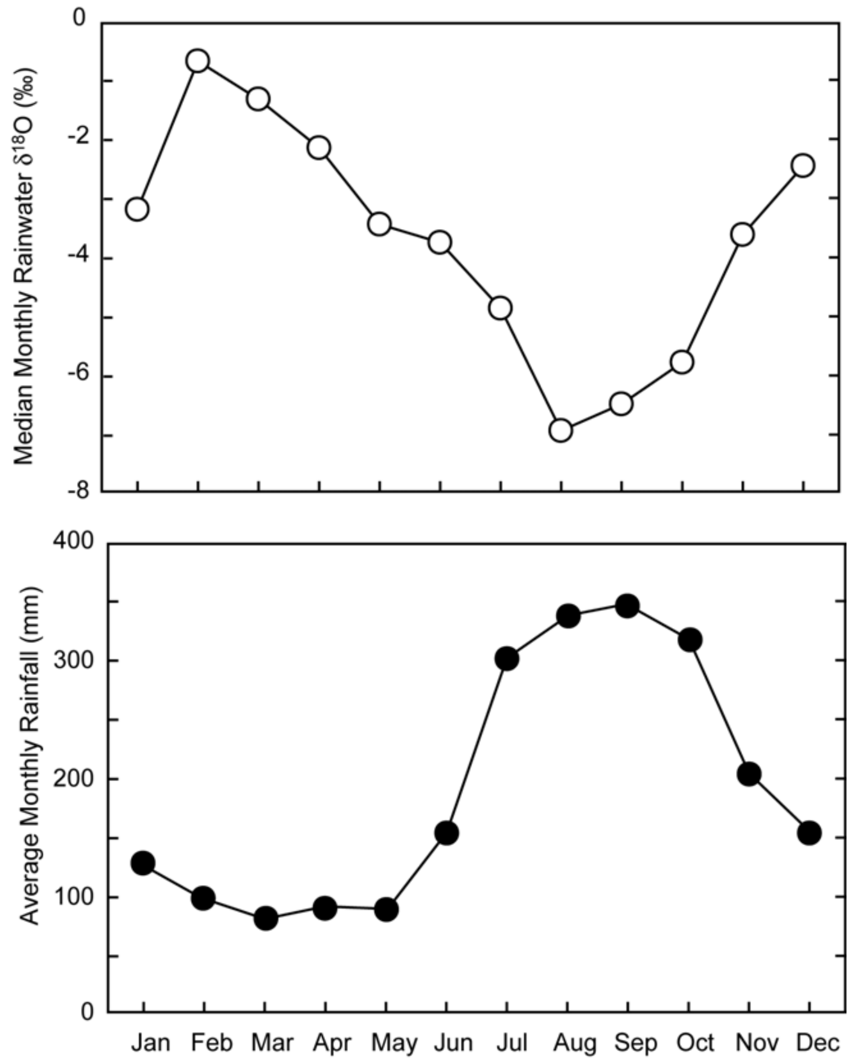

Figure 3-17. Seasonal variations of rainwater oxygen isotopic compositions on Guam (1961-1977). Rainwater $\delta^{18}O$ values are lower during peakwet season months (July through October). Based on data from IAEA/WMO (1998).

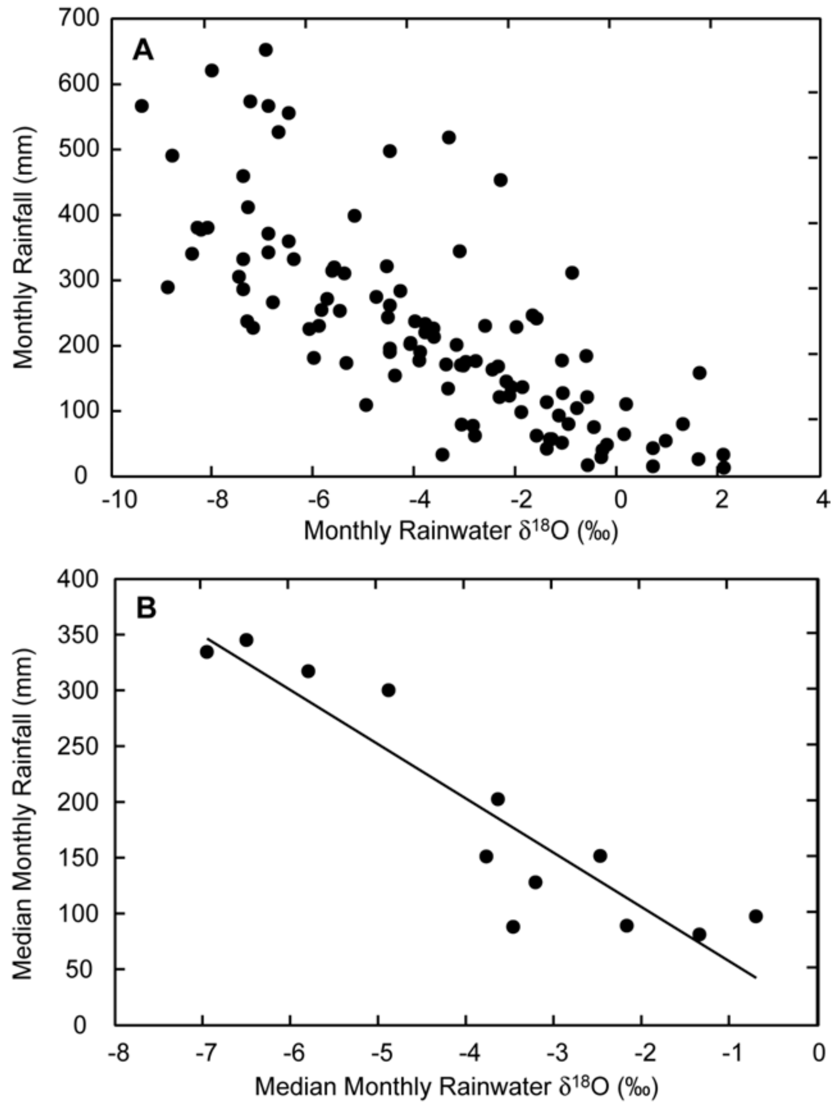

Figure 3-18. The oxygen isotopic composition of Guam rainwater varies as a function of the amount of rainfall.

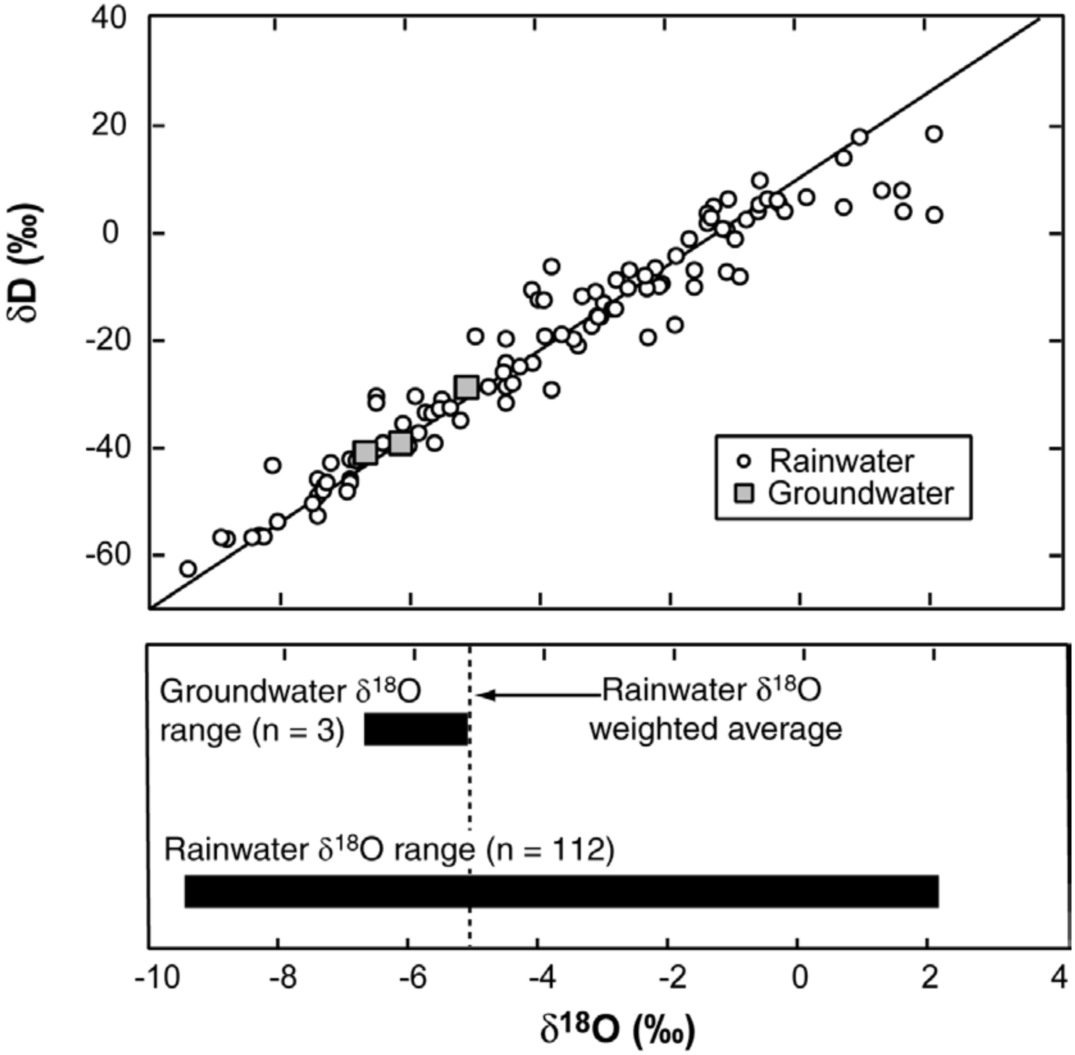

Figure 3-19. The $\delta^{18}O$-δD compositions of rainwater and groundwater associated with the limestone aquifer of northern Guam. Rainwater data from IAEA/WMO (1998).

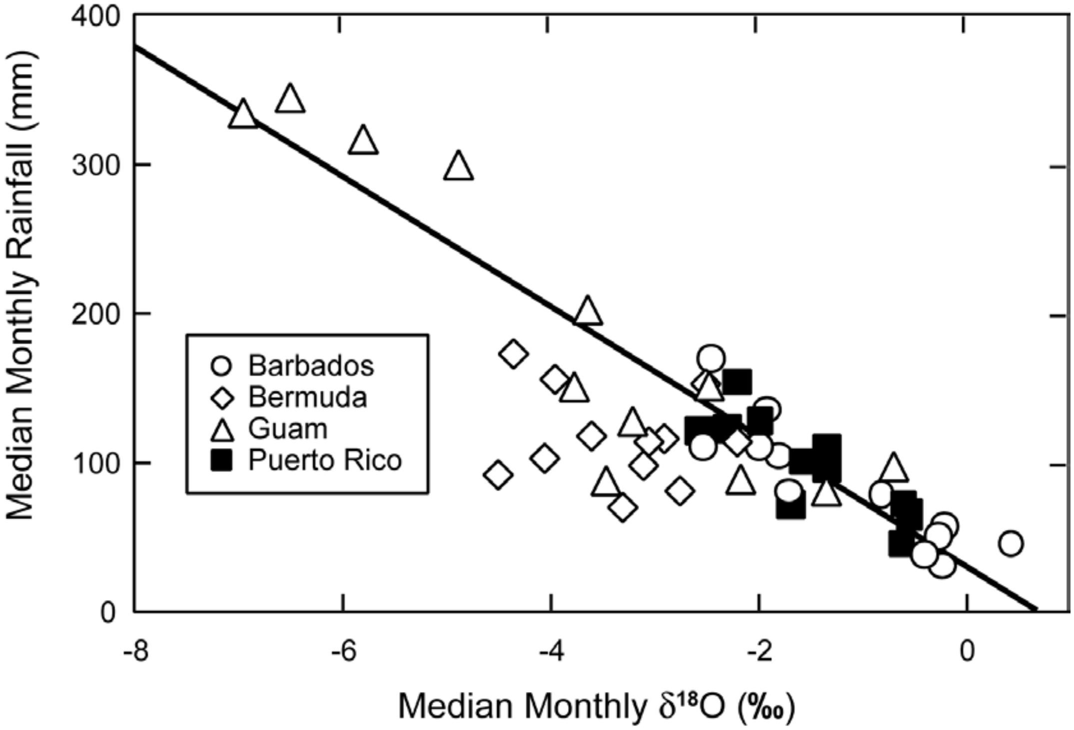

Figure 3-20. Similar relationships between rainfall and rainwater $\delta^{18}O$ values exist on tropical islands, e.g., Barbados, Guam and Puerto Rico. This relationship apparently does not occur on Bermuda, an islandwith a temperate climate. This relationship has implications for whether rainwater oxygen isotopes can be used as a tool to estimate recharge amounts, seasonality and spatial distribution (Based on data from IAEA/WMO, 1998).

CHAPTER 4: THE SPATIAL DISTRIBUTION OF FERTILIZER NITROGEN INPUTS TO A TROPICAL KARST AQUIFER

ABSTRACT

Elevated nitrogen concentrations in groundwater are usually associated with influxes of nitrogen from anthropogenic sources, such as domestic wastewater or fertilizer. The aims of this study are to: 1) estimate the amount of fertilizer nitrogen contributing to elevated groundwater nitrogen concentrations in the Pleistocene limestone aquifer on Barbados, a karst island aquifer; and 2) investigate spatial variations of nitrogen inputs to the aquifer. These aims are achieved by investigating the various components that constitute the nitrogen budget of an aquifer. These nitrogen components include uptake by plants, soil, volatilization, and nitrogen associated with human activities, such as nitrogenous fertilizers and domestic wastewater. Understanding the nitrogen budget at the scale of an island aquifer potentially adds insight into the global nitrogen budget.

The results of this study indicate that nitrogen in Barbados groundwater is primarily derived from the widespread application of nitrogenous fertilizers. Nitrogen budget calculations in this study suggest that the overall contribution from domestic wastewater to groundwater in the areas studied is small relative to nitrogen fluxes from the leaching of fertilizers, although elsewhere wastewater may be an important source of groundwater nitrogen. The spatial distribution of average

nitrogen leaching rates on Barbados mimics groundwater recharge rates. This indicates that nitrogen leaching is: 1) more intense in areas characterized by higher groundwater recharge rates; and 2) recharge plays a greater role in determining the spatial distribution of nitrogen inputs to the aquifer than land use.

INTRODUCTION

There is a worldwide historic trend of increasing nitrate in surface water and groundwater (Schlesinger, 1991). This trend has been attributed to human activities, such as increasing use of nitrogen fertilizers and urbanization, especially during the twentieth century (Schlesinger, 1991). On the scale of a small island aquifer, the study of the nitrogen cycle involves consideration of the same nitrogen sources and sinks considered at the global scale. These sources and sinks are human activity, vegetation, atmosphere, soil, groundwater and surface water. At the global scale, groundwater does not play a major role in the nitrogen cycle because at that scale groundwater is a much smaller reservoir than the atmosphere or surface water. On the other hand, on a small karst island where there is little surface water flow, groundwater plays a significant role in the nitrogen cycle of that island.

High infiltration rates and enhanced porosity make karst aquifers especially susceptible to contamination as a result of human activities. Nitrogen contamination of groundwater has potential adverse health effects, such as methemoglobinemia ("Blue Baby Syndrome"), and ecological effects, especially eutrophication (Tchobanoglous and Schroeder, 1985). This contamination is often the result of over-application of nitrogenous fertilizers, contamination by human or animal waste, or a combination of the two. Effective management of groundwater resources requires identification of different sources of nitrogen and understanding of the spatial distribution of nitrogen inputs to the aquifer. Sources of nitrogen inputs into aquifers are typically related to land use and enter the underlying aquifer with infiltrating water. Consequently, one can predict that the spatial and temporal distribution of nitrogen inputs to an aquifer should also be related to the spatial distribution of recharge. If there can be a means to predict recharge as a function of seasonality or other factors, this may be a way to predict effects of nitrogen pollution. Determination of the spatial and seasonal distribution of recharge for Barbados has already been achieved using oxygen isotopes (Jones et al., 2000). This study is probably the first to indicate that both the spatial and temporal distribution of fertilizer nitrogen entering the aquifer are similar to the distribution of recharge.

The Pleistocene limestone aquifer of Barbados is the primary source of potable water on the island, consequently nitrogen contamination could adversely affect the water supply. Most of the land on the island is used to cultivate crops, or residential and commercial land use. Under natural conditions, groundwater nitrate concentrations are typically <3 mg l^{-1} NO_3-N. Groundwater nitrate concentrations greater than 3 mg l^{-1} NO_3-N are attributed to the influx of additional nitrogen from anthropogenic sources such as fertilizers and wastewater (Bachman, 1984).

On Barbados, the occurrence of nitrogen concentrations exceeding 3 mg l^{-1} NO_3-N in groundwater (4 - 10 mg l^{-1} NO_3-N) is ubiquitous, however, these elevated nitrogen concentrations generally fell below the World Health Organization drinking water standards (10 mg l^{-1} NO_3-N) in the areas studied. Determining the sources and distribution of nitrogen contamination in aquifers is important especially when the aquifer under investigation is an important source of potable water. Additionally, understanding nitrogen fluxes through aquifers may give insights into the effects of recharge processes on groundwater geochemistry because nitrogen inputs into an aquifer are associated with inflow of infiltrating water. This is particularly applicable to karst aquifers that are vulnerable to contamination due to rapid, discrete recharge through karst features. Studying nitrogen in groundwater will also provide information on major anthropogenic sources of dissolved constituents in groundwater by establishing a relationship between groundwater compositions and land use. Understanding the spatial distribution of nitrogen inputs will indicate areas of an aquifer that are more susceptible to contamination not only by fertilizers but also other agricultural chemicals, such as pesticides.

The parts of the Pleistocene limestone aquifer studied in this investigation are located in less populated areas on the island. The elevated nitrogen concentrations have previously been assumed to be primarily derived from the widespread use of nitrogenous fertilizers in the cultivation of crops, primarily sugar cane (Klohn-Crippen Consultants Ltd., 1997; Jones et al., 1998). These elevated nitrogen concentrations have been assumed to reflect the almost uniform distribution of cultivated crops throughout the island, accounting for about 60% of land use.

The purpose of this study is to estimate the nitrogen budget of the Pleistocene limestone aquifer of Barbados with the aim of: 1) evaluating potential nitrogen sources and sinks; 2) estimating the proportion of applied fertilizer nitrogen that is leached from the soil to the underlying aquifer; and 3) determining the spatial distribution of nitrogen inputs to Barbados groundwater. This research is part of a larger study of the groundwater hydrology and geochemistry of the Pleistocene limestone aquifer of Barbados that primarily focuses on the northwestern and southeastern parts of the island (Banner et al., 1994; 1996; Jones et al., 1998; 2000). This aquifer is well suited for the study of nitrogen fluxes in groundwater because of its well-characterized hydrogeology and hydrogeochemistry (Senn, 1946; Tullstrom, 1964; Harris, 1971; Stanley Associates Engineering Ltd., 1978; Mwansa and Barker, 1996; Klohn-Crippen Consultants Ltd., 1997; Smart and Ketterling, 1997; Jones et al., 1998; 2000). Estimation of nitrogen fluxes requires knowledge of groundwater fluxes through the aquifer. Spatial and temporal variations in recharge were estimated by Jones et al. (2000) study.

Nitrogen Attenuation

Nitrate concentrations in groundwater are generally influenced by the loading of nitrogen and attenuation by denitrification. Denitrification reduces nitrogen concentrations by converting nitrate to easily volatilized nitrogen gases, usually under anaerobic conditions. Nitrification is the process that converts ammonia commonly present in wastewater and fertilizers to nitrate under aerobic conditions. This process generally has no overall effect on total nitrogen concentrations because it simply converts the nitrogen from one form, ammonia, to another, nitrate (Tchobanoglous and Schroeder, 1985).

Nitrification .... $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$ (4-1)

Denitrification .... $4NO_3^- + 5C + 2H_2O \rightarrow 2N_{2(g)} + 4HCO_3^- + CO_2$ (4-2)

STUDY AREA

Climate

The average annual rainfall on Barbados varies from about 1,000 mm yr^{-1} in the north and southeast to more than 2,000 mm yr^{-1} at the center of the island (Fig. 4-1). The wet season extends from June to December and typically accounts for

60% of average annual rainfall. Dry season rainfall is associated with local convection due to moist air flowing over the heated island (Malkus, 1963). During the wet season, rainfall occurs due to the combined effects of moisture associated with: 1) tropical weather systems, such as tropical depressions and hurricanes; 2) the proximity of the Inter-Tropical Convergence Zone (ITCZ); and 3) local convection effects.

Geology and Hydrogeology

The Pleistocene limestone aquifer of Barbados is composed of Pleistocene coral reef limestone underlain by Tertiary age deep-sea sediments that act as an aquitard. This aquifer occurs in the northern, western and southern portions of the island. Due to continuous uplift, the coral reef limestone was deposited outwards from the center of the island forming a series of terraces that decrease in age with decreasing elevation (Taylor and Mann, 1991). There are three main groups of terraces, the Lower Reef, Middle Reef and Upper Reef Terraces separated by the First and Second High Cliffs, respectively (Fig. 4-2).

The Pleistocene limestone aquifer is highly permeable due to the high effective primary and secondary porosity of the limestone. Recharge to the aquifer takes the form of diffuse and discrete infiltration through the soil and underlying limestone to the water table that occurs close to the base of the Pleistocene limestone (Fig. 4-3). Due to the relatively thin saturated zone, the topography of the top of the aquitard controls the groundwater flow paths within the aquifer. Groundwater generally flows from the elevated central portions of the island, westward and southward towards the coast. Discharge from this aquifer primarily takes the form of groundwater discharge along the coastline.

The major element compositions of Barbados groundwater vary from Ca-HCO_3 compositions in inland areas to Na-Cl compositions along the coast (Jones et al., 1998). This range of compositions reflects the impacts of limestone dissolution during infiltration and along flow paths, and freshwater-seawater mixing near the coast, respectively.

Soils

The soils that overly the aquifer on Barbados are primarily the insoluble residue left after weathering of: 1) volcanic ash originating from the Lesser Antilles volcanic arc located about 200 km to the west; 2) Saharan dust; 3) Pleistocene coral reef limestone; and 4) Tertiary deep-sea sediments (Muhs, 1987; 1990; Borg and Banner, 1996). Soils occurring above the Second High Cliff have infiltration rates of approximately 250 mm h^{-1} (Tullstrom, 1964; Fig. 4-4). Below the Second High Cliff, at elevations less than 100 m, infiltration capacities through the soils range from 12.5 mm h^{-1} to 250 mm h^{-1}, but typically are approximately 50 mm h^{-1} (Tullstrom, 1964). Differences in soil infiltration capacities can be attributed to differences in soil maturity. The predominant clay mineral present in relatively immature soils that occur at lower elevations is smectite and the lower permeability of these soils can be attributed to the shrink-swell properties of smectite. More mature soils occurring at higher elevations are primarily composed of kaolinite or mixtures of kaolinite and smectite (Vernon and Carroll, 1965; Beaven and Dumbleton, 1966). The Pleistocene limestone is much more permeable than the overlying soils with infiltration rates of 700 mm h^{-1} to 70,000 mm h^{-1} (Tullstrom, 1964; Smart and Ketterling, 1997). In theory, variations of soil permeability with elevation may play a role in nitrogen removal from the soil by denitrification. The effects denitrification are dependent on the occurrence of anaerobic conditions and the residence time of water in the soil zone. These conditions are more likely to occur in soils characterized by relatively low infiltration capacities, such as those that occur at lower elevations on Barbados.

Land use

Agriculture in the form of crop cultivation accounts for approximately 60% of land use on Barbados (Fig. 4-5). In parts of northwestern and southeastern Barbados, agriculture accounts for 70 - 75% of the land use. During any year, more than 80% of this agricultural land is used for the cultivation of sugar cane with the remainder either left fallow or used for food crops (Klohn-Crippen Consultants Ltd., 1997). The rearing of livestock on Barbados is primarily at a subsistence level and accounts for relatively minor land use compared to the cultivation of crops (Klohn-Crippen Consultants Ltd., 1997). The bulk of the population of Barbados resides in the southern and southwestern parts of the island. In the study areas, moderate to densely populated areas account for 10 - 15% of the land. However, except for a few small areas along the Second High Cliff in the southeast, these populated areas are primarily restricted to the coast, down-gradient of most of the wells sampled in this study. Consequently, one could expect that in the areas under investigation the primary source of nitrogen in the groundwater would be from fertilizers used in the cultivation of crops because the other major potential source of nitrogen is relatively small. This study investigates whether estimated nitrogen fluxes can be used to confirm this hypothesis.

GROUNDWATER AND RAINWATER SAMPLING

In this investigation, groundwater samples were collected at 32 sites (29 wells, 2 caves and a spring) in southeastern and northwestern Barbados in July-August 1994 and January 1996 (Fig. 4-2). This sampling schedule was followed to reflect groundwater conditions during wet and dry seasons in groundwater catchments with contrasting flow-path lengths. Hydraulic gradients are steeper and groundwater flow paths shorter in the groundwater catchments in northwestern Barbados than in the southeast. Forty nine rainwater samples were collected at Site A between March 1997 and July 1998 (Fig. 4-2).

The nitrate concentrations in the rainwater and groundwater samples collected in this investigation were analyzed using single column ion chromatography (IC) at the University of Texas at Austin. Analytical uncertainty for the NO_3 analyses was ≤5% (2σ). Nitrate concentrations in the groundwater lie within the range 4 - 9 mg l^{-1} NO_3-N in northwestern groundwater catchments and 5 - 10 mg l^{-1} NO_3-N in the southeastern part of the island (Table 4-1). Ammonium concentrations in groundwater samples were measured in the field using a Milton Roy spectronic mini 20 field spectrophotometer with an accuracy of ±1%. There is no apparent spatial relationship between groundwater nitrate concentrations at specific locations and groundwater flow paths, although nitrate concentrations generally increase with elevation (Fig. 4-8). This indicates a non-point source of groundwater nitrogen.

NITROGEN BUDGET COMPONENTS

The nitrogen budget constructed here takes into account the different major sources and sinks of anthropogenic nitrogen on Barbados. Potential sources of soil nitrogen are: 1) nitrogenous fertilizers used to cultivate crops, such as sugar cane and vegetables; 2) rainwater; 3) domestic wastewater, particularly in densely populated areas; and 4) soil organic material. Major potential sinks for soil nitrogen include: 1) uptake by plants; 2) leaching from the soil to the groundwater; and 3) volatilization in the form of emissions of N_2, NH_3, and nitrogen oxide gases. The contribution of each of these sources and sinks is estimated here.

Rainwater

The nitrate concentrations in Barbados rainwater samples range from below the detection limit of 0.02 mg l^{-1} NO_3-N (milligrams of nitrate nitrogen per liter) to as high as 0.45 mg l^{-1} NO_3-N, with a weighted average of 0.08 mg l^{-1} NO_3-N. An average rainwater nitrate concentration for use in nitrogen budget calculations was weighted based on daily rainfall. Based on data from Puerto Rico, NH_4 concentrations in rainwater contribute approximately 20 % of nitrogen in rainwater (National Atmospheric Deposition Program, 2001). This would result in an estimated total rainwater N flux of 1.4 kg-N ha^{-1} yr^{-1} on Barbados. The range of nitrate concentrations reflects seasonal fluctuations generally related to the amount of rainfall. Rainwater nitrate concentrations are higher during the dry season than wet season (Fig. 4-6). This seasonal fluctuation can be attributed in part to greater dilution of sea water aerosols dissolved in rainwater during the wet season. There are no apparent differences between wet and dry season groundwater nitrogen concentrations (Table 4-1).

Nitrogenous Fertilizers

Fertilizers are applied early in the sugar cane growing season, over a period of time ranging from May through September (Klohn-Crippen Consultants Ltd., 1997). Ammonium sulfate is the primary nitrogenous fertilizer used on Barbados. Relatively small quantities of urea, potassium nitrate and manure are also used. A survey by Klohn-Crippen Consultants Ltd. (1997) showed fertilizer application of 1.2×10^{2} - 1.3×10^{2} kg-N ha^{-1} yr^{-1} for sugar cane on large sugar plantations and suggested that fertilizer applications for other crops were 4 - 5 times higher.

Wastewater

Domestic wastewater from densely populated areas is potentially a major source of nitrogen in the aquifer. In rural parts of Barbados, about half of the households dispose of untreated domestic wastewater in deep pits locally known as "suckwells" while the remainder dispose of wastewater in shallow septic pits or septic tanks (Barbados Ministry of Health et al., 1991). Suckwells are dug to depths of up to 25 m into the limestone with the aim of achieving rapid infiltration and are thus potentially significant sources of nitrogen in the aquifer. This study initially assumes that nitrogen fluxes from domestic wastewater are negligible because the populations in the areas under investigation are concentrated along the coast, down-gradient from most of the sampled wells. Studies by Stanley Associates Engineering Ltd. (1978), the Barbados Ministry of Health et al. (1991) and Klohn-Crippen Consultants Ltd. (1997) suggest that domestic wastewater presents a relatively small risk of contributing nitrogen to Barbados groundwater due to: 1) the relatively low population density in rural areas (3.5 persons ha^{-1}); 2) the infrequent detection of fecal coliform; and 3) attenuation by denitrification under anaerobic conditions that exist in shallow septic pits, suckwells, and soakaways.

Volatilization

Volatilization of nitrogenous fertilizers takes the form of emissions of nitrogen gases (N_2, NO, N_2O, and NH_3). This process is a significant sink in the nitrogen budgets of both natural and agricultural ecosystems (Wahhab et al., 1957; Siegel et al., 1982; Keller et al., 1983; Eichner, 1990; Veldkamp et al., 1998). Emissions of these gases are greatest immediately after fertilization, declining over several weeks or months as soil nitrogen is depleted (Hall et al., 1996).

Nitrogen oxide gases, NO and N_2O, are by-products of both nitrification and denitrification (Davidson, 1993). Emissions of the respective gases are related to soil moisture. Increased soil moisture due to irrigation or rainfall is usually accompanied by increased fluxes of nitrogen oxide gases from the soil, decreasing over several days or weeks (Hall et al., 1996). This occurs because nitrifying and denitrifying bacteria are more active when soil moisture increases (Davidson et al., 1993). The size of these emissions is dependent on: 1) changes in soil moisture; 2) the amount of fertilizer nitrogen present in the soil; and 3) the amount of organic material in the soil (Hall et al., 1996). Anaerobic conditions in relatively moist soils result in denitrification which produces $NO \gg N_2O$ while aerobic conditions in drier soils preferentially produce N_2O by the process of nitrification (Bremner and Blackmer, 1978; Davidson, 1993; Hutchinson et al., 1993). The amount of N_2O released from soils fertilized with ammonium sulfate is directly related to the amount of fertilizer applied (Bremner and Blackmer, 1978). Nitrogen oxide gas emissions from fertilized fields under tropical or subtropical conditions generally lie within the range 1 – 5 kg-N ha^{-1} yr^{-1} (Bremner and Blackmer, 1978; Mosier and Hutchinson, 1981; Cates and Keeney, 1987; Johansson and Sanhueza, 1988; Veldkamp et al., 1998; Hutchinson et al., 1993). These emission rates are generally higher than emission rates observed in natural settings (0.6 – 3.6 kg-N ha^{-1} yr^{-1}) but lower than the maximum emission rates observed for sugar cane of 29 kg-N ha^{-1} yr^{-1} (Cates and Keeney, 1987; Johansson and Sanhueza, 1988; Hutchinson et al., 1993; Matson et al., 1996; Veldkamp et al., 1998).

The type of soil present plays a role in NH_3 gas emissions. Generally, NH_3 emissions are greater from sandy soils than loamy or clayey soils (Wahhab et al., 1957). Emissions of NH_3 gas from ammonium sulfate fertilizer are also related to moisture loss from the soil and soil pH. These gas emissions range from 0% of applied nitrogen at pH 5.5 to 15 - 25% at pH 8.5 (Wahhab et al., 1957). Loss of soil moisture may result in NH_3 emissions that account for 10 - 60% or 10 - 40% of applied nitrogen in sandy and sandy loam soils, respectively.

Nitrogen gas emissions have been measured using isotopically-labeled nitrogen in field experiments (Siegel et al., 1982). In these experiments highly enriched ^{15}N-labeled KNO_3 fertilizer was applied to soil and gas samples were collected from enclosed chambers inserted 14 cm into the soil. These experiments showed isotopically-labeled N_2 gas emissions rising with increased soil moisture and temperature but decreasing over time. Measured emissions of N_2 gas from experimental plots lie within the range 0.9 - 90 kg-N ha^{-1} yr^{-1}.

The above ranges of nitrogen and nitrogen oxide gas emission rates can be used to constrain losses of nitrogen from the soil due to volatilization. In the absence of direct measurements, these ranges of emission rates for the respective gases can be used to estimate a range of total volatilization losses from fertilized soils.

Soil

Soil can act as a source or sink for nitrogen depending on whether there is net annual depletion or accumulation of nitrogen. In this study it is assumed that the nitrogen content of the soil is at steady-state and that all the nitrogen from the different sources is taken up by the sinks. In other words, there is no net annual change in soil nitrogen concentrations. Such steady-state conditions are consistent with observations of nitrogen concentrations in Barbados soils. Nitrogen concentrations in Barbados soil water rise sharply in response to the application of nitrogenous fertilizers and gradually return to pre-fertilization concentrations over a period of months (Fig. 4-7; Klohn-Crippen Consultants Ltd., 1997). This fluctuation of soil-water nitrogen concentrations indicates that the residence time of fertilizer nitrogen in the soil is approximately five months.

NITROGEN BUDGET CALCULATIONS

In this study, nitrogen budgets for groundwater catchments in southeastern and northwestern Barbados were calculated with the aim of investigating: 1) the relative contribution of the different nitrogen sources and sinks averaged over the entire groundwater catchment under investigation; and 2) the relative contribution to groundwater of nitrogen leached from the three main groups of terraces within the respective groundwater catchments. Land usage data was obtained by digitizing 1:10,000 topographic maps and analyzing the land use data using Geographic Information Systems (Fig. 4-5).

Nitrogen Sources

Rainwater

The following equation was used to estimate nitrogen fluxes from rainwater.

$$\text{Nitrogen Flux}_{RW} = \text{Area}_{Catchment} \times \text{Rainfall}_{Average\ annual} \times \text{Nitrogen Conc.}_{RW} \quad (4\text{-}3)$$

Where:

$\text{Nitrogen Flux}_{RW}$ = Nitrogen flux from rainwater (kg-N yr^{-1})

$\text{Area}_{Catchment}$ = Area of groundwater catchment (m^2)

$\text{Rainfall}_{Average\ annual}$ = Average annual rainfall for Barbados (m yr^{-1})

$\text{Nitrogen Conc.}_{RW}$ = Average nitrogen concentration in rainwater (kg-N m^{-3})

Fertilizers

In this study, it is assumed that sugar cane is cultivated on 100% of agricultural land within the respective groundwater catchments and nitrogenous fertilizer is applied on agricultural land with a loading of 117, 132, or 580 kg-N ha^{-1} yr^{-1}. The justification for these assumptions is that at any time sugar cane accounts for 80-90% of the agricultural land within the two study areas and therefore agricultural practices associated with this crop will have by far the greatest influence on the nitrogen budget. The three fertilizer application rates used in these calculations represent typical nitrogen loading for ammonium sulfate and ammonium sulfate/potassium carbonate fertilizers used on Barbados, and an estimate of 1996 fertilizer sales, respectively, (Klohn-Crippen Consultants Ltd., 1997). The fertilizer application rate based on 1996 fertilizer sales assumes that none of the fertilizer was re-exported. The following equation was used to estimate nitrogen fluxes from applied fertilizers.

$$\text{Nitrogen Flux}_{\text{Fertilizer}} = \text{Area}_{\text{Agriculture}} \times \text{Nitrogen fertilizer loading} \quad .. (4\text{-}4)$$

Where:

Nitrogen Flux $_{\text{Fertilizer}}$ = Nitrogen flux from applied fertilizer (kg-N yr^{-1})

Area $_{\text{Agriculture}}$ = Area of agricultural land in groundwater catchment (m^2)

Nitrogen fertilizer loading = Applied fertilizer nitrogen (kg-N m^{-2} yr^{-1})

Nitrogen Sinks

Plant Uptake (Sugar cane)

The harvested portion of fertilized sugar cane plants contains 48 - 63 kg-N ha^{-1} (Gascho et al., 1986). As mentioned above, it is assumed that all agricultural land is used to cultivate sugar cane. In other words, nitrogen uptake rates by non-sugar cane crops are assumed to be similar to sugar cane. The nitrogen uptake fluxes by plants were estimated using the following equation.

$$\text{Nitrogen Flux}_{\text{Uptake}} = \text{Area}_{\text{Agriculture}} \times \text{Nitrogen uptake rate} \quad \text{.......} \ (4\text{-}5)$$

Where:

$\text{Nitrogen Flux}_{\text{Uptake}}$ = Nitrogen taken up by crops (kg-N yr^{-1})

$\text{Area}_{\text{Agriculture}}$ = Area of agricultural land in groundwater catchment (m^2)

Nitrogen uptake rate = Nitrogen uptake by crops (kg-N m^{-2} yr^{-1})

Groundwater

The flux of groundwater nitrogen is an indicator of the amount of nitrogen leached from the soil by the infiltrating water that recharges the aquifer. This assumes that no denitrification is taking place within the aquifer. Assuming that annual groundwater discharge is equal to annual recharge, the amount of nitrogen leached from the soil can be estimated based on average groundwater nitrogen concentrations and average recharge rates for the respective groundwater catchments. The assumption of groundwater discharge equal to recharge is based on the relatively small seasonal and interannual water-level fluctuations that occur in the Pleistocene limestone aquifer that indicate relatively uniform amounts of groundwater in storage. The recharge rates, expressed as a percentage of average annual rainfall, were estimated based on groundwater and rainwater oxygen isotopic compositions (Jones et al., 2000). The groundwater nitrogen fluxes were estimated using the following equation.

$$\text{Nitrogen Flux}_{GW} = \text{Nitrogen Conc.}_{GW} \times \text{Groundwater Discharge} \quad (4\text{-}6)$$

Where:

Nitrogen Flux $_{GW}$ = Groundwater nitrogen flux (kg-N yr^{-1})

Nitrogen conc. $_{GW}$ = Nitrogen concentration in groundwater (kg-N m^{-3})

Groundwater Discharge = Groundwater discharge from catchment (m^3 yr^{-1})

Volatilization

It is assumed that: 1) N_2 emissions take place at 0.9, 9.0, or 90 kg-N ha^{-1} yr^{-1}; 2) nitrogen oxide gases emissions take place at 1.0, 5.0 or 29 kg-N ha^{-1} yr^{-1}; and 3) NH_3 emissions account for 15 – 25% of applied nitrogen or emission rates of approximately 20 – 150 kg-N ha^{-1} yr^{-1}. These emission rates represent minimum, intermediate and maximum emission rates for the respective gases taken from the literature as discussed in the Nitrogen Budget Components section above. Additionally, it is assumed that volatilization fluxes from uncultivated land are insignificant. The nitrogen fluxes due to volatilization were estimated using the following equation.

$$\text{Nitrogen Flux}_{\text{Gas}} = \text{Area}_{\text{Agriculture}} \times \text{Nitrogen emission rate} \quad \text{....... (4-7)}$$

Where:

Nitrogen Flux $_{\text{Gas}}$ = Nitrogen gas emission flux (kg-N yr^{-1})

Area $_{\text{Agriculture}}$ = Area of agricultural land in groundwater catchment (m^2)

Nitrogen emission rate = Nitrogen gas emission rate (kg-N m^{-2} yr^{-1})

Spatial Distribution of Leached Nitrogen

In order to investigate the spatial distribution of nitrogen leached from the soil, Equations 4-3 to 4-7 were used to estimate the magnitude of the nitrogen sources and sinks within each major terrace present in the respective groundwater catchments. For each terrace, the nitrogen leaching rate was estimated: 1) by assuming that leaching accounts for the difference between the sum of nitrogen inputs and the sum of nitrogen outputs to plant uptake and volatilization (Eq. 4-8); and 2) based on groundwater nitrogen concentrations and estimated recharge (Eq. 4-9).

$$\text{Nitrogen Flux}_{\text{Leach}} = \text{Nitrogen Flux}_{\text{Sources}} - \text{Nitrogen Flux}_{\text{Sinks}} \text{...... (4-8)}$$

$$\text{Nitrogen Flux}_{\text{Leach}} = \text{Nitrogen Flux}_{\text{GW (out)}} - \text{Nitrogen Flux}_{\text{GW (in)}} \text{... (4-9)}$$

Where:

Nitrogen Flux $_{Leach}$ = Nitrogen leached from soil (kg-N yr^{-1})

Nitrogen Flux $_{Sink}$ = Nitrogen taken up by sinks (kg-N yr^{-1})

Nitrogen Flux $_{Source}$ = Nitrogen released from sources (kg-N yr^{-1})

Nitrogen Flux $_{GW\ (out)}$ = Nitrogen flux out of aquifer (kg-N yr^{-1})

Nitrogen Flux $_{GW\ (in)}$ = Nitrogen flux from up-gradient (kg-N yr^{-1})

Equation 4-9 uses a mass-balance approach to estimate the amount of nitrogen leached from each of the three main terraces by estimating the groundwater nitrogen flux and then subtracting groundwater nitrogen fluxes originating from up-gradient terraces.

RESULTS

Nitrogen Budgets of Groundwater Catchments

Table 4-2 shows the nitrogen budget for the groundwater catchments of northwestern and southeastern Barbados, based on estimated annual nitrogen fluxes from or into the major potential sources and sinks, respectively. It should be noted that these results represent average nitrogen fluxes for the respective groundwater catchments.

Given an average annual rainfall of 1,500 mm, rainwater nitrogen input to the groundwater catchments is negligible (1.4 kg-N ha^{-1} yr^{-1}). Rainwater nitrogen inputs are thus small compared to anthropogenic sources of nitrogen, such as nitrogenous fertilizers (Table 4-2). The nitrogenous fertilizer loading used in these nitrogen budgets results in nitrogen fluxes (117 – 580 kg-N ha^{-1} yr^{-1}) that account for almost all of the nitrogen input to the catchments. Within the areas under investigation, estimates of sugar cane nitrogen uptake used in the calculations ranged from 48 to 63 kg-N ha^{-1} yr^{-1}. Estimates of nitrogen loss by volatilization indicate that N_2, nitrogen oxide and NH_3 gas emissions together account for 20 – 26 kg-N ha^{-1} yr^{-1}. Estimates for volatilization show that this process primarily takes the form of nitrogen oxide (1 – 29 kg-N ha^{-1} yr^{-1}) and NH_3 (18 – 150 kg-N ha^{-1} yr^{-1}) emissions from the soil with lesser amounts of N_2 gas emissions (0.9 – 90 kg-N ha^{-1} yr^{-1}). Mass-balance calculations based on estimated nitrogen source and sink fluxes (Eq. 4-8) indicate nitrogen leaching rates of approximately 26 to 190 kg-N ha^{-1} yr^{-1} (Table 4-3). These leaching estimates are higher than nitrogen leaching estimates based on groundwater nitrogen fluxes (Eq. 4-9) of 12 - 27 kg-N ha^{-1} yr^{-1}.

Intra-Catchment Nitrogen Budgets

Estimated nitrogen fluxes for the main terraces occurring within the groundwater catchments of southeastern and northwestern Barbados are shown in Tables 4-4 and 4-5. The nitrogen input and output rates are the same as those used above. The amount of nitrogen involved in the nitrogen budget of each terrace varies with the relative surface area of the terrace and the relative amount of land used for agriculture within each terrace. In southeastern Barbados, estimated nitrogen leaching based on nitrogen source and sink fluxes are approximately 49 to 250 kg-N ha^{-1} yr^{-1} and 31 to 150 kg-N ha^{-1} yr^{-1} in the Upper and Middle Reef Terraces, respectively (Table 4-6). The Lower Reef Terrace is absent in southeastern Barbados. In northwestern Barbados, estimates of leached nitrogen vary from 39 to 190 kg-N ha^{-1} yr^{-1} in the Upper Reef Terrace, decreasing to 22 to 110 kg-N ha^{-1} yr^{-1} in the Lower Reef Terrace. The nitrogen leaching estimates based on groundwater fluxes (Eq. 4-9) are generally lower than those based on estimated source and sink fluxes (Eq. 4-8). In southeastern Barbados, nitrogen leaching estimates based on groundwater nitrogen fluxes vary from 15 to 24 kg-N ha^{-1} yr^{-1} and 13 to 38 kg-N ha^{-1} yr^{-1} in the Upper and Middle Reef Terraces, respectively, while in northwestern Barbados, the ranges are 13 to 22 kg-N ha^{-1} yr^{-1}, 6.4 to 35 kg-N ha^{-1} yr^{-1}, and 110 kg-N ha^{-1} yr^{-1} in the Upper, Middle and Lower Reef Terraces, respectively (Tables 4-6 and 4-7).

DISCUSSION

Despite water-table depths exceeding 50 m, the effects of vadose zone denitrification are unlikely to be significant on Barbados because the highly porous limestone is highly permeable and well aerated. These conditions produce aerobic conditions, and relatively short residence-times of infiltrating water in the vadose zone, and consequently result in little denitrification (Mueller et al., 1995). The results of infiltration tests by Mwansa and Barker (1996) and Smart and Ketterling

(1997) indicate that water residence time in the vadose zone on Barbados ranges from several minutes to a few days for water infiltrating through sinkholes or drainage wells. Residence times associated with diffuse infiltration are undoubtedly longer. The soils on Barbados are composed primarily of clay and have infiltration capacities of up to 250 mm h^{-1} (Tullstrom, 1964). These are much less permeable than the underlying limestone. Consequently, one would expect that the potential for the occurrence of waterlogging and associated anaerobic conditions conducive to significant denitrification is much greater in the soil portion of the vadose zone than in the underlying limestone. The elevated NO_3 in Barbados groundwater can be explained by the recharge processes. Recharge to the limestone aquifer primarily occurs by rapid discrete infiltration of runoff through karst features, such as sinkholes and dry valleys (Jones et al., 2000). The recharging water bypasses the soil and consequently it is unlikely that NO_3 concentrations in the infiltrating water will be significantly reduced by denitrification.

The application of fertilizers on Barbados coincides with the wet season when recharge to the underlying aquifer takes place (Jones et al., 2000). Consequently, applied fertilizers are susceptible to both increased leaching and ultimately an increase in their contribution to the groundwater nitrogen fluxes. This problem has the potential to be greatest at higher elevations where the soils are more permeable and at lower elevations where recharge is apparently greatest

(Jones et al., 2000). On Barbados, the effects of denitrification in the soil are potentially greater at lower elevations where the soils are less permeable, and less well-drained. However, the presence of numerous drainage wells, particularly in sugar cane fields, indicates the potential for transmission of fertilizer nitrogen to the aquifer in runoff during periods of heavy rainfall. The relative effects of soil permeability and recharge processes on nitrogen entering the aquifer will be discussed later.

On Barbados, one would expect relatively large NH_3 emissions because soil pH is within the range 7 – 8 and there is greater potential for NH_3 emissions at higher elevations from the higher permeability soils (Vernon and Carroll, 1965; Wahhab et al, 1957). Volatilization from fertilized fields is difficult to estimate because: 1) potential competition for nitrogen among the emissions of N_2, NH_3 and nitrogen oxide gases; and 2) gas emissions vary spatially and temporally with the combined effects of soil pH and soil moisture. The highest N_2 emission rate used in the nitrogen budget calculations (90 kg-N ha^{-1} yr^{-1}) was observed in laboratory and field experiments at the University of Illinois by Siegel and others (1982). This emission rate reflects short-lived initial fluxes and is probably not representative of longer-term average nitrogen gas fluxes from the soil.

Nitrogen Budgets of Groundwater Catchments

Sugar cane nitrogen uptake predicted by the nitrogen budget calculations for Barbados (8 - 54% of applied nitrogen) overlaps with measured sugar cane nitrogen uptake rates at other sites (Hunsigi, 1993). Hunsigi concluded that depending on the fertilization procedure, sugar cane nitrogen uptake accounts for 44 - 80%, averaging 60% of available nitrogen. Mass-balance calculations by Klohn-Crippen Consultants Ltd. (1997) suggested that 40 - 50% of fertilizer nitrogen on Barbados is leached from the soil to the aquifer. These leaching rates indicate nitrogen fluxes of 50 - 300 kg-N ha^{-1} yr^{-1}, that are higher than the leaching rates of 10 - 30 kg-N ha^{-1} yr^{-1} indicated by groundwater nitrogen fluxes in this investigation (Table 4-3). The higher leaching rates can be attributed to the fact that Klohn-Crippen did not consider the possible effects of nitrogen losses due to volatilization of the applied fertilizer. These losses could result in nitrogen fluxes of 20 to 260 kg-N ha^{-1} yr^{-1}. In other words, nitrogen volatilization fluxes may be equal to or exceed leaching.

Two mass-balance methods were used to estimate the amount of nitrogen being leached from the soil and contributing to groundwater nitrogen concentrations. The first method was based on estimated nitrogen source and sink fluxes (Eq. 4-8) while the second method was based on groundwater nitrogen fluxes (Eq. 4-9). There is general agreement between the results of both methods, especially when using the low and intermediate source and sink fluxes even though in some cases these fluxes differ by a factor of 2-3 (Fig. 4-9). This agreement suggests that overall additional nitrogen inputs from domestic wastewater are relatively small in these lightly populated parts of Barbados. Large nitrogen inputs from a source not included in the calculation, such as domestic waste water, should result in groundwater nitrogen fluxes that significantly exceed the values determined by Eq. 4-8. In the areas investigated, major sources of domestic wastewater nitrogen are either relatively small point sources or limited to a narrow strip along the coast. Point sources may produce narrow plumes that are not readily detected in wells. Contamination in the densely populated areas along the coast may not be apparent due to the presence of few wells. Comparison of water samples collected from the beaches along the west coast of Barbados with groundwater collected from inland wells indicate elevated fecal coliform in the beach water samples (DELCAN, 1995). This elevated fecal coliform is indicative of domestic wastewater contamination along the coast.

Variations in Nitrogen Leaching Within Groundwater Catchments

Figure 4-8 shows that nitrogen fluxes to the aquifer in the groundwater catchments under investigation increase down-gradient while at the same time, average groundwater nitrogen concentrations decrease. The apparent inverse relationship between groundwater nitrogen fluxes and nitrogen concentrations can be explained by higher recharge rates at lower elevations (Jones et al., 2000). This results in greater dilution and therefore lower nitrogen concentrations coupled with larger groundwater fluxes.

In each groundwater catchment under investigation, the amount of nitrogen associated with the nitrogen sources and sinks varies with the area of the terrace and the proportion of land used for agriculture (Tables 4-4 to 4-7). Consequently, the nitrogen budget in terraces with larger surface areas will involve more nitrogen than in smaller terraces. With the exception of rainwater nitrogen, the fluxes associated with the nitrogen sinks and sources used in these nitrogen budget calculations are all associated with agricultural land. Consequently, these nitrogen fluxes are dependent on the proportion of the catchment used for cultivation of crops. In the groundwater catchments under investigation, agricultural land use increases with elevation. In southeastern Barbados, crop land accounts for approximately 85% of the Upper Reef Terrace, decreasing to about 70% in the much larger Middle Reef Terrace. In northwestern Barbados, crop land accounts for 77%, 65%, and 40% of the Upper, Middle and Lower Reef Terraces, respectively. The overall effect of the distribution of agricultural land use on Barbados is that nitrogen input estimates decrease at lower elevations in the northwest and increase in the southeast (Tables 4-6 and 4-7). However, the relative area of residential or commercial land use, an alternative source of nitrogen, increases at lower elevations from 12% to 21% in southeastern Barbados and 5% to

14% in the northwest. Decreasing agricultural land use together with increasing residential land use implies that at lower elevations the potential for significant anthropogenic nitrogen inputs from domestic wastewater increases relative to fertilizer inputs.

Estimated nitrogen leaching rates based on observed groundwater nitrogen concentrations are generally lower than leaching rates predicted by the nitrogen sources and sinks used in the nitrogen budget calculations (Fig. 4-9a). However, like the catchment-wide calculations, there is general agreement between the two results for each terrace, especially when low and intermediate nitrogen source and sink fluxes are used. This indicates that in most areas, the highest fertilizer application rate of 580 kg-N ha^{-1} yr^{-1} is unrealistically high and over-estimates nitrogen leaching by over-estimating nitrogen inputs. The exception to this rule occurs in the Lower Reef Terrace in northwestern Barbados where the nitrogen leaching rate based on one groundwater composition coincides with the leaching rate based on the highest nitrogen source and sink fluxes. The groundwater nitrogen fluxes imply that: 1) the rates of nitrogen leaching from the soil increase 5 - 10% down-gradient; and 2) there is little difference between nitrogen leaching rates in northwestern and southeastern Barbados.

The measured down-gradient trend contradicts the leaching patterns predicted by the nitrogen source and sink fluxes, where nitrogen leaching decreases down-gradient. This occurs because nitrogen source and sink fluxes are controlled by land-use patterns while groundwater nitrogen fluxes are controlled by the spatial distribution of recharge. The down-gradient increase in nitrogen leached from the soil can be explained by more intense leaching associated with the higher recharge rates at lower elevations that more than compensate for less agricultural land. In other words, nitrogen leaching rates on Barbados are controlled more by recharge processes than land use (Fig. 4-9b). This intense leaching is made possible by rapid discrete infiltration where: 1) the Pleistocene limestone is exposed (Jones et al., 2000); and 2) the presence of drainage wells in sugar cane fields may result in rapid transmission of fertilizer nitrogen dissolved in runoff water to the water table. The distribution of drainage wells on Barbados has not been mapped, but one can speculate that these drainage wells are more common at lower elevations where the soils are less well-drained (Fig 4-4).

It should be noted that the extremely high leaching rate for the Lower Reef Terrace in northwestern Barbados is based on one groundwater sample. The nitrogen fluxes in the other terraces investigated can be explained by low and intermediate nitrogen source and sink fluxes. The nitrogen fluxes responsible for the groundwater nitrogen flux in the Lower Reef Terrace far exceed those of the rest of the groundwater catchment. This could suggest nitrogen influxes from an additional source rather than higher fertilization rates. The Lower Reef Terrace has a higher ratio of urban to agricultural land use than the two up-gradient terraces and the groundwater sample was collected from a shallow well that is located immediately down-gradient from a residential area. It therefore must be considered that the excess nitrogen could be derived from domestic wastewater. Nitrogen isotopes may be used as tracers to indicate whether the source of nitrogen in groundwater is inorganic nitrogenous fertilizer or human or animal waste (Kreitler, 1975). This is possible because each of these potential nitrogen sources is characterized by a distinct range of nitrogen isotopic compositions. However, interpretation of nitrogen isotopic data are complicated by multiple sources of nitrogen or fractionation due to nitrification or denitrification (Spalding et al., 1994; Kellman and Hillaire-Marcell, 1997; DiGnazio et al., 1998; Feast et al., 1998).

The parts of this study that determine the fate of applied fertilizer nitrogen by means of estimated nitrogen fluxes to the atmosphere, aquifer, and vegetation have implications for investigations of the global nitrogen cycle. These estimates of nitrogen uptake by vegetation and nitrogen losses from the soil by leaching and volatilization represent on a small scale, processes that contribute to the global nitrogen budget.

CONCLUSIONS

This study investigates the relative contribution of nitrogen sources and sinks in the soil to the nitrogen budget of groundwater catchments on Barbados. The contributions of the respective nitrogen sources and sinks are determined by evaluating estimated nitrogen fluxes associated with potential nitrogen sources and sinks that occur in the respective study areas. These estimated fluxes are used to determine: 1) the fate of nitrogenous fertilizers applied to agricultural fields including the proportion of applied fertilizer that is leached from the soil and contributes to groundwater nitrogen concentrations; 2) the spatial distribution of fertilizer nitrogen inputs to a karst aquifer; and 3) the impact of land use in general and fertilizer application in particular on groundwater compositions. Identifying parts of an aquifer with high nitrogen influxes is vital to developing land use regulation to preserve groundwater quality.

The potential sources of nitrogen identified in this study are rainwater, nitrogenous fertilizers, and domestic wastewater, while the potential nitrogen sinks are: 1) nitrogen uptake by plants, especially sugar cane; 2) leaching of nitrogen from the soil by recharge water; and 3) volatilization of soil nitrogen in the form of NH_3, N_2 and nitrogen oxide gas emissions (Fig. 4-10). Evaluation of the contributions of the potential nitrogen sources indicates that on Barbados the widespread use of nitrogenous fertilizers on agricultural land is the predominant source of nitrogen in the soil and groundwater. The contribution of nitrogen from domestic wastewater, a point source, to the groundwater is relatively small overall but may be an important source of nitrogen locally. Nitrogen fluxes from domestic wastewater are most apparent where groundwater nitrogen fluxes are higher than that predicted by leaching of fertilizer nitrogen. The uptake of nitrogen by plants, such as sugar cane, is the primary nitrogen sink. Nitrogen losses to volatilization and leaching, however, are also significant. Nitrogen losses from the soil by volatilization in the form of NH_3 and nitrogen oxide gases account for approximately 15 – 40% of nitrogen inputs and far exceed estimated emissions of N_2 gas (1 – 7%). On Barbados, groundwater nitrogen fluxes indicate that approximately 15 - 30% of applied fertilizer nitrogen in the soil is lost by leaching. This nitrogen enters the aquifer during recharge periods.

The spatial distribution of average nitrogen leaching rates within groundwater catchments in southeastern and northwestern Barbados indicate that leaching rates vary more as a function of recharge rates than as a function of agricultural land use. On Barbados, agricultural land use increases with elevation. This should result in lower nitrogen inputs at lower elevations. Groundwater nitrogen fluxes, however, indicate that the leaching of fertilizer nitrogen increases at lower elevations. This increase in nitrogen fluxes corresponds to increases in groundwater recharge rates at lower elevations.

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Table 4-1. Nitrate and ammonia concentrations in groundwater and vadose water samples collected on Barbados.

Site No.	Well	Date	NH_4 (mg l^{-1} N)	NO_3 (mg l^{-1} N)
19	Alleynedale Hall Plantation	7/28/94	BDL	7.25
19	Alleynedale Hall Plantation	1/5/96	0.09	7.22
20	Alleynedale II	1/4/96	0.03	6.65
21	Barrows Childrens Home	8/7/94	1.13	1.25
21	Barrows Childrens Home	1/5/96	0.16	3.71
1	Bowmanston Pumping Station (Drip)	8/5/94	0.69	8.38
1	Bowmanston Pumping Station (Drip)	1/9/96	BDL	7.19
2	Bowmanston Pumping Station (Stream)	8/5/94	0.23	6.36
2	Bowmanston Pumping Station (Stream)	1/9/96	BDL	6.82
22	Bromefield Plantation	7/24/94	0.30	5.22
22	Bromefield Plantation	1/7/96	BDL	5.04
23	Carlton Pumping Station	1/3/96	0.03	8.13
3	Carmichael Plantation	1/8/96	0.16	5.95
4	Claybury Plantation	7/23/94	0.09	9.25
5	Congo Road	8/3/94	0.38	5.59
6	Easy Hall Plantation	7/23/94	BDL	6.38
6	Easy Hall Plantation	1/2/96	BDL	6.78
7	Edgecumbe Plantation	7/22/94	0.09	7.67
7	Edgecumbe Plantation	1/3/96	0.26	7.09
24	Farm Plantation	1/4/96	BDL	6.75
8	Halton Plantation	7/23/94	BDL	7.22
8	Halton Plantation	1/9/96	BDL	5.09
9	Hampton Plantation	7/30/94	0.09	5.79
9	Hampton Plantation	1/3/96	BDL	6.72
10	Henley Plantation	7/23/94	BDL	5.93
11	Home Agricultural Station	8/4/94	0.16	6.95
11	Home Agricultural Station	1/9/96	0.13	6.51

Table 4-1. (Cont.)

Site No.	Well	Date	NH_4 (mg l^{-1} N)	NO_3 (mg l^{-1} N)
12	Kendal Plantation	8/2/94	0.23	8.59
12	Kendal Plantation	1/3/96	0.09	9.80
13	Little Bentleys	7/21/94	0.16	8.17
14	Marshall Trading	8/2/94	0.57	0.71
25	Mount Gay Distillery	7/29/94	BDL	6.11
25	Mount Gay Distillery	1/8/96	0.26	4.95
15	Mount plantation, The	7/23/94	BDL	6.15
26	Mullins Bay	1/6/96	0.30	5.99
16	Pollard Mill	8/2/94	0.30	5.53
16	Pollard Mill	1/8/96	0.45	4.91
27	Portland Plantation	1/5/96	0.09	5.67
28	Rock Hall Plantation	1/4/96	0.03	6.43
17	Ruby	8/4/94	0.16	7.11
17	Ruby	1/2/96	BDL	7.64
29	Sailor Gully Cave	1/10/96	0.45	0.92
18	Thicket Cave	8/2/94	--	19.4
18	Three Houses Spring	7/27/94	0.16	6.70
18	Three Houses Spring	1/2/96	BDL	7.57
30	Trents Plantation	8/7/94	--	8.97
31	Welchtown Plantation	8/3/94	0.53	9.00
31	Welchtown Plantation	1/5/96	0.16	8.93
32	White Hall	1/4/96	BDL	7.57

Table 4-2. Nitrogen mass-balance calculations for two groundwater catchments on Barbados. Low, intermediate (Interm.), and high nitrogen flux estimates are made for each nitrogen source or sink.

NITROGEN SOURCES							
RAINWATER							
Catchment	Catchment Area (m^2)	NO_3 ($mg\ l^{-1}$)			Flux ($kg\text{-}N\ yr^{-1}$)		
Northwest	49,701,000	0.36			6,060		
Southeast	83,027,000	0.36			10,120		
FERTILIZERS							
Catchment	Agriculture (m^2)	Loading ($kg\text{-}N\ m^{-2}\ yr^{-1}$)			Flux ($kg\text{-}N\ yr^{-1}$)		
		Low	Interm.	High	Low	Interm.	High
Northwest	34,298,000	0.0117	0.0132	0.0580	401,000	453,000	1,989,000
Southeast	62,355,000	0.0117	0.0132	0.0580	730,000	823,000	3,617,000

Table 4-2. (Cont.)

NITROGEN SINKS							
GROUNDWATER							
Catchment	Catchment Area (m^2)	NO_3 (mg l^{-1})	Av Recharge (%)	Recharge (m^3 yr^{-1})	Flux (kg-N yr^{-1})		
					Low	Interm.	High
Northwest	49,701,000	26.8	21	15,420,000	58,000	93,000	128,000
Southeast	83,027,000	30.0	22	27,043,000	103,000	183,000	225,000
SUGARCANE							
Catchment	Agriculture (m^2)	N Uptake (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Northwest	34,298,000	4.8E-03		6.3E-03	165,000		216,000
Southeast	62,355,000	4.8E-03		6.3E-03	299,000		393,000
VOLATILIZATION (NO and N_2O)							
Catchment	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Northwest	34,298,000	1.0E-04	5.0E-04	2.9E-03	3,400	17,100	100,000
Southeast	62,355,000	1.0E-04	5.0E-04	2.9E-03	6,200	31,200	181,000
VOLATILIZATION (NH_3)							
Catchment	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Northwest	34,298,000	1.8E-03	3.3E-03	1.5E-02	61,000	115,000	499,000
Southeast	62,355,000	1.8E-03	3.3E-03	1.5E-02	111,000	208,000	907,000
VOLATILIZATION (N_2)							
Catchment	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Northwest	34,298,000	9.0E-05	9.0E-04	9.0E-03	3,000	31,000	309,000
Southeast	62,355,000	9.0E-05	9.0E-04	9.0E-03	6,000	56,000	561,000

Table 4-3. Low, intermediate and high estimates of fertilizer nitrogen leaching for two groundwater catchments on Barbados.

Catchment	Nitrogen Inputs (Rainwater + Fertilizer)					
	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Northwest	407,000	459,000	1,995,000	8.2E-03	9.2E-03	4.0E-02
Southeast	740,000	833,000	3,627,000	8.9E-03	1.0E-02	4.4E-02
	Nitrogen Outputs (Plant Uptake + Volatilization)					
Catchment	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Northwest	232,000	327,000	1,123,000	4.7E-03	6.6E-03	2.3E-02
Southeast	422,000	595,000	2,042,000	5.1E-03	7.2E-03	2.5E-02
	Nitrogen Leached = Nitrogen Inputs - Nitrogen Outputs					
Catchment	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Northwest	175,000	131,000	872,000	3.5E-03	2.6E-03	1.8E-02
Southeast	318,000	238,000	1,585,000	3.8E-03	2.9E-03	1.9E-02
	Nitrogen Leached = Groundwater Nitrogen Flux					
Catchment	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Northwest	58,000	93,000	128,000	1.2E-03	1.9E-03	2.6E-03
Southeast	103,000	183,000	225,000	1.2E-03	2.2E-03	2.7E-03

Table 4-4. Nitrogen budget for the respective terraces within groundwater catchments located in southeastern Barbados.

NITROGEN SOURCES							
RAINWATER							
Terrace	Terrace Area (m^2)	NO_3 (mg l^{-1})			Flux (kg-N yr^{-1})		
Upper	35,140,000		0.36			4,300	
Middle	62,410,000		0.36			7,600	
FERTILIZERS							
Terrace	Agriculture (m^2)	Loading (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	34,120,000	0.0117	0.0132	0.0580	399,000	450,000	1,979,000
Middle	37,836,000	0.0117	0.0132	0.0580	443,000	499,000	2,194,000

Table 4-4. (Cont.)

NITROGEN SINKS							
GROUNDWATER							
Terrace	Terrace Area (m2)	NO_3 (mg l^{-1})	Av Recharge (%)	Recharge (m^3 yr^{-1})	Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	35,140,000	32.82	18	9,435,000	54,000	70,000	86,000
Middle	62,410,000	29.06	24	25,439,000	83,000	159,000	235,000
SUGARCANE							
Terrace	Agriculture (m^2)	N Uptake (kg-N m^{-2})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	34,120,000	4.8E-03		6.3E-03	164,000		215,000
Middle	37,836,000	4.8E-03		6.3E-03	182,000		238,000
VOLATILIZATION (NO and N_2O)							
Terrace	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	34,120,000	1.0E-04	5.0E-04	2.9E-03	3,400	17,000	99,000
Middle	37,836,000	1.0E-04	5.0E-04	2.9E-03	3,800	19,000	110,000
VOLATILIZATION (NH_3)							
Terrace	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	34,120,000	1.8E-03		1.5E-02	60,500		496,000
Middle	37,836,000	1.8E-03		1.5E-02	67,500		551,000
Upper	34,120,000	9.0E-05	9.0E-04	9.0E-03	3,100	30,700	307,000
Middle	37,836,000	9.0E-05	9.0E-04	9.0E-03	3,400	34,000	341,000

Table 4-5. Nitrogen budget for the respective terraces within groundwater catchments located in northwestern Barbados.

NITROGEN SOURCES							
RAINWATER							
Terrace	Terrace Area (m^2)	NO_3 (mg l^{-1})			Flux (kg-N yr^{-1})		
Upper	23,882,000	0.36			2,900		
Middle	21,173,000	0.36			2,600		
Lower	4,117,000	0.36			500		
FERTILIZERS							
Terrace	Agriculture (m^2)	Loading (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	18,299,000	0.0117	0.0132	0.0580	214,000	246,000	1,061,000
Middle	13,407,000	0.0117	0.0132	0.0580	157,000	177,000	778,000
Lower	1,721,0002	0.0117	0.0132	0.0580	20,100	22,700	100,000

Table 4-5. (Cont.).

NITROGEN SINKS							
GROUNDWATER							
Terrace	Terrace Area (m^2)	NO_3 (mg l^{-1})	Av Recharge (%)	Recharge (m^3 yr^{-1})	Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	23,882,000	29.95	17	6,161,000	31,400	41,700	51,900
Middle	21,173,000	27.18	21	7,846,000	13,600	44,300	74,900
Lower	4,117,000	26.12	30	8,120,000		44,500	
SUGARCANE							
Terrace	Agriculture (m^2)	N Uptake (kg-N m^{-2})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	18,299,000	4.8E-03		6.3E-03	87,800		115,000
Middle	13,407,000	4.8E-03		6.3E-03	64,400		84,500
Lower	1,721,000	4.8E-03		6.3E-03	8,300		10,800
VOLATILIZATION (NO and N_2O)							
Terrace	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	18,299,000	1.0E-04	5.0E-04	2.9E-03	1,800	9,200	53,100
Middle	13,407,000	1.0E-04	5.0E-04	2.9E-03	1,300	6,700	38,900
Lower	1,721,000	1.0E-04	5.0E-04	2.9E-03	180	860	5,000
VOLATILIZATION (NH_3)							
Terrace	Agriculture (m^2)	N Emissions (kg-N m^{-2} yr^{-1})			Flux (kg-N yr^{-1})		
		Low	Interm.	High	Low	Interm.	High
Upper	18,299,000	1.8E-03		1.5E-02	32,600		266,000
Middle	13,407,000	1.8E-03		1.5E-02	24,000		195,000
Lower	1,721,000	1.8E-03		1.5E-02	3,100		25,100
Upper	18,299,000	9.0E-05	9.0E-04	9.0E-03	1,600	16,500	165,000
Middle	13,407,000	9.0E-05	9.0E-04	9.0E-03	1,200	12,100	121,000
Lower	1,721,000	9.0E-05	9.0E-04	9.0E-03	160	1,500	15,500

Table 4-6. Calculations of fertilizer nitrogen leaching rates in groundwater catchments located southeastern Barbados.

Nitrogen Inputs (Rainwater + Fertilizer)						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	403,000	455,000	1,983,000	1.1E-02	1.3E-02	5.6E-02
Middle	450,0000	507,000	2,202,000	7.2E-03	8.1E-03	3.5E-02
Nitrogen Outputs (Plant Uptake + Volatilization)						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	231,000	272,000	1,117,000	6.6E-03	7.7E-03	3.2E-02
Middle	256,000	302,000	1,239,000	4.1E-03	4.8E-03	2.0E-02
Nitrogen Leached = Nitrogen Inputs - Nitrogen Outputs						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	173,000	183,000	866,000	4.9E-03	5.2E-03	2.5E-02
Middle	194,000	205,000	963,000	3.1E-03	3.3E-03	1.5E-02
Nitrogen Leached = Groundwater Nitrogen Flux						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	54,300	70,000	85,600	1.5E-03	2.0E-03	2.4E-03
Middle	82,700	159,000	235,000	1.3E-03	2.5E-03	3.8E-03

Table 4-7. Calculations of fertilizer nitrogen leaching rates in groundwater catchments located northwestern Barbados.

Nitrogen Inputs (Rainwater + Fertilizer)						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	217,000	244,000	1,064,000	9.1E-03	1.0E-02	4.5E-02
Middle	159,000	180,000	780,000	7.5E-03	8.5E-03	3.7E-02
Lower	20,600	23,200	100,000	5.0E-03	5.6E-03	2.4E-02
Nitrogen Outputs (Plant Uptake + Volatilization)						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	124,000	146,000	599,000	5.2E-03	6.1E-03	2.5E-02
Middle	91,000	107,000	439,000	4.3E-03	5.1E-03	2.1E-02
Lower	11,700	13,800	56,400	2.8E-03	3.3E-03	1.4E-02
Nitrogen Leached = Nitrogen Inputs - Nitrogen Outputs						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	93,100	98,500	465,000	3.9E-03	4.1E-03	1.9E-02
Middle	68,600	72,500	341,000	3.2E-03	3.4E-03	1.6E-02
Lower	9,000	9,500	44,000	2.2E-03	2.3E-03	1.1E-02
Nitrogen Leached = Groundwater Nitrogen Flux						
Terrace	Flux (kg-N yr^{-1})			Flux (kg-N m^{-2} yr^{-1})		
	Low	Interm.	High	Low	Interm.	High
Upper	31,500	41,700	51,900	1.3E-03	1.7E-03	2.2E-03
Middle	13,600	44,300	74,900	6.4E-04	2.1E-03	3.5E-03
Lower		44,500			1.1E-02	

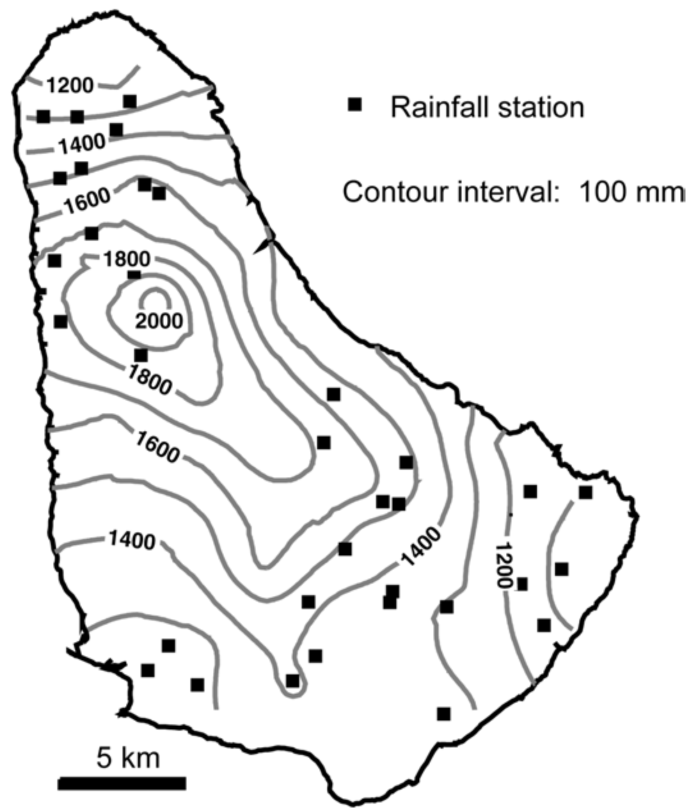

Figure 4-1. Distribution of annual rainfall (1992) on Barbados. Based on rainfall data obtained from the Caribbean Institute of Meteorologyand Hydrology.

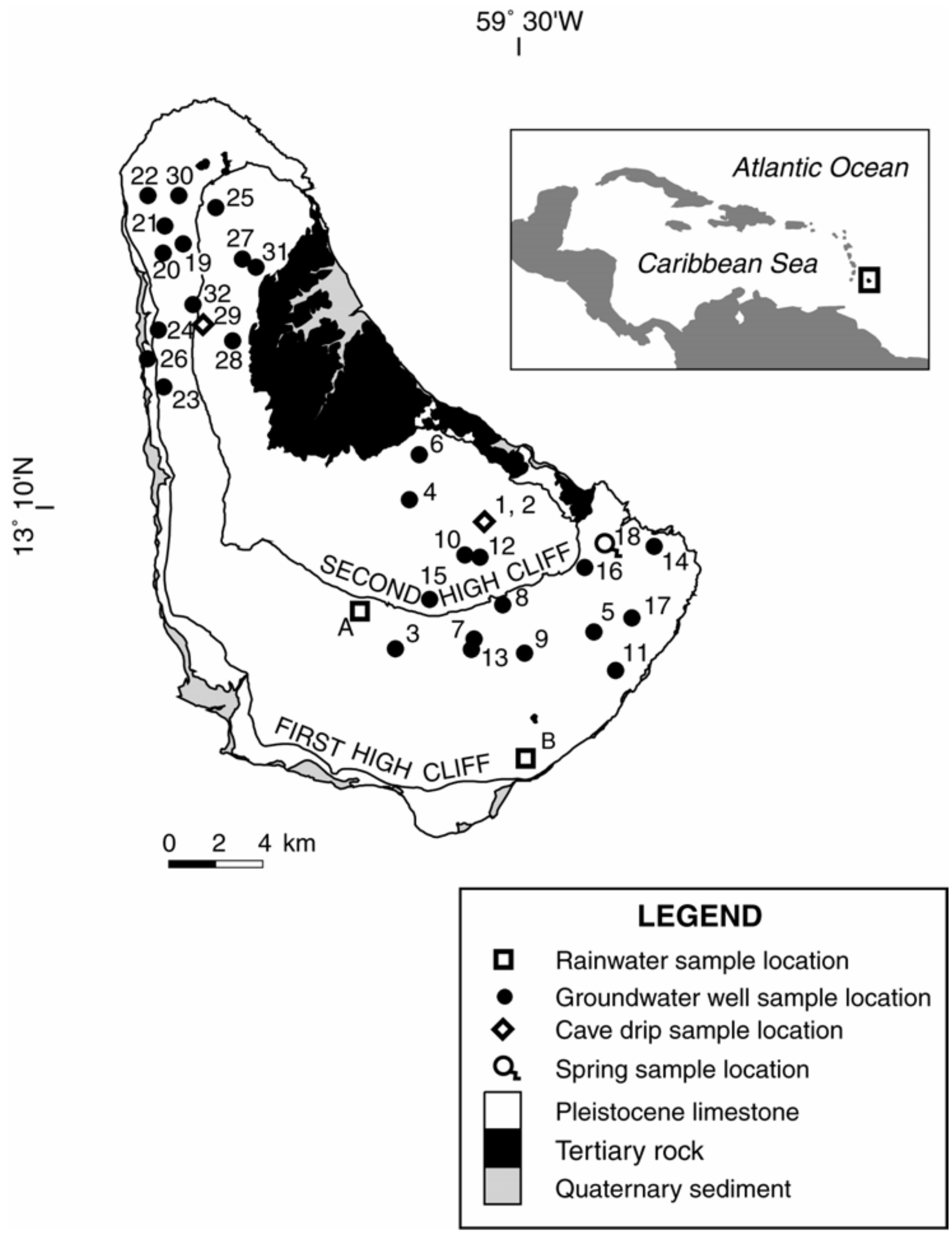

Figure 4-2. Location and geologic map of Barbados. The Pleistocene limestonethat comprises the aquifer occurs in the northern, western and southern portions of Barbados. Adapted from 1:50,000 geologic map (Directorate of Overseas Surveys, 1983).

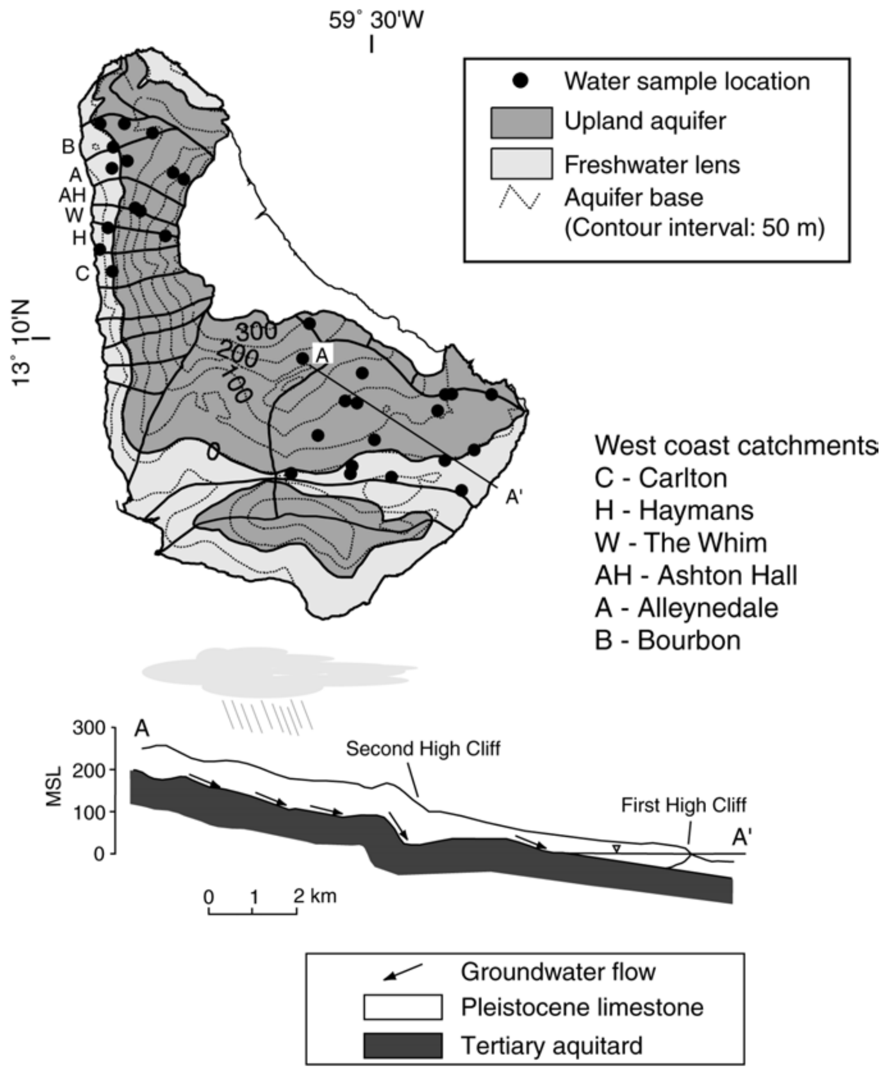

Figure 4-3. Hydrogeologic map of Barbados. The Pleistocene limestone aquifer is divided into several groundwater catchments due to the topography of the Pleistocene-Tertiary contact. The distribution of sampled wells indicate the groundwater catchments investigated in this study while the contours shown indicate the elevation of the base of the Pleistocene limestone (Adapted from Stanley Associates, 1978; Barbados Ministry of Health et al., 1991).

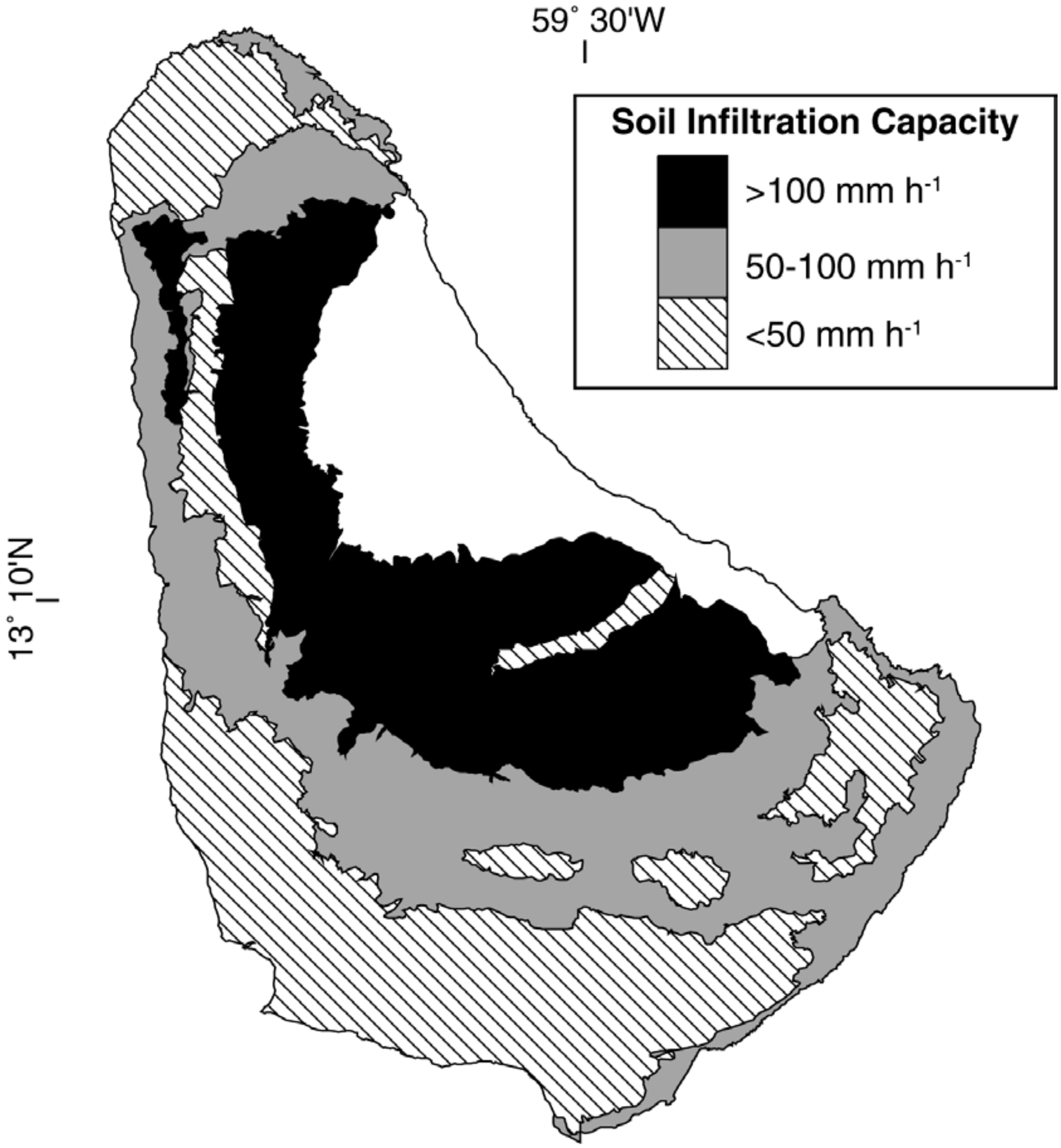

Figure 4-4. The infiltration capacities of soils developed over the Pleistocene limestone aquifer. Barbados soil infiltration capacities tend to increase with elevation. The most permeable soils occur above the Second High Cliff. Adapted from Vernon and Carroll, 1965; Tullstrom, 1964).

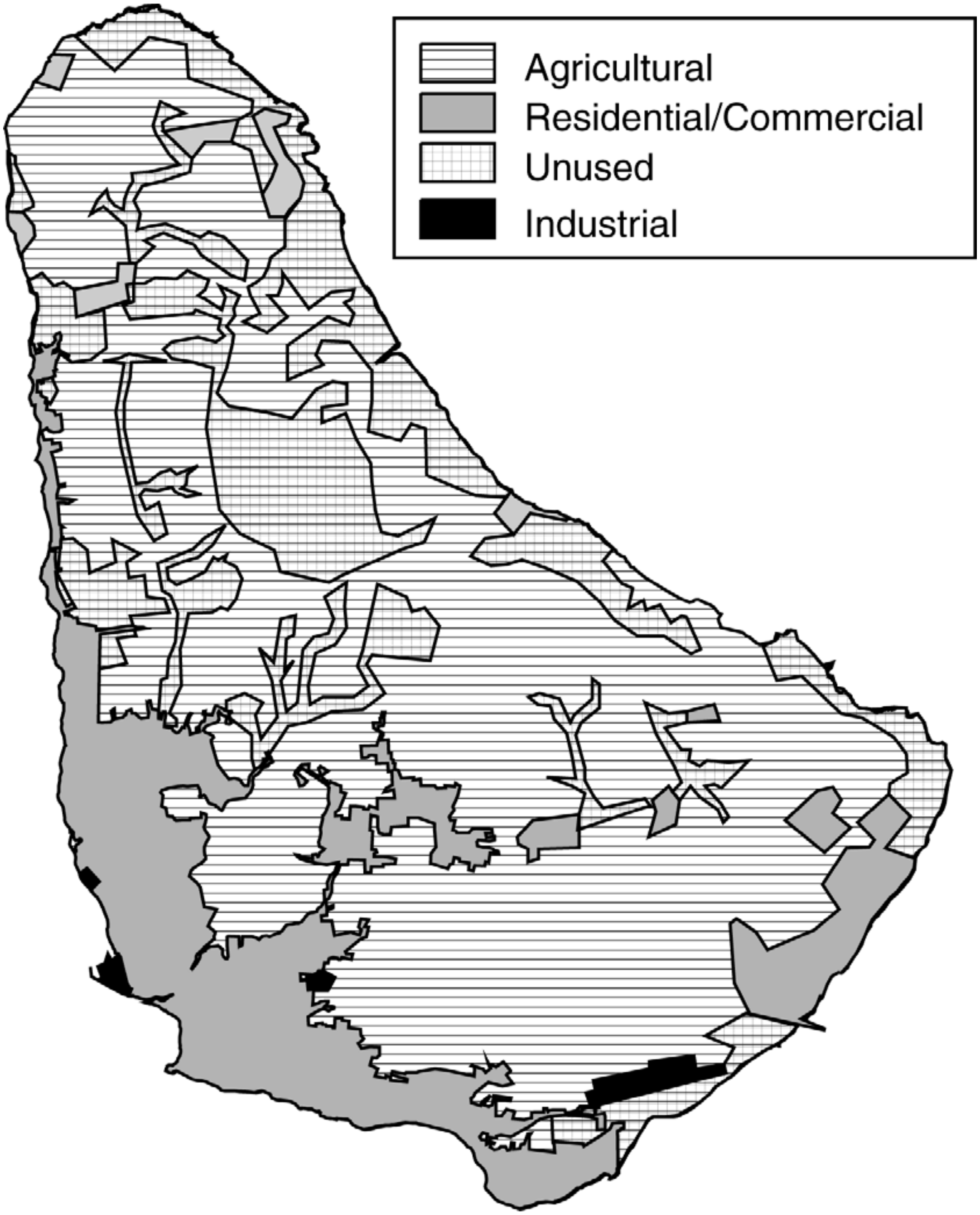

Figure 4-5. Land use on variations Barbados. On Barbados, agriculture accounts for approximately 60% of the land. Adapted from Directorate of Overseas Surveys 1:10,000 topographic maps.

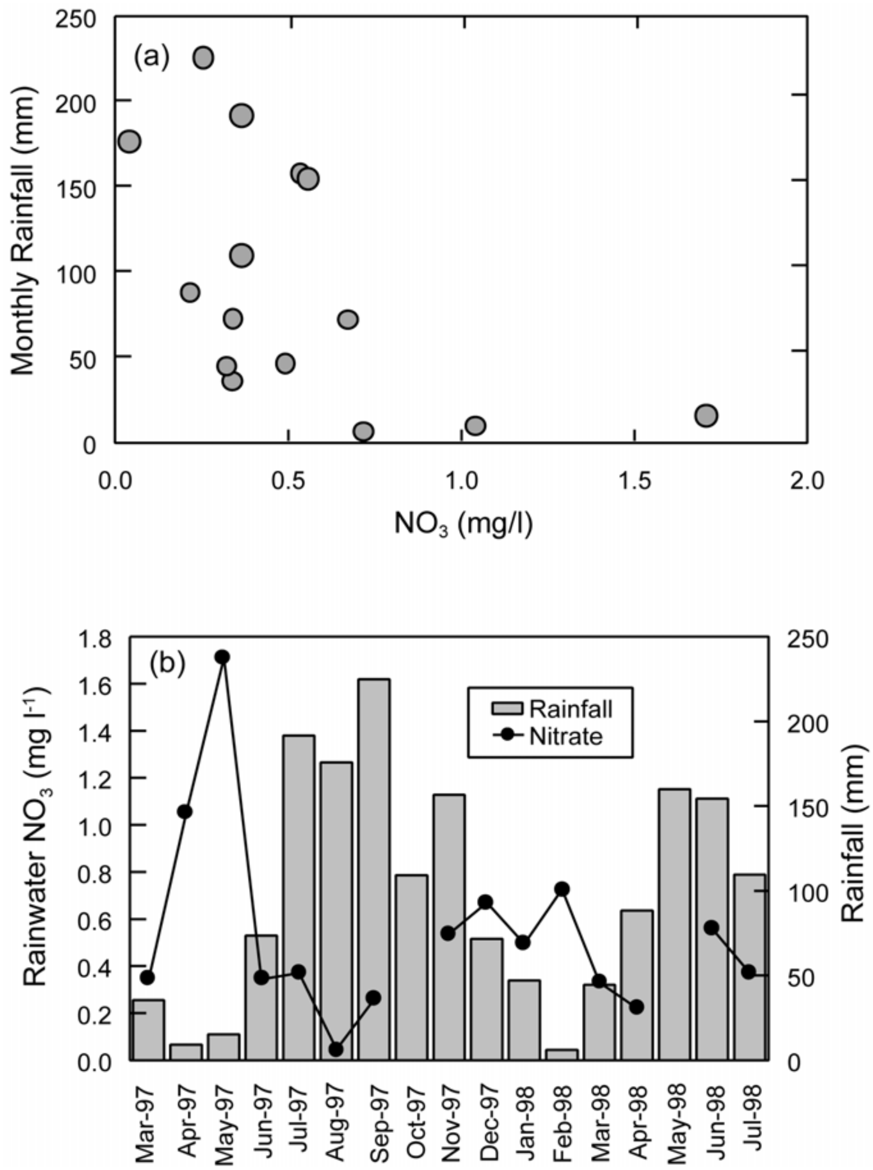

Figure 4-6. (a) Average monthly rainwater nitrate concentrations on Barbados generally decrease with increasing monthly rainfall. (b) Average monthly rainwater nitrate concentrations fluctuate seasonally such that nitrate concentrations are generally higher during the dry season than the wet. These rainwater samples were collected at Site A (Fig. 3-3).

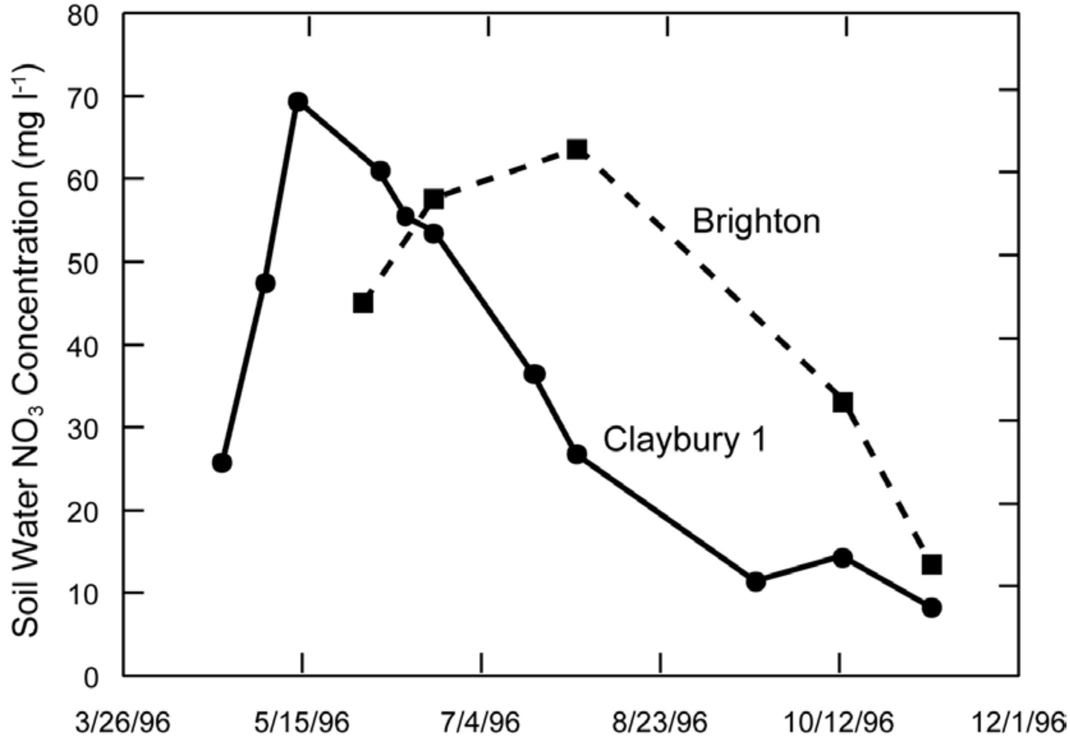

Figure 4-7. Soil water nitrate concentrations vary over time. These samples were collected at a depth of 1.5 meters near Sites 3 and 4 (Fig. 3-3). These fields, located at Brighton and Claybury Plantations, were used to cultivate sugar cane and vegetables, respectively. Nitrate concentrations rise in response to fertilizer application that most likely took place in May and April, 1996, respectively (based on data from Klohn-Crippen Consultants Ltd., 1997).

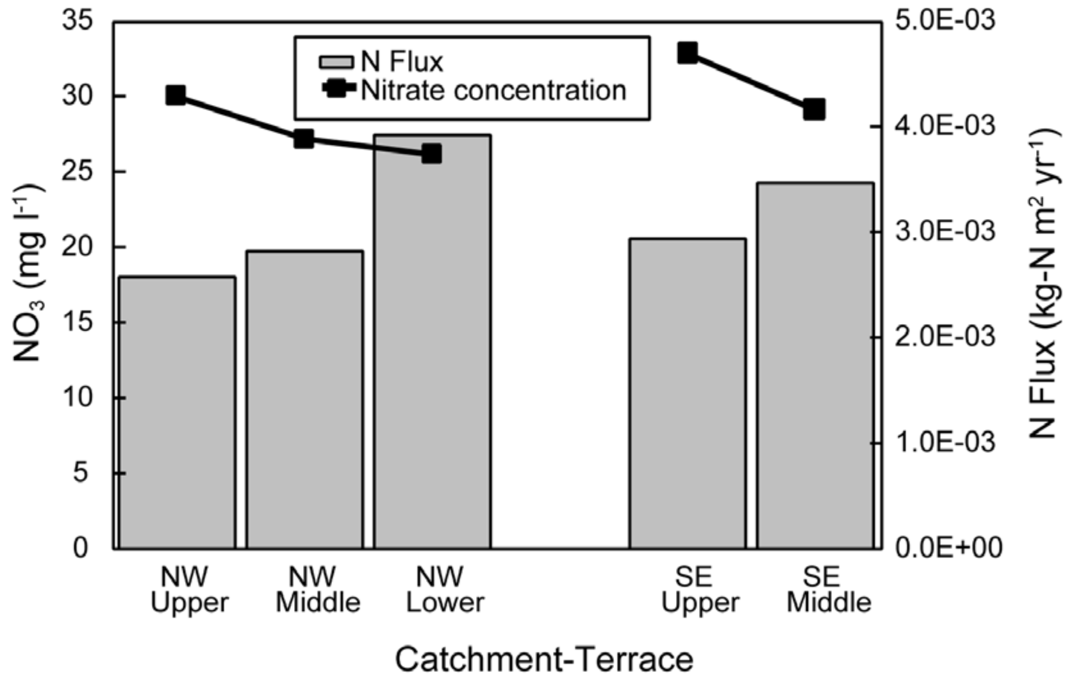

Figure 4-8. Average groundwater nitrate concentrations in Barbados groundwater catchments decrease down-gradient while at the same time groundwater nitrogen fluxes through the aquifer increase. This occurs due to enhanced recharge occurring at lower elevations.

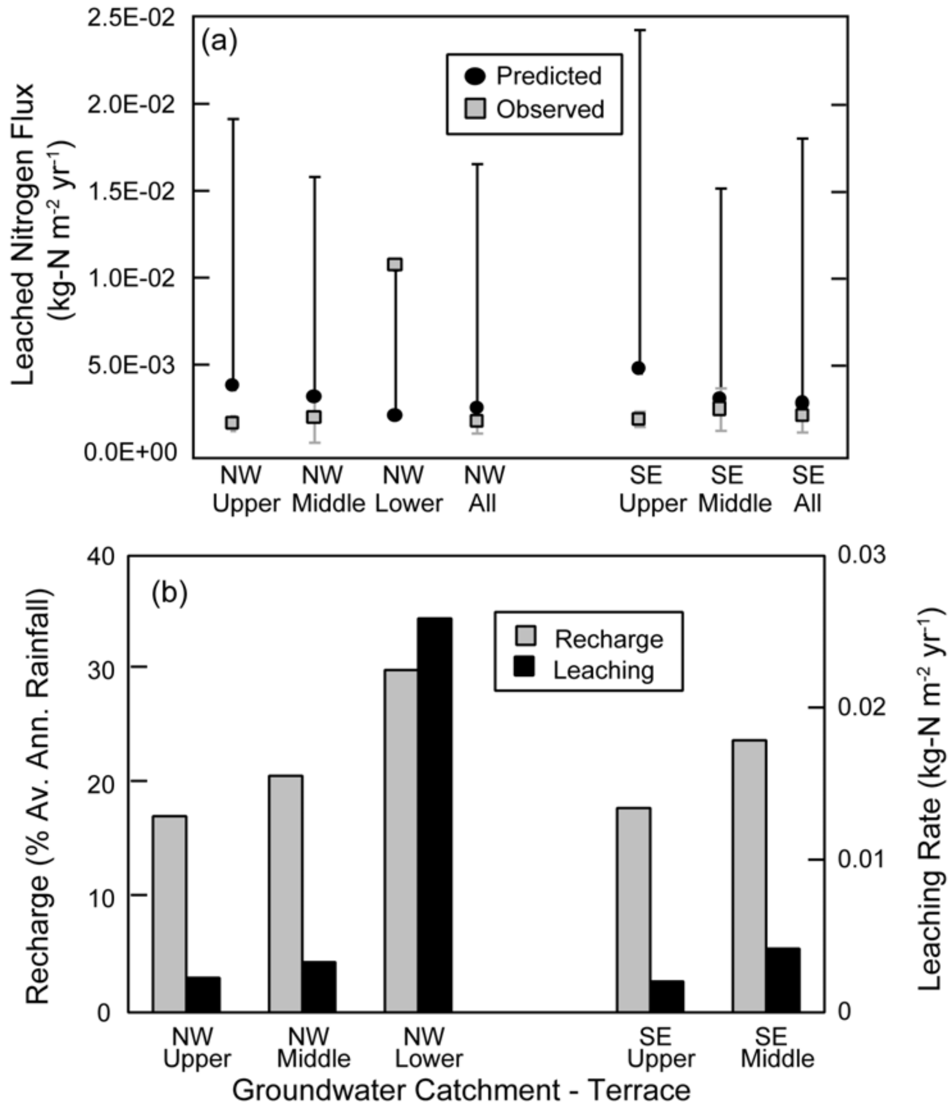

Figure 4-9. (a) Nitrogen leached from the soil is predicted by estimated nitrogen sources and sinks and by observed groundwater nitrogen concentrations. The predicted leaching rates are generally higher than leaching rates based on observed groundwater nitrogen concentrations. The bars represent the range of estimated nitrogen leaching. These leaching rates are averaged over the entire terrace. (b) Comparison of nitrogen leaching and recharge rates indicates that nitrogen leaching rates increase at lower elevations in response to increased recharge.

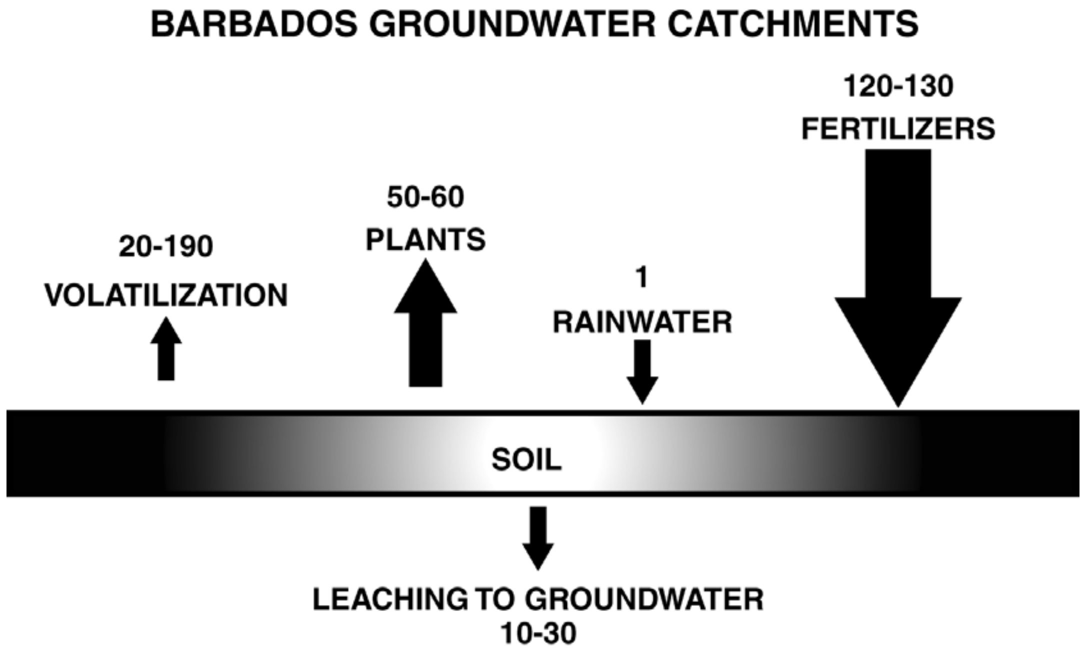

Figure 4-10. The nitrogen budget for groundwater catchments on Barbados. Nitrogenous fertilizer is the predominant source of nitrogen while uptake by plants, leaching and NH_3 emissions are the primary sinks. The numbers represent nitrogen fluxes expressed in kg ha^{-1} yr^{-1}.

CHAPTER 5: CONTROLS ON THE GROUNDWATER GEOCHEMISTRY OF AN ISLAND AQUIFER: THE PLEISTOCENE LIMESTONE AQUIFER OF BARBADOS

ABSTRACT

In this investigation, major and trace element and isotopic compositions of groundwater in a karst aquifer on Barbados are evaluated. The aim of this study is to determine which processes are responsible for observed groundwater compositions, and how and why these processes vary spatially and seasonally. To achieve this aim, the impact of factors, such as soil, aquifer and aquitard rock compositions, recharge processes, groundwater flow paths, groundwater mixing and anthropogenic inputs, on groundwater compositions is investigated.

The results of this investigation indicate that groundwater compositions are the sum of multiple geochemical processes. On Barbados, three main processes influence groundwater compositions: 1) mixing; 2) recharge; and 3) interaction with soil, and aquifer and aquitard rock. Groundwater mixing involves mixing fresh groundwater with seawater or groundwater discharging from the underlying aquitard. Groundwater discharge from the underlying aquitard has not previously been identified in this aquifer. Recharge processes are reflected in groundwater nitrate derived from leached fertilizer, and strontium isotopes characterized by soil-influenced compositions. Strontium isotopes also allow us to distinguish groundwater interaction with aquifer and aquitard rocks of varying compositions

that are encountered along groundwater flow paths. The predominance of soil-influenced strontium isotopic compositions, especially in up-gradient parts of the aquifer indicate that the impact of interaction between groundwater and relatively stable low-Mg calcite is small.

The three main processes, mixing, recharge, and interaction with soil and aquifer or aquitard rock, are all influenced to varying degrees by groundwater hydrology. The extent of groundwater mixing is a function of advection and diffusion, while interaction with soil or aquifer and aquitard rock is influenced by groundwater flow paths and residence times.

INTRODUCTION

The purpose of this research is to address the following questions: 1) what process or processes influence groundwater compositions observed in limestone aquifers; 2) how do groundwater compositions vary spatially and temporally; and 3) what factors or processes are responsible for these variations? Differences between the major and trace element and isotopic compositions of groundwater and rainwater may be the product of a single geochemical process, or the cumulative effects of multiple geochemical processes that take place during recharge and along groundwater flow paths. These geochemical processes potentially involve factors such as soil compositions, aquifer and aquitard rock compositions, recharge processes, groundwater flow paths, groundwater mixing and land use. These factors may be responsible for spatial and seasonal variations of groundwater compositions observed within aquifers. It has been widely recognized that some geochemical processes taking place in aquifers, for example, nitrification and denitrification, are influenced by microbes (Chapelle, 1993). It is possible that microbes play a role in many other geochemical processes. Identifying the role of microbes in geochemical process lies outside of the scope of this study which will be restricted to simply identifying geochemical processes taking place in the aquifer under investigation. The aim of this study is to increase our understanding of the natural groundwater geochemical processes taking place in a limestone aquifer. This is achieved by: 1) evaluating spatial and seasonal changes in groundwater major and trace element and isotopic compositions; and 2) investigating the relationships between these changes and the factors listed above.

The Pleistocene limestone aquifer of Barbados is a relatively small, unconfined karst aquifer characterized by short flow paths up to 10 kilometers long. This aquifer is well suited for studies investigating factors influencing groundwater geochemistry because it has a simple flow system. Additionally, the aquifer hydrogeology and hydrogeochemistry are well characterized (Senn, 1946; Tullstrom, 1964; Harris, 1971; Banner et al., 1994). The short flow paths in this aquifer result in short groundwater residence times and rapid responses to anthropogenic inputs. This paper primarily investigates the natural geochemical processes affecting groundwater compositions in this aquifer. These geochemical processes are responsible for most constituents present in the groundwater.

Most groundwater originates as rainwater. In the absence of significant evaporation, water-rock interaction, mixing, etc., groundwater O and H isotopic compositions reflect the composition of the initial rainwater. In contrast, dissolved constituents in groundwater primarily reflect the compositions of the rocks encountered during recharge and along flow paths, or mixing with other waters. The most significant anthropogenic inputs in Barbados groundwater take the form of NO_3 primarily derived from nitrogenous fertilizers (Jones et al., 1998).

In geologically young limestone aquifers, such as the Pleistocene limestone aquifer on Barbados, groundwater major element compositions are primarily the products of dissolution of metastable carbonate minerals, aragonite and high-Mg calcite, coupled with precipitation of low-Mg calcite (Harris, 1971). This results in progressive enrichment of groundwater in Mg and Sr along groundwater flow paths (Banner et al., 1994). These patterns occur in response to the presence of relatively unaltered Sr- and Mg-rich limestone along the coasts, especially in southern Barbados. Elsewhere in the aquifer, diagenetic alteration has converted most of the aragonite present in the limestone to low-Mg calcite (Matthews, 1968). Near the coasts, groundwater compositions are characterized by gradually increasing Na and Cl concentrations due to mixing with seawater (Harris, 1971).

In addition to groundwater major element compositions, interaction between groundwater and limestone is also reflected in groundwater Sr isotopes. Previous studies on Barbados indicate that spatial variation of groundwater Sr isotopes reflect a combination of water-rock interactions: 1) dissolution; 2) aragonite-calcite conversion; and 3) recrystallization (Banner et al, 1994). In this study, soil was implicated as a potential source of Sr.

Carbon isotopic compositions of limestone on Barbados display a wide range of values (Allan and Matthews, 1977). This range of values represents vadose- or soil-influenced compositions indicated by low $\delta^{13}C$ values and phreatic compositions that retained marine signatures and consequently have $\delta^{13}C$ values ~0‰. The low calcite $\delta^{13}C$ values are the product of subaerial diagenesis because of the contribution of soil C to limestone by infiltrating water (Allan and Matthews, 1977).

Monthly groundwater sampling of public water supply wells in previous studies has suggested that there are no clear seasonal patterns in groundwater major element compositions (Stanley Associates Engineering, 1978a; DELCAN, 1995). Temporal variations of groundwater major element compositions have been observed at pumping stations located in the freshwater lens portion of the aquifer. This variation has been attributed to increased pumping rates during the dry season (Stanley Associates Engineering, 1978a). Increased salinity occurs because underlying brackish and saline water is drawn into the pumping wells (Stanley Associates Engineering, 1978a).

Understanding natural groundwater geochemical processes is important in order to resolve anthropogenic processes that may also be influencing groundwater compositions. The evaluation of multiple geochemical and isotopic tracers indicate that the major and trace element and isotopic compositions of groundwater in the Pleistocene limestone aquifer of Barbados are the cumulative result of multiple processes taking place in different parts of the flow system rather than a single continuous geochemical evolution process. This is deduced by determining the sources of different geochemical constituents in the groundwater.

STUDY AREA

Climate

The average annual rainfall on Barbados varies from about 1,000 mm yr^{-1} in the north and southeast to more than 2,000 mm yr^{-1} at the center of the island (Fig. 5-1). On Barbados, the wet season extends from June to December. Wet season rainfall typically accounts for 60% of average annual rainfall (Jones et al., 2000).

Geology and Hydrogeology

The Pleistocene limestone aquifer of Barbados is composed of Pleistocene coral reef limestone underlain by Tertiary deep-sea sedimentary rocks that act as an aquitard. This aquifer occurs in the northern, western and southern portions of the island. Due to continuous uplift, the coral reef limestone was deposited outwards from the center of the island forming a series of terraces that decrease in age with decreasing elevation (Taylor and Mann, 1991). There are three main groups of terraces, the Lower Reef, Middle Reef and Upper Reef Terraces separated by the First and Second High Cliffs, respectively (Fig. 5-2). The Second High Cliff is an important site for recharge to the aquifer (Jones et al., 2000).

The Pleistocene limestone is composed of largely of stable low-Mg calcite, however less stable high-Mg calcite and aragonite occur especially at lower elevations (Matthews, 1968). The spatial distribution of aragonite and high-Mg calcite is related to the age of the limestone and the extent of diagenetic alteration that converts aragonite and high-Mg calcite to low-Mg calcite. Consequently, the younger limestones in the lower terraces tend to contain more aragonite and high-Mg calcite than older limstones at higher elevations (Matthews, 1968). Aragonite and high-Mg calcite occur at lower elevations in western Barbados than in the southeast (Matthews, 1968). This can be attributed to the more intense diagenesis in the west. The Tertiary deep-sea sedimentary rocks that underly the Pleistocene limestone are composed of smectite-nanno-rad-foram marl and radiolarian mudstone, and interbedded volcanogenic turbidites and waterlaid tuffs (Saunders et al., 1984).

There are nine soil types that overlie and were largely formed by weathering of the Pleistocene limestone. These soils display variable hydrologic properties and mineral compositions, and are generally 1-2 m thick. In addition to material derived from the Pleistocene limestone, the soils contain sediment derived from the Tertiary rock units that occur on the island, volcanic ash derived from the volcanic arc located to the west and Saharan dust. (Vernon and Carroll, 1965; Muhs et al., 1987). These soils are largely composed of 60-75 % clay, although some sandy soils may contain as little as 25 % clay. The clay minerals vary from stable kaolinite at higher elevations to less stable smectite at lower elevations following patterns similar to the Pleistocene limestone mineralogy (Vernon and Carroll, 1965).

The Pleistocene limestone aquifer is highly permeable due to the high effective primary and secondary porosity of the limestone (Senn, 1946; Tullstrom, 1964). Recharge to the aquifer takes the form of rapid diffuse and discrete infiltration through the soil and underlying limestone to the water table which occurs close to the base of the Pleistocene limestone (Jones et al., 2000). The topography of the top of the aquitard controls the groundwater flow paths within the aquifer (Fig. 5-3). This occurs because the aquifer is unconfined and has a relatively thin saturated zone. Groundwater generally flows from the elevated central portions of the island, westward and southward towards the coast. Discharge from this aquifer primarily takes the form of groundwater discharge along the coast. Some discharge also takes place from springs that occur where the Pleistocene-Tertiary contact crops out along the eastern margin of the aquifer and from a few springs that occur where the Pleistocene limestone is thin and the water table intersects the land surface.

The Pleistocene limestone aquifer is divided into two hydrologic zones referred to as the Stream- and Sheet-water zones, depending on whether the top of the aquitard lies above or below sea level, respectively (Fig. 5-3). The Stream-water zone forms the upland portions of the aquifer where groundwater forms a thin saturated zone, a few meters thick, at the base of the Pleistocene limestone (Senn, 1946). The term 'Stream water' refers the occurrence of underground streams in this part of the aquifer. The Stream-water zone constitutes the bulk of the areal extent of the Pleistocene limestone aquifer, whereas the Sheet-water zone primarily occurs within 1 – 2 km of the coast. In the Sheet-water zone, groundwater occurs in freshwater lenses. In this part of the aquifer, the water table is close to sea level (Senn, 1946). In addition to hydrologic zones, this aquifer is subdivided into groundwater catchments (Stanley Associates Engineering Ltd., 1978b). Ridges in the topography of the aquitard form hydrologic divides and thus control groundwater flow paths in the aquifer.

METHODS

As part of this investigation, rainwater, groundwater and vadose water samples were collected and analyzed for major and trace element concentrations and O, H, C, and Sr isotopes. The groundwater and vadose water samples were collected from wells, a spring and cave drips (Fig. 5-2; Table 5-1). Rainwater samples were collected at Site A during 1997 and 1998 (Fig. 5-2). These rainwater samples supplement rainwater data collected as part of the Global Network for Isotopes in Precipitation (GNIP) program from 1959 through 1992.

Groundwater and Vadose Water Sampling

Groundwater samples were collected from 32 sites on Barbados (Fig. 5-2). These samples were collected from pumping wells, or in the absence of a pump, using acid-cleaned teflon bailers. The sample sites are located within groundwater catchments in northwestern and southeastern Barbados. These areas were chosen because they provide contrasting hydrologic and geologic conditions, such as different groundwater flow-path lengths, hydraulic gradients, and limestone compositions. In northwestern Barbados, groundwater flow-paths are shorter and overall hydraulic gradients are steeper than in the southeast (Fig.5-3). The Pleistocene limestone in northwestern Barbados has also undergone more intense diagenetic alteration than limestone of equivalent age in the southeast (Matthews, 1968). Most groundwater samples were collected during July/August 1994 and January 1996. These samples represent relatively dry and wet conditions, respectively. Additional groundwater samples were collected periodically from January 1996 through February 1997 from selected wells located in different parts of the aquifer. These samples were collected to investigate seasonal variations of groundwater compositions. These sites, Alleynedale Hall (Site 19), Hampton (Site 9), and Kendal Plantations (Site 12), and Home Agricultural Station (Site 11), each represent different conditions that occur within the aquifer (Fig. 5-2). Kendal Plantation is located above the Second High Cliff in the Stream-water zone. Alleynedale Hall is located at the boundary between the Sheet- and Stream-water zones. Hampton Plantation is located in the center of the Sheet-water zone while Home Agricultural Station is located near the coast.

Vadose zone water samples were collected from three caves located at Bowmanston Pumping Station (Site 1), Thicket (Site 18), and Sailors Gully (Site 29; Fig. 5-2). These water samples were collected directly from drips using polypropylene bottles. The water samples from slow drips in the Thicket and Sailors Gully caves required leaving the collection bottles for 2 - 3 days.

Rainwater Sampling

Rainwater samples were collected at Sample Site A during 1997 and 1998 (Fig. 5-2). The simple rainwater collection apparatus consists of a bucket with a lid, a glass funnel, and a 250-ml glass collection bottle. The funnel fits into a hole cut in the bucket lid and the rainwater is collected in the glass bottle. This apparatus was placed at a location away from obstructions and overhangs, such as trees, in order to minimize any solid debris from falling into the sampler. These samples were transferred from the 250-ml collection bottle to 60-ml amber vials within several hours of rainfall events, and were immediately refrigerated after being sealed with Parafilm™. Most sample vials represent rainfall during a single day, however, in about 15% of the samples, rainwater collected during consecutive small rainfall events was pooled together in a single vial (Table A-1).

Soil sampling

Soil samples were collected as part of this investigation with the aim of determining the impact of soil compositions on groundwater compositions. Seven soil samples were collected throughout the study areas (Fig. 5-2). These soil samples were collected in areas adjacent to selected groundwater sample locations in northwestern and southeastern Barbados.

Analytical Methods

The water and soil samples that were collected as part of this investigation were analyzed for major and trace element and C, O, H, and Sr isotopic compositions. Field parameters, pH and temperature, were measured using a Fisher Scientific Accumet® model 1002 pH/Eh meter equiped with a combination pH electrode with Ag/AgCl reference and a temperature probe. Alkalinity was also measured in the field by titrating a 25-ml water sample with 0.1N HCl to the pH 4.5 end-point using a 2-ml Gilmont microburet. Cation concentrations were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) while anion concentrations were determined using single column ion chromatography (IC) at the University of Texas at Austin. The charge-balance for 45 out of 51 water samples analyzed is within ±5%. A total of 1 out of 51 analyzes have charge balances exceeding 10%. Strontium isotopic compositions of the water samples were determined using a Finnigan-MAT model 261 thermal ionization mass spectrometer in static multi-collection mode at the University of Texas at Austin. Analytical uncertainty (2σ external) of the $^{87}Sr/^{86}Sr$ analyses based on NBS-SRM 987 standards was ±0.000029 (1996 analyses), ±0.000032 (1997 analyses), and ±0.000012 (2000 soil analyses). The analytical uncertainty of 2000 analyses are lower than earlier analyses because the 1996 and 1997 analyses were determined by static multicollection mode while the 2000 analyses were determined by dynamic multicollection mode. Mean $^{87}Sr/^{86}Sr$ values of the NBS-

SRM 987 standard are 0.710237 (n=19), 0.710195 (n=4) and 0.710265 (n=4) in 1996, 1997, and 2000, respectively. The $^{87}Sr/^{86}Sr$ analyses from these three periods were normalized to a standard $^{87}Sr/^{86}Sr$ value of 0.710250. Groundwater and rainwater samples were analyzed for their O isotopic compositions at the Colorado School of Mines, Southern Methodist University and University of Arizona by a modification of the CO_2 equilibration technique (Epstein and Mayeda, 1953) as described in Socki et al. (1992). Analytical precision (1σ external), based on analyses of laboratory standards and duplicate samples is ±0.15‰, ±0.1‰ and ±0.09‰ at the Colorado School of Mines, Southern Methodist University and University of Arizona, respectively. The H isotopic compositions of the rainwater and groundwater samples were determined at Southern Methodist University and University of Arizona using a method similar to Bigeleisen et al. (1952). Analytical precision (1σ external) based on standard runs is ±1.4‰ and ±1‰ at Southern Methodist University and the University of Arizona, respectively. Carbon isotopes were analyzed at the Colorado School of Mines in the stable isotope laboratory of John Humphrey following methods given in Craig (1957). Analytical precision (1σ external) for these analyses is ±0.12‰.

RESULTS

Rainwater Geochemistry

Geochemical compositions of rainwater samples collected as part of this study display a range of concentrations that vary seasonally (Fig. 5-4; Table 5-2). Concentrations of dissolved constituents in Barbados rainwater are higher during dry season months, January through May, than during the wet season. The relationship between dissolved constituent concentrations in rainwater and the amount of rainfall is not linear (Fig. 5-5). There is a wide range of rainwater Cl concentrations associated with daily rainfall less than 15 mm (1 - 35 mg l^{-1}) while rainwater associated with daily rainfall exceeding 15 mm has Cl concentrations of 1 - 7 mg l^{-1}.

The O and H isotopic compositions of Barbados rainwater collected in this study display a range of compositions. The $\delta^{18}O$ and δD values lie in the range –2.5 to +0.5‰ and –16.7 to +11.2‰, respectively. This range of values (n = 11) is smaller than the range of values in the larger GNIP dataset (n = 244). In both cases, the $\delta^{18}O$ and δD values lie along the Global Meteoric Water Line and display a negative correlation with the amount of rainfall (Jones et al., 2000). The O and H isotopic compositions of Barbados rainwater and their relationship with groundwater compositions is discussed in detail in Jones et al (2000).

Groundwater and Vadose Water Geochemistry

Major and Trace Elements

On Barbados, groundwater and vadose water major element compositions form a range that lies between Ca-HCO_3 and Na-Cl geochemical facies (Fig. 5-6; Table A-5). Major element compositions of groundwater in the Stream-water zone are primarily Ca-HCO_3 while in the Sheet-water zone groundwater has a wider range of compositions from Ca-HCO_3 to Na-Cl. Vadose water compositions are similar to groundwater. Vadose water major element compositions vary from compositions approaching evaporated rainwater at Thicket Cave to compositions similar to the adjacent groundwater at Bowmanston Pumping Station (Fig. 5-6).

Periodic groundwater sampling at four locations over a period of a year indicate relatively uniform concentrations of dissolved constituents at the two Stream-water zone sample sites, Alleynedale Hall and Kendal Plantations. Groundwater major element concentrations at the Sheet-water zone sample sites, Home Agricultural Station and Hampton Plantation, display apparent seasonal cycles with higher concentrations from September through November. These seasonal fluctuations are more apparent at Home Agricultural Station than at Hampton Plantation (Fig. 5-7).

Carbon Isotopes

Barbados groundwater is characterized by a relatively narrow range of O isotopic compositions (-5 to –2 ‰ SMOW) and much larger range of C isotopic compositions of -13 to -2‰ PDB (Fig. 5-8; Table A-6). The range of groundwater $\delta^{13}C$ values approaches that of Barbados limestone samples collected by Banner (unpublished). The C isotopic compositions of groundwater samples collected in July-August 1994, prior to the peak of the wet season (August-November) were compared with the groundwaters collected at the same sites in January 1996, at end the wet season (Table 5-3). At eight out of fifteen sites differences in groundwater $\delta^{13}C$ values were larger than analytical uncertainty of ±0.12‰. At approximately half of these eight sites, the 1996 groundwater $\delta^{13}C$ value was lower than the 1994 value. Groundwater $\delta^{13}C$ values display no apparent relationship with location along groundwater flow paths. Comparison of $\delta^{13}C$ values of groundwater and vadose water collected at Bowmanston Pumping Station indicate lower $\delta^{13}C$ values for the groundwater (-9.1‰) than vadose water (-7.4‰).

Oxygen and Hydrogen Isotopes

The groundwater O and H isotopic compositions of Barbados groundwater form a narrower range than rainwater $\delta^{18}O$ values (Jones et al., 2000). Groundwater $\delta^{18}O$ values mostly lie in the range –4 to –2‰ while δD values lie in the range –21 to –9‰. There is a tendency for Barbados groundwater to have higher $\delta^{18}O$ values at lower elevations, however, there is no statistically significant relationship between groundwater $\delta^{18}O$ values and elevation. Periodic groundwater sampling as part of this study indicates that there are no apparent seasonal fluctuations of groundwater oxygen isotopic compositions.

Strontium Trace Element and Isotope Geochemistry

The Sr isotopic compositions of Barbados groundwater and aquifer and aquitard rocks are expressed relative to the $^{87}Sr/^{86}Sr$ ratio of modern seawater as follows:

$$\delta^{87}Sr = [(^{87}Sr/^{86}Sr_{sample})/\ (^{87}Sr/^{86}Sr_{seawater}) - 1] \times 10^5, \qquad (5\text{-}1)$$

where the $\delta^{87}Sr$ value of modern seawater is 0.

In northwestern Barbados, groundwater Sr/Ca ratios are relatively uniform throughout the catchments, displaying a relatively narrow range of values. In the southeast, groundwater Sr/Ca ratios increase gradually at elevations above 50 m (Sr/Ca <0.01) and rapidly at lower elevations to Sr/Ca values >0.15 (Fig. 5-9). Groundwater Mg/Ca ratios display trends similar to Sr/Ca ratios in the respective catchments (Fig. 5-10). Comparison of Mg/Ca and Sr/Ca ratios of aquifer and aquitard rock indicate that in both cases high Mg/Ca ratios are associated with high

Sr/Ca ratios (Fig. 5-14). Tertiary aquitard rock generally has higher Mg/Ca ratios than the Pleistocene limestone aquifer rock.

Barbados groundwater δ^{87}Sr values lie in the range -35 to –6 (Fig. 5-11; Table A-6). In most parts of the study areas, groundwater δ^{87}Sr values are >-25, however in some areas groundwater δ^{87}Sr values lie in the range –25 to –40. These low groundwater δ^{87}Sr values occur in parts northwestern and southeastern Barbados (Fig. 5-12). There are no apparent seasonal or interannual variations of groundwater δ^{87}Sr values.

Soil Geochemistry

Barbados soil leachates generally become increasingly depleted in Mg and Sr with increasing elevation, displaying patterns similar to the Pleistocene limestone (Fig. 5-13). Barbados soil leachates display δ^{87}Sr values of –22.6 to +8.5, a range that overlaps with both the ranges groundwater and Pleistocene limestone compositions of –35 to –6 and –9 to +2, respectively (Fig. 5-11). These soil leachate δ^{87}Sr values are in most cases slightly higher than groundwater δ^{87}Sr values and lower than Pleistocene limestone δ^{87}Sr values at equivalent elevations.

DISCUSSION

Rainwater

The dissolved constituents in Barbados rainwater are derived from sea-water aerosols. These rainwater compositions are typical of oceanic settings (Berner and Berner, 1996). Seasonal fluctuations of Barbados rainwater major element and isotopic compositions display an apparent inverse relationship with rainfall amounts. The non-linear relationship between rainfall and major element concentrations, such as Cl, NO_3, and SO_4, indicates that the occurrence of lower concentrations of dissolved constituents in rainwater during the wet season is not simply due to increased dilution. A better explanation for this seasonal fluctuation is the rapid removal of airborne sea-water aerosols during rainfall events. During 1997-98, rainwater associated with daily rainfall of <10 mm displayed a wide range of Cl concentrations (1 - 36 mg l^{-1}). Intense rainfall exceeding 10 mm day^{-1}, is characterized by rainwater Cl concentrations that are ≤7 mg l^{-1}. These lower concentrations can be attributed to sea-water aerosol removal from the atmosphere during the early stages of rainfall events (Berner and Berner, 1996). Groundwater constituents derived from rainwater, for example Cl, accumulate in the soil during the dry season and are only flushed into the aquifer during recharge periods that occur at the peak of the wet season (Jones et al., 2000).

Groundwater

Major and Trace Elements

The range of groundwater major element compositions on Barbados represent compositional changes along flow paths. In the Stream-water zone, groundwater major element compositions tend towards Ca-HCO_3 type waters that are attributable to limestone dissolution (Table Fig. 5-6). Groundwater in the Sheet-water zone displays a wider range of water types (Na-Cl to Ca-HCO_3) that overlaps with Stream-water zone groundwater compositions. In the Sheet-water zone, Ca-HCO_3 type groundwater primarily occurs along the landward margin of the zone, reflecting the inflow of groundwater from the Stream-water zone. Groundwater major element compositions change from Ca-HCO_3 to Na-Cl types towards the coast. These groundwater compositional changes occur due to increasing mixing of fresh groundwater with seawater.

Vadose waters display a range of major element compositions, varying from a rainwater-type composition at Thicket Cave to groundwater-type compositions at Bowmanston Pumping Station. This range of compositions is apparently related to the depth of the cave below land surface. The cave at Thicket is relatively shallow, overlain by about 10 meters of limestone. The Sailors Gully cave occurs in a dry valley at the base of a channel approximately 30 meters deep and the Bowmanston cave is the deepest of the three caves occurring at a depth of >80 meters. The vadose water compositions change from rainwater to groundwater compositions with increasing depth (Fig. 5-6). This trend can be explained by increasing effects of interaction between infiltrating water and the limestone.

Seasonal fluctuations of groundwater major element compositions are more apparent in the coastal zone, as represented by Home Agricultural Station, than in the inland parts of the aquifer, as represented by Hampton, Alleynedale Hall and Kendal Plantations (Fig 5-7). The seasonal fluctuations can be attributed to seasonal thinning and thickening of the freshwater lens and freshwater-seawater mixing zone (Steinen et al., 1978). Seasonal variations of the freshwater lens and mixing zone are associated with seasonal variations of the groundwater inflow from the Stream-water zone. The freshwater lenses and mixing zones become thicker in response to the wet season influx of recharge water and thinner during the dry season due to less fresh groundwater entering Sheet-water zone. Sheet-water zone groundwater tends to be more saline during peak wet season months (September through November) when the mixing zone is thicker (Fig. 5-7). The thicker mixing zone can be attributed to turbulent groundwater flow associated with the rapid influx of large volumes of groundwater associated with discrete recharge at the peak of the wet season (Jones et al., 2000). This results in more mixing of the fresh groundwater with the underlying seawater and consequently higher salinity of groundwater in the freshwater lens. This effect would diminish over time as lesser amounts of groundwater enter the Sheet-water zone, resulting in less turbulence and therefore less mixing. Groundwater Na concentrations can be used as an indicator of fresh groundwater-seawater mixing. Chloride mass-balance considerations indicate that groundwater at Hampton, Kendal, and Alleynedale Hall Plantations contain 0.2 – 0.3%, 0.3 – 0.4%, and 0.2 – 0.5% seawater, respectively. Home Agricultural Station groundwater is composed of approximately 2% seawater during dry season months (January through March) and 2.6 – 2.7% seawater during wet season months (September through November). At the Home Agricultural Station, groundwater Ca, Mg and Sr concentrations display seasonal fluctuations similar to Na. Despite this similarity, Ca, Mg and Sr are also derived from the aquifer rock and therefore can not be used to estimate seawater mixing.

There are no apparent seasonal fluctuations of groundwater oxygen isotopic compositions. The lack of groundwater oxygen isotopic fluctuations can be explained by the occurrence of a brief period of recharge coinciding with the peak of the wet season (Jones et al., 2000). Consequently, groundwater $\delta^{18}O$ values primarily reflect the oxygen isotopic composition of rainwater during the recharge period (Jones et al., 2000). Freshwater-seawater mixing of up to 2% on Barbados as based on Na concentrations discussed above should result in a $\delta^{18}O$ value shift of <0.02‰, is less than the analytical uncertainty and much smaller than the observed range of groundwater $\delta^{18}O$ values (~2‰).

Carbon Isotopes

Barbados groundwater displays a range of $\delta^{13}C$ values that approximately coincide with the range of Pleistocene limestone $\delta^{13}C$ values (Fig. 5-8). There is no apparent pattern to the spatial or temporal variations of groundwater $\delta^{13}C$ values. The variations of limestone $\delta^{13}C$ values represent variability in the relative influence of soil C that is reflected in relatively low and high $\delta^{13}C$ values above and below the water table, respectively (Allan and Matthews, 1977).

Machel (2000) suggests that low $\delta^{13}C$ values of Barbados dolomite could occur due to oxidation of methane in parts of southeastern Barbados. The methane is assumed to be derived from localized seepage of fluids, possibly including oil and water, from an underlying petroleum reservoir (Machel and Burton, 1994). This hypothesis is based on the occurrence of several biodegraded oil seeps within the aquitard rock. This hypothesis can not be used to explain low $\delta^{13}C$ values of Barbados groundwater because: 1) widespread, active methane seepage has not been identified on Barbados; 2) Machel and Burton (1994) indicate that groundwater from the underlying petroleum reservoir is characterized by high $\delta^{13}C$ values (+7 to +10‰); and 3) in a shallow aquifer, soil processes outlined by Allan and Matthews (1977) are the most obvious and therefore the most likely source of low $\delta^{13}C$ values in groundwater via recharge of vadose water. Variation of groundwater $\delta^{13}C$ values can also occur due to variation of vegetation types or soil productivity. These factors are unlikely to influence Barbados groundwater $\delta^{13}C$ values because the groundwater represents recharge over a period of a few years. Vegetation changes, especially changes due to climate, take place over periods of decades or centuries. Seasonal fluctuations of soil productivity result in fluctuations of soil CO_2 concentrations and $\delta^{13}C$ values (Rightmire, 1978). The $\delta^{13}C$ values of Barbados groundwater will be influenced primarily by the $\delta^{13}C$ value of soil CO_2 at the peak of the wet season, when conditions are favorable for recharge. Additionally, humid tropical climates are unlikely to experience large fluctuations of soil productivity, unlike temperate climates where soil productivity decreases during winter months.

Strontium Trace Element and Isotope Geochemistry

Previous research has shown that groundwater geochemical processes taking place in Barbados include dissolution and recrystallization of the Pleistocene limestone aquifer rock, as well as aragonite-calcite conversion, especially at lower elevations (Banner et al., 1994). Barbados groundwater Sr/Ca and Mg/Ca ratios generally increase down-gradient with increasing residence time. This spatial distribution also mimicks trends observed in both the Pleistocene limestone and soils that are encountered along flow paths (Figs. 5-10; 5-11; 5-15). These trends are the products of the occurrence of younger, less diagenetically altered limestone at lower elevations. This limestone is characterized by relatively high Mg and Sr.

Weathering of the limestone produces similar trends in the resultant soils, although Sr and Mg concentrations are lower in the soils than in the parent limestone (Fig.5-13).

Comparison of groundwater Sr/Ca ratios in northwestern and southeastern Barbados indicate that northwestern groundwater Sr/Ca ratios are almost uniform throughout the catchment while southeastern groundwater Sr/Ca ratios decrease with increasing elevation (Fig.5-9). Similarly, the range of Mg/Ca ratios in northwestern groundwater is much smaller than in the southeastern catchments (Fig.5-10). These differences can be explained by groundwater Sr/Ca and Mg/Ca ratios that mimic the composition of the soils and aquifer rock. In northwestern Barbados, the Pleistocene limestone has undergone more intensive diagenesis than in the southeast. This diagenetic alteration results in preferential removal of Sr and Mg from the limestone and creates a mineralogically more stable aquifer rock (Matthews, 1968; Banner et al., 1994). Consequently, the limestone displays generally lower Sr/Ca and Mg/Ca ratios in the northwest than in other parts of the island. Most groundwater and soil Mg/Ca ratios lie between Pleistocene limestone and Tertiary aquitard compositions suggesting possible inputs from both aquifer and aquitard rocks or mineral-solution reactions, such as conversion of aragonite to calcite or high-Mg calcite to low-Mg calcite, that drive fluid Mg/Ca and Sr/Ca higher than rock compositions (Fig. 5-14).

Barbados soil, vadose water and groundwater Sr isotopic compositions generally lie between Pleistocene limestone and Tertiary rock compositions (Fig. 5-11). One would expect that the range of soil, vadose water and groundwater δ^{87}Sr values reflects interaction between vadose water and groundwater and Pleistocene aquifer rock and Tertiary aquitard rock (Banner et al., 1994). Additionally, the soil δ^{87}Sr values are probably also influenced by material derived from Saharan dust and volcanic ash (Banner et al., 1994). The Pleistocene and Tertiary Sr sources have characteristic ranges of δ^{87}Sr values of –10 to +2 and –200 to -50, respectively, reflecting Pleistocene through Tertiary seawater Sr isotopic compositions.

The Sr isotopic compositions of most groundwater samples collected in this study indicate a predominant influence of Pleistocene limestone aquifer rock or soil. There are a few groundwater samples that have δ^{87}Sr values less than –25 (Fig. 5-11). This indicates a greater Tertiary aquitard influence on the Sr isotopic compositions of these samples. These Tertiary aquitard-influenced groundwaters occur in isolated down-gradient parts of the Stream-water zone (Fig. 5-12). This greater aquitard influence is suggestive of groundwater flow through the aquitard rock. Higher Mg/Ca ratios in aquitard-influenced groundwaters could be attributed to tertiary aquitard rock that generally has higher Mg/Ca ratios than most low-Mg Pleistocene limestone (Fig. 5-14). In the absence of δ^{87}Sr data, this evidence is not definitive because high-Mg calcite and aragonitic limestones can also produce high Mg/Ca ratios in groundwater.

Comparison of groundwater Sr/Ca ratios and Sr isotopic compositions in the two study areas indicate that interaction between groundwater, soil and aquifer or aquitard rock produces groundwater compositions that follow trends that apparently approach soil, aquifer or aquitard rock strontium isotopic compositions along groundwater flow paths, respectively (Fig. 5-15). The groundwater Sr/Ca ratios and Sr isotopic compositions in the respective groundwater catchments lie along different trends. In both catchments, groundwater are characterized by a similar range of δ^{87}Sr values, however, in the northwest, the groundwater is characterized by a narrower range of Sr/Ca ratios. This mimics the range of aquifer rock compositions that the groundwater encounters in the respective groundwater catchments.

Geochemical modeling

In order to better investigate the water-rock interaction in the Pleistocene limestone aquifer, geochemical modeling was conducted based on Banner et al. (1989, 1994). Geochemical modeling of selected constituents indicates expected groundwater compositional changes during infiltration and along groundwater flow paths for given soil leachate, and aquifer and aquitard rock compositions. The geochemical processes modeled are: 1) dissolution of low-Mg calcite in Pleistocene aquifer and Tertiary aquitard rock; 2) recrystallization of low-Mg calcite in Pleistocene aquifer and Tertiary aquitard rock; and 3) transformation of aragonitic limestone to low-Mg calcite in Pleistocene aquifer rock (Table 5-4). This geochemical modeling differs from Banner (1994) because in addition to groundwater interaction with aquifer rock calcite and aragonite, the models also take into consideration interaction with the underlying aquitard. This modeling also uses a soil leachate composition as the initial fluid composition instead of a groundwater composition. Consequently, the geochemical processes modeled in this study are a more complete representation of the geochemical processes taking place in the aquifer.

In each geochemical process modeled, a median soil leachate composition (Easy Hall, Site 6) was used as the initial groundwater composition. This composition coincidently is derived from a soil sample collected at the uppermost part of the southeastern groundwater catchment. The low-Mg calcite and aragonitic limestone aquifer rock and Tertiary aquitard rock compositions used in these simulations were taken from Banner et al. (1994). The exchange reaction distribution coefficients, $K_D^{Sr/Ca}$, used in these simulations were 0.045 for transformation of aragonite to calcite and 0.05 for recrystallization of low-Mg calcite Pleistocene aquifer and Tertiary aquitard rock (Banner, 1995). The exchange reaction distribution coefficient defines the relationship between Sr and Ca concentrations in equilibrated solid and liquid phases.

Geochemical modeling indicates expected changes in groundwater compositions associated with progressive interaction between the initial soil leachate and the respective aquifer and aquitard rock compositions (Fig. 5-16). Dissolution or recrystallization of aquitard rock results in progressively lower groundwater δ^{87}Sr values, coupled with relatively small changes in groundwater Sr/Ca ratios. Dissolution or recrystallization of low-Mg calcite results in higher groundwater δ^{87}Sr values but these changes are not as dramatic as those that result from recrystallization or dissolution of aragonite (Fig. 5-16). All of these processes will also produce the progressively higher groundwater Mg/Ca ratios observed in the aquifer.

In order to better constrain geochemical processes taking place in the aquifer, one must also consider the geology and groundwater hydrology. The spatial distribution of aragonitic and low-Mg calcite limestone and aquitard-influenced groundwater suggests that: 1) dissolution of the respective aquifer and aquitard rocks may occur throughout the aquifer; 2) recrystallization of low-Mg calcite limestone primarily occurs at higher elevations where these rocks are more abundant; 3) aragonite-calcite conversion occurs at low elevations where these aragonitic limestone is most abundant; and 4) interaction between groundwater and aquitard rock is most apparent at lower elevations in parts of the aquifer, especially in the northwestern catchments, where aragonitic limestone is absent.

Initial comparison of the results of geochemical modeling with groundwater Sr isotopic and Sr/Ca ratio data indicate that the groundwater Sr isotopic compositions and associated Sr concentrations observed in the aquifer may be influenced by initial soil leachate compositions or can be produced by a combination of aquifer and aquitard rock dissolution, recrystallization and aragonite-calcite conversion (Fig. 5-16). Groundwater compositions can be grouped into three categories, soil-, aquifer rock-, and aquitard-influenced compositions based on their δ^{87}Sr values (Fig. 5-16). These soil-, aquifer rock-, and aquitard-influenced groundwater compositions are represented by δ^{87}Sr value ranges of –25 to –10, greater than –10, and less than –25, respectively. The range of soil-influenced groundwater coincides with the range where soil δ^{87}Sr values differ from Pleistocene limestone.

Soil- versus limestone-influenced groundwater Sr isotopic compositions are likely results of different infiltration paths (Musgrove, 2000). Rapid infiltration through karst features is likely to result in soil-influenced groundwater compositions due to rapid transit through the vadose zone, largely bypassing the limestone. Consequently, soil-influenced groundwater would be expected adjacent to points of discrete recharge to the aquifer. This hypothesis is supported by Jones et al. (2000), who concluded that on Barbados recharge to the aquifer primarily occurs due to discrete recharge associated with heavy rainfall.

In order to test the results of the geochemical modeling, down-gradient variation of observed groundwater Sr/Ca and δ^{87}Sr compositions along selected flow paths was compared with compositional trends predicted by the modeling. Tracing groundwater compositional changes along four selected flow paths (I through IV) indicates that actual interaction between groundwater and aquitard or aquifer rock along flow paths is a complex series of processes rather than the single process implied by geochemical modeling (Fig. 5-17). Along groundwater flow path I, groundwater Sr compositions display soil-influenced compositions up-gradient and aquitard-influenced compositions at the end of the flow path. The clustering of these groundwater compositions indicate a rapid change from soil- to aquitard-influence along this flow path. Flow path II indicates a similar clustering of soil-influenced groundwater Sr isotopic compositions but on this flow path aquifer rock influences become apparent along the coast. Flow path III, located in southeastern Barbados, displays some similarities to flow path I. Flow path III probably provides better resolution than flow path I. Along flow path III, Sr isotopic compositional changes indicate changes from soil-influenced compositions to aquifer rock-influenced compositions up-gradient, and aquitard-influence down-gradient. It should be noted that on both flow paths I and III, none of the sample sites are located within the freshwater lens portion of the aquifer. Three of the four groundwater samples along flow path IV display compositions indicative of aquifer rock influences. The fourth sample has a soil-influenced Sr isotopic composition and thus indicates a nearby discrete recharge point.

Comparison of the Sr isotopic compositions along flow paths II and IV indicate a larger aquifer rock influence along flow path IV. This is not surprising because flow path IV is located in southeastern Barbados where the Pleistocene limestone is less altered and therefore less mineralogically stable than in the northwest (flow path II).

The aquitard-influenced groundwater Sr isotopic compositions, observed on flow paths I and III, that occur in down-gradient parts of the aquifer are indicative of an influx of groundwater flow through fractures within the aquitard rock that is forced upward as it encounters the coastal freshwater-seawater interface (Fig. 5-18). Groundwater flow through the aquitard has not previously been identified. In the absence of a groundwater influx from within the aquitard, geochemical variations in groundwater flowing along through the aquifer rock, along the top of the aquitard rock, would be similar to those observed on flow paths II and IV. It is unlikely that the low δ^{87}Sr values are the result of groundwater derived from the underlying petroleum reservoir, despite a groundwater sample from the petroleum reservoir collected as part of this study has a low δ^{87}Sr value of –170. Mass-balance calculations based on Cl concentrations in groundwater in the Pleistocene limestone aquifer (97%) and the petroleum reservoir (3%) would produce $\delta^{87}Sr$ values much higher than those observed in aquitard-influenced groundwater.

Groundwater Sr/Ca ratios and $\delta^{87}Sr$ values indicate that the influence of soil on groundwater exceeds that of the aquifer and aquitard rock in most of the aquifer, especially in the northwest (Fig.5-12). Aquifer and aquitard rock influences are most apparent at low elevations. This suggests that the impact of groundwater interaction with stable low-Mg calcite is relatively small, and aquifer rock influences are most likely the product of aragonite-calcite conversion or aragonite dissolution.

CONCLUSIONS

The results of this study indicate that groundwater geochemical compositions are the sum of multiple processes. Dissolved constituents of groundwater are largely but not exclusively derived from interaction with soil, aquifer and aquitard rock. Spatial variations of groundwater geochemical compositions are primarily related to spatial variation of aquifer rock compositions, and the degree of mixing with seawater or groundwater derived from the aquitard. Seasonal variations of groundwater compositions are largely related to climatic effects that impact groundwater hydrology.

The effects of seawater mixing are apparent due to spatial and temporal variation of groundwater major element compositions. These effects take the form of down-gradient compositional changes from Ca-HCO_3 to Na-Cl compositions, as well as seasonal compositional fluctuations along the coast. The seasonal fluctuations take the form of increased seawater mixing in coastal areas during the wet season due to an influx of recharge water into the freshwater lens portion of the aquifer. This effect declines during the dry season.

Recharge processes are reflected in groundwater nitrate, $\delta^{18}O$ and $\delta^{87}Sr$ values. Groundwater $\delta^{18}O$ values on Barbados generally increase with recharge amounts (Jones et al., 2000). Nitrate fluxes through the aquifer display a general relationship with recharge estimates based on groundwater $\delta^{18}O$ values (Chapter 4). Soil-influenced groundwater $\delta^{87}Sr$ values can be attributed to discrete recharge through karst features, bypassing vadose limestone.

The Ca-HCO_3 composition of most Barbados groundwater is indicative of calcite dissolution in limestone aquifers. Investigation of other groundwater constituents, such as C and Sr isotopes together with Sr/Ca and Mg/Ca ratios provide additional information on interaction between groundwater and soil and aquifer and aquitard rock encountered along flow paths. Groundwater C and Sr isotopes and Sr/Ca and Mg/Ca ratios are influenced by the compositions of the soil or Pleistocene limestone and consequently display similar down-gradient compositional trends. Based on the respective ranges of Sr isotopic compositions of soils, aquifer and aquitard rock, Barbados groundwater can be grouped into soil-, aquifer rock-,and aquitard-influenced Sr isotopic compositions. This indicates that: 1) most groundwater Sr isotopic compositions are influenced by soil; 2) the influence of low-Mg calcite limestone is relatively small; 3) aquifer rock and aquitard influences are most apparent in down-gradient parts of the aquifer. Aquifer rock-influenced groundwater can be attributed to interaction with less stable carbonate minerals, such as aragonite, while aquitard-influenced groundwater is attributable to mixing of aquifer groundwater with groundwater flowing upward from the underlying aquitard. This mixing process has not previously been identified in this aquifer.

Major and trace element and isotopic compositions of Barbados groundwater reflect three main processes: 1) mixing; 2) recharge processes; and 3) interaction with soil, aquifer or aquitard rock. All three of these processes are in some way related to the groundwater hydrology of the aquifer. Mixing is related to groundwater advection and diffusion while groundwater interaction with aquifer and aquitard rocks characterized by different compositions is indicative of groundwater flow paths that result in groundwater encountering these rocks.

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Table 5-1. Groundwater and vadose water sample sites. The site numbers correspond to location numbers in Figure 5-2.

Site No.	Well	Parish	Hydrologic Zone	Elevation (m)	Well Depth (m)
1,2	Bowmanston Pumping Station	St. John	Stream	185	
3	Carmichael Plantation	St. George	Stream	56	50.2
4	Claybury Plantation	St. John	Stream	232	
5	Congo Road	St. Philip	Sheet	40	40.9
6	Easy Hall Plantation	St. Joseph	Stream	295	
7	Edgecumbe Plantation	St. Philip	Sheet	65	65.8
8	Halton Plantation	St. Philip	Stream	85	59.1
9	Hampton Plantation	St. Philip	Sheet	37	37.8
10	Henley Plantation	St. John	Stream	168	79.7
11	Home Agricultural Station	St. Philip	Sheet	30	
12	Kendal Plantation	St. John	Stream	165	80.6
13	Little Bentleys	Christ Church	Sheet	52	52.3
14	Marshall Trading	St. Philip	Stream	35	
15	Mount Plantation, The	St. George	Stream	160	69.8
16	Pollard Mill	St. Philip	Stream	85	15.7
17	Ruby	St. Philip	Sheet	35	32.3
18	Thicket Cave	St. Philip	Drip	65	NA
18	Three Houses Spring	St. Philip	Stream	50	
19	Alleynedale Hall Plantation	St. Peter	Sheet	63	52.9
20	Alleynedale II	St. Lucy	Sheet	50	
21	Barrows Childrens Home	St. Lucy	Sheet	53	
22	Bromefield Plantation	St. Lucy	Sheet	47	
23	Carlton Pumping Station	St. James	Sheet	55	
24	Farm Plantation	St. Peter	Sheet	45	
25	Mount Gay Distillery	St. Lucy	Stream	125	76.0
26	Mullins Bay	St. Peter	Sheet	4	5.0
27	Portland Plantation	St. Peter	Stream	175	57.2
28	Rock Hall Plantation	St. Peter	Stream	235	
29	Sailors Gully Cave	St. Peter	Drip	120	NA
30	Trents Plantation	St. Lucy	Stream	65	
31	Welchtown Plantation	St. Peter	Stream	205	53.8
32	White Hall	St. Peter	Stream	100	

Table 5-1. (Cont.)

Site No.	Well	1994			1996		
		Date	Depth-to-Water (m)	Water-Table Elevation (m)	Date	Depth-to-Water (m)	Water-Table Elevation (m)
1,2	Bowmanston Pumping Station	8/5/94	--	--	1/9/96	--	--
3	Carmichael Plantation	7/25/94	46.6	9.1	1/8/96	45.4	6.6
4	Claybury Plantation	7/23/94	46.5	185.5			
5	Congo Road	8/3/94	39.3	0.7			
6	Easy Hall Plantation	7/23/94	59.6	235.4	1/2/96	59.5	235.5
7	Edgecumbe Plantation	7/22/94	--	--	1/3/96	62.3	2.7
8	Halton Plantation	7/23/94	58.5	26.5	1/9/96	--	--
9	Hampton Plantation	7/30/94	35.7	1.3	1/3/96	34.7	2.3
10	Henley Plantation	7/23/94	78.0	90.0			
11	Home Agricultural Station	8/4/94	29.0	1.0	1/9/96	29.0	1.0
12	Kendal Plantation	8/2/94	77.7	87.3	1/3/96	77.4	87.6
13	Little Bentleys	7/21/94	--	--			
14	Marshall Trading	8/2/94	--	--			
15	Mount Plantation, The	7/23/94	67.2	92.8			
16	Pollard Mill	8/2/94	15.2	69.8	1/8/96	15.2	69.8
17	Ruby	8/4/94	34.6	0.4	1/2/96	35.5	-0.5
18	Thicket Cave	8/2/94	NA	NA			
18	Three Houses Spring	7/27/94	0.0	50.0	1/2/96	0.0	50.0
19	Alleynedale Hall Plantation	7/28/94	49.3	13.8	1/5/96	47.5	15.5
20	Alleynedale II				1/4/96	48.8	1.2
21	Barrows Childrens Home	8/7/94	50.4	2.6	1/5/96	49.8	3.2
22	Bromefield Plantation	7/24/94	45.4	1.4	1/7/96	44.5	2.5
23	Carlton Pumping Station				1/3/96	54.7	0.3
24	Farm Plantation				1/4/96	45.1	-0.1
25	Mount Gay Distillery	7/29/94	66.1	58.9	1/8/96	64.0	61.0
26	Mullins Bay				1/6/96	4.3	-0.3
27	Portland Plantation	8/4/94	56.1	119.3	1/5/96	54.9	115.1
28	Rock Hall Plantation				1/4/96	49.7	185.3
29	Sailors Gully Cave				1/10/96	NA	NA
30	Trents Plantation	8/7/94	27.1	37.5			
31	Welchtown Plantation	8/3/94	41.1	163.9	1/5/96	40.2	164.8
32	White Hall				1/4/96	34.1	65.9

Table 5-2. Selected dissolved constituents and isotopic compositions of Barbados rainwater collected at Site A (Fig. 5-2).

Date	**Rainfall (mm)**	**Cl (ppm)**	**NO_3 (ppm)**	**SO_4 (ppm)**	**$\delta^{18}O$ (‰) (SMOW)**	**δD (‰) (SMOW)**	**$^{87}Sr/^{86}Sr$**	**$\delta^{87}Sr$**
7/25/94*	0.51	7.15	0.48	1.97			0.709608	61.1
3/23-24/97	2.50	18.12	0.40	4.16	-0.34	-3.8		
3/24-26/97	5.25	7.38	0.32	1.99	0.45	9.3		
3/24-26/97	5.25				0.38	11.2		
3/30-31/97	11.50				-0.16	0.7		
4/13-30/97	6.50	16.04	1.05	4.24	-0.27	7.1		
4/23-24/97	0.00				-0.36	4.9		
5/1-5/97	3.25	31.02	1.71	7.42				
5/12-15/97	0.00	26.65	1.20	5.99	0.02	-0.4		
5/15-20/97	0.25	11.05	0.09	2.07				
6/10-12/97	3.00	8.18	0.44	3.55	-2.25	-2.3		
6/22-23/97	14.25	1.64	0.30	0.67	-2.52	-16.7		
6/27-29/97	0.50	28.47	1.03	5.11	-1.26	0.3		
7/14/97	15.25	5.82	0.36	1.35	-1.89	-10.9		
7/27/97	3.25	10.79	0.39	2.09				
7/27/97	3.25	11.00	0.56	2.30				
7/28/97	17.25	6.95	0.38	1.90				
7/28/97	17.25	6.95	0.33	1.54				
8/22/97	8.25	1.31	0.17	0.41				
8/26/97	22.25	0.88	0.00	0.62				
9/1/97	4.32	3.82	0.46	1.42				

Table 5-2. (Cont.)

Date	Rainfall (mm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)	$\delta^{18}O$ (‰) (SMOW)	δD (‰) (SMOW)	$^{87}Sr/^{86}Sr$	$\delta^{87}Sr$
9/6/97	97.28	1.46	0.25	0.67				
11/7/97	0.25	2.62	0.82	1.88				
11/12/97	9.91	5.34	0.53	1.34				
11/26/97	0.51	10.74	0.37	2.00				
11/28/97	9.14	11.60	0.39	2.23				
11/29/97	9.91	7.10	0.68	1.63				
11/30/97	0.25	6.19	0.70	1.59				
12/3/97	30.99	3.03	0.37	1.30				
12/10/97	1.25	28.45	1.22	4.44				
12/17/97	5.08	5.91	0.29	1.34				
12/20-21/97	7.11	5.28	0.46	1.50				
12/31/97	8.89	32.31	2.02	5.65				
1/2/98	2.56	10.07	0.32	1.68				
1/8/98	3.33	10.65	0.19	1.99				
1/15/98	7.18	6.12	0.39	1.31				
1/27/98	2.82	15.96	1.28	3.16				
2/14/98	0.26	21.74	1.09	5.76				
2/17/98	1.54	7.93	0.55	1.98				
2/18/98	1.54	22.31	0.84	4.68				
3/27/98	0.51	14.23	0.42	2.66				
3/28/98	0.76	16.64	0.27	3.43				
4/16/98	1.02	36.45	2.00	7.31				
4/19/98	64.26	4.05	0.18	0.86				
4/20/98	5.00	9.30	0.38	1.63				
6/18/98	2.60	16.67	1.44	3.47				
6/21/98	9.91	18.79	0.42	2.39				
6/22/98	3.81	6.99	0.69	1.73				
6/28/98	2.54	9.52		2.50				
7/2/98	20.77	6.95	0.15	1.66				

Table 5-3. Carbon isotopic compositions of groundwater samples collected from sample sites in both 1994 and 1996.

WELL	δ^{13}C		
	1994	**1996**	**Difference**
Alleynedale Hall Pltn	-8.08	-8.24	-0.16
Barrow Children's Home	-2.46	-6.61	-4.15
Bowmanston PS (Stream)	-9.16	-9.10	+0.06
Bromefield Pltn	-5.36	-6.97	-1.61
Easy Hall Pltn	-10.53	-10.92	-0.39
Edgecumbe Pltn	-9.02	-7.43	+1.59
Halton Pltn	-8.73	-9.05	-0.32
Hampton Pltn	-9.53	-9.21	+0.32
Home Agriculture Stn	-6.64	-8.74	-2.10
Kendal Pltn	-6.03	-9.09	-3.06
Mount Gay Distillery	-8.86	-9.10	-0.24
Pollard Mill	-7.74	-4.29	+3.45
Ruby	-10.24	-9.17	+1.07
Three Houses Spring	-5.13	-7.55	-2.42
Welchtown Pltn	-5.17	-5.45	-0.28

Table 5-4. Compositions of the groundwater and aquifer and aquitard rocks used to simulate down-gradient changes in groundwater Sr concentrations and Sr isotopic compositions in response to changing limestone compositions and hydrologic conditions.

	δ^{87}Sr	**Sr/Ca**	**Sr (ppm)**	**Ca (ppm)**
Soil leachate (Easy Hall) Pltn	-14.1	0.0018	0.128	30.4
Low-Mg limestone	-5.2	0.0037	1,480	182,607
Aragonitic limestone	0.0	0.0220	8,500	176,381
Tertiary pelagic rock 1	-51.8	0.0022	845	175,344

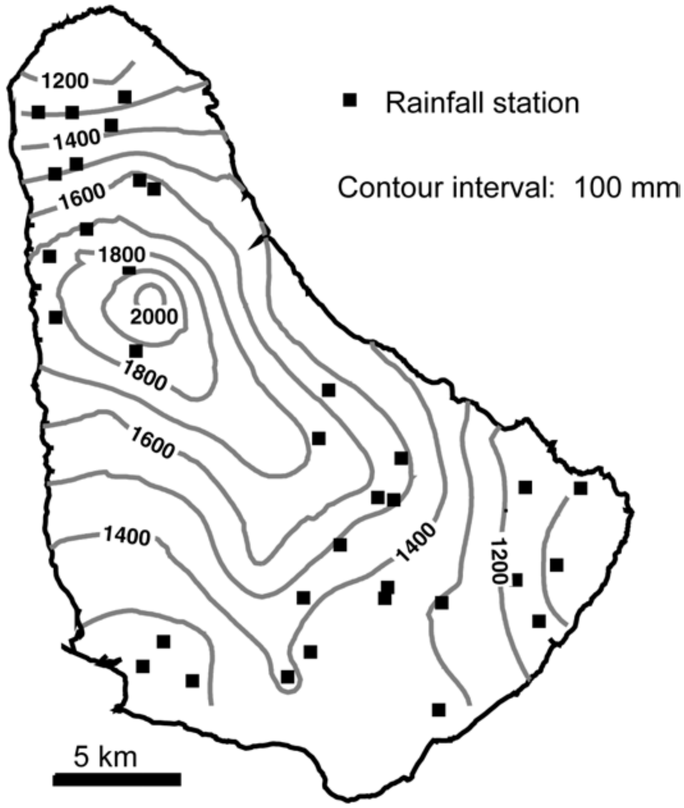

Figure 5-1. Map showing the distribution of annual rainfall (1992) on Barbados. Based on unpublished rainfall data obtained from the Caribbean Institute of Meteorology and Hydrology.

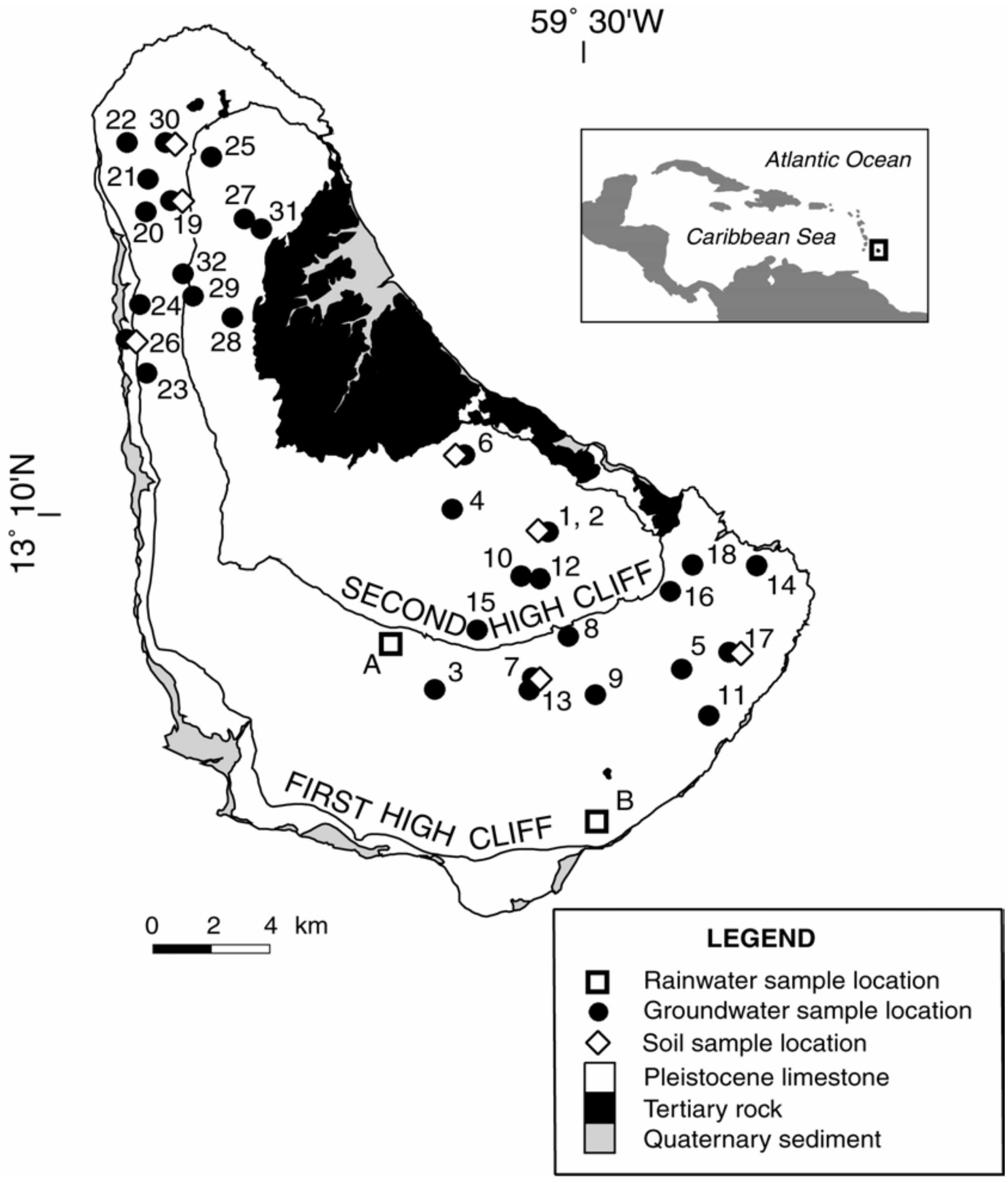

Figure 5-2. Geologic map of Barbados. The Pleistocene limestone that comprises the aquifer occurs in the northern, western and southern portions of the island. Adapted from Directorate of Overseas Surveys 1:50,000 geologic map (1983).

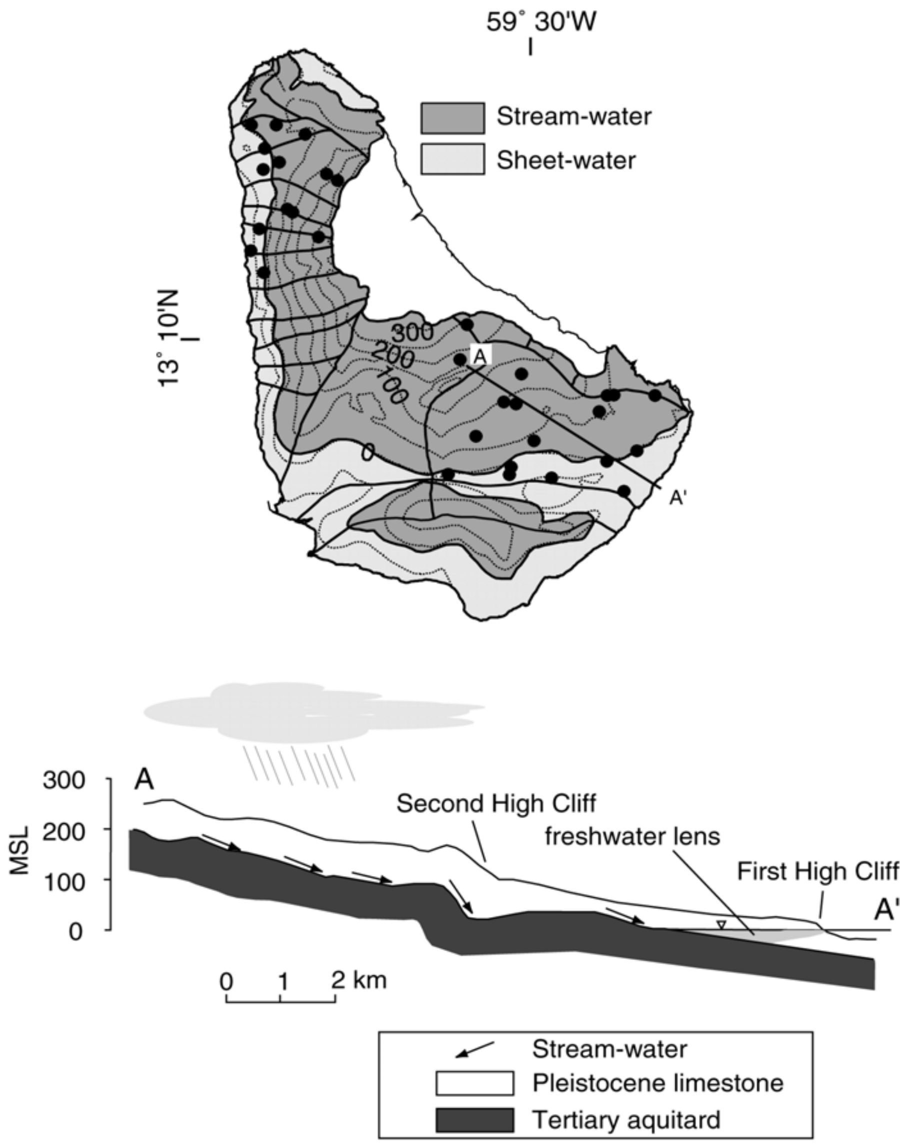

Figure 5-3. Hydrogeologic map of Barbados. The Pleistocene limestone aquifer is divided into several groundwater catchments due to the topography of the Pleistocene-Tertiary contact. The distribution of sampled wells indicate the groundwater catchments investigated in this study while the contours shown indicate the elevation of the base of the Pleistocene limestone (Adapted from Stanley Associates, 1978; Barbados Ministry of Health et al., 1991).

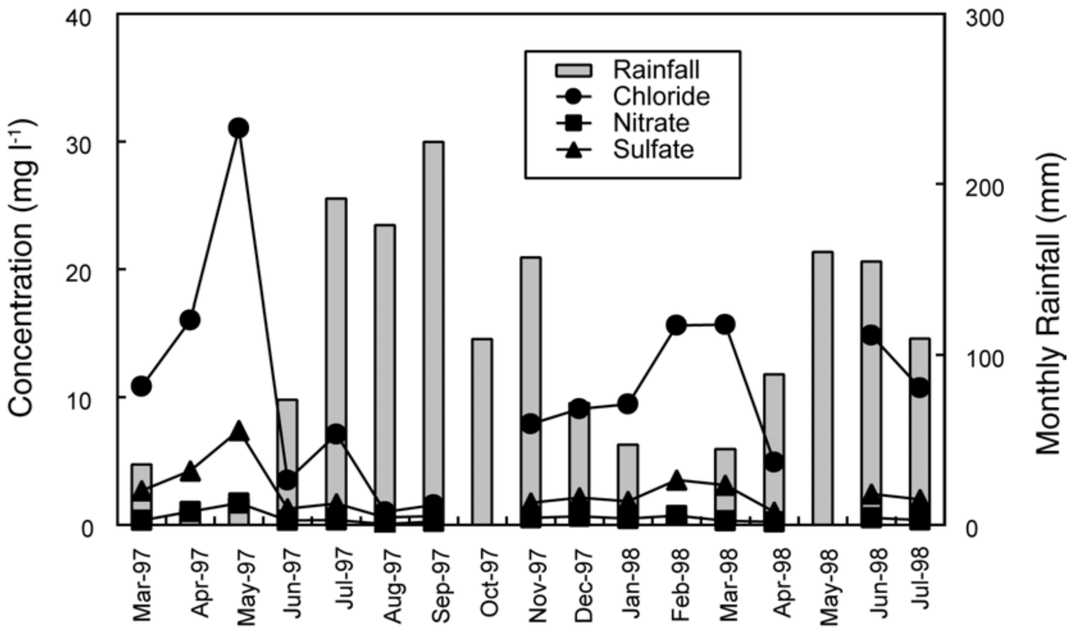

Figure 5-4. The concentrations of chloride, nitrate, and sulfate in Barbados rain-water fluctuate seasonally. These concentrations are generally higher during the dry season and lower during the wet season. Wet season concentrations are lower due to the combined effects of dilution and removal of airborne sea salt aerosols by rainfall.

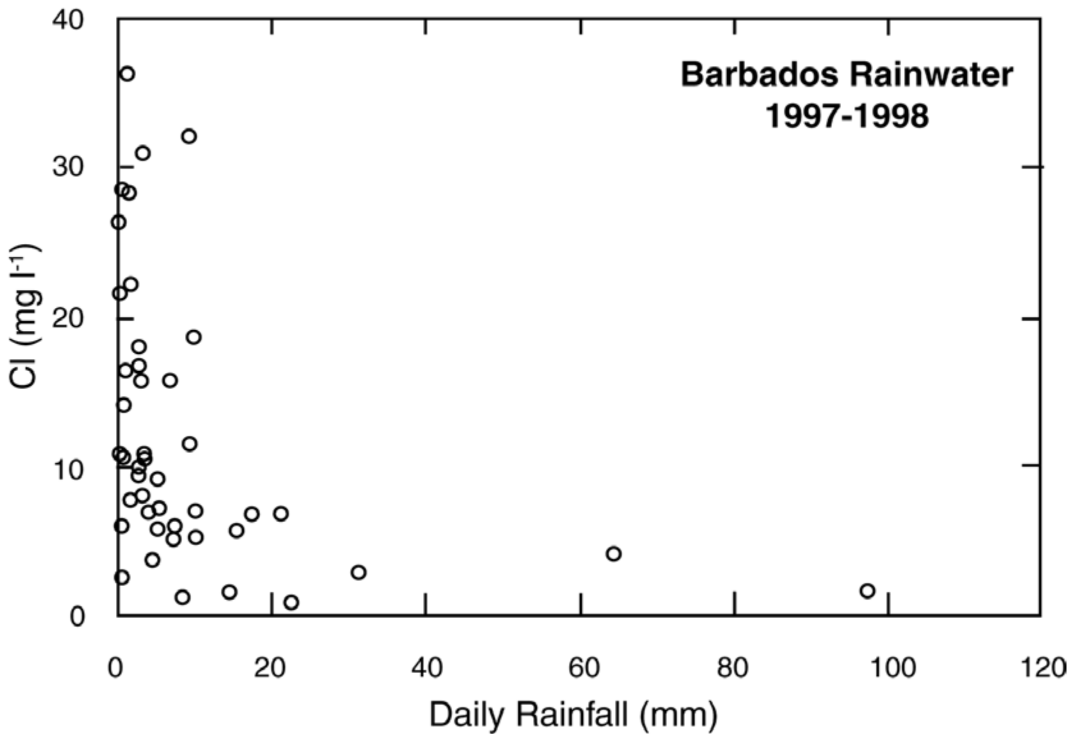

Figure 5-5. The relationship between rainwater Cl concentrations and rainfall amounts is not linear, indicating that the observed seasonal fluctuations are not simply due to dilution of dissolved seawater aerosols.

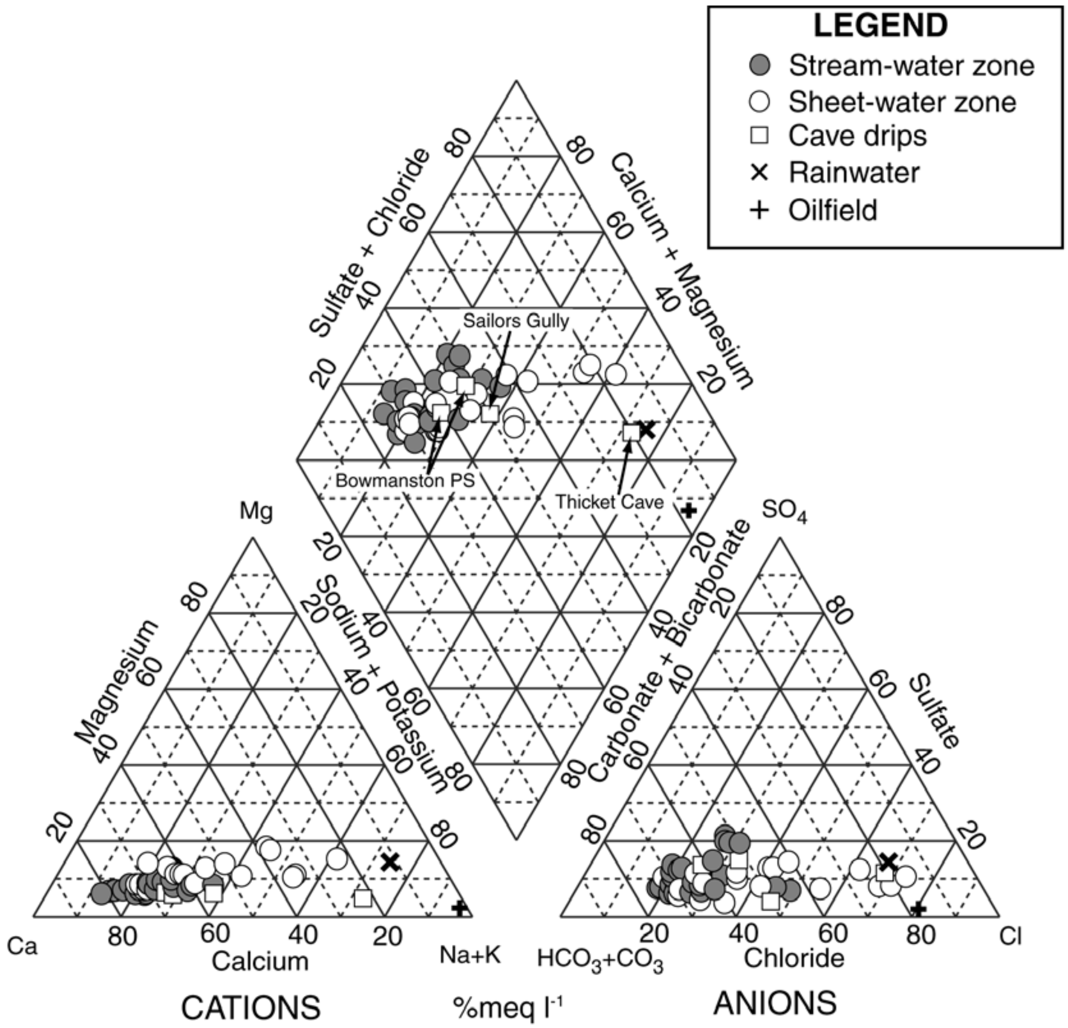

Figure 5-6. Piper diagram showing the range of Barbados groundwater, rainwater, and vadose water major element compositions. Stream-water zonegroundwater compositions indicate dissolution of limestone. The wider range of Sheet-water zone groundwater represents the effects ofmixing groundwater from the Stream-water zone and seawater. Vadosewater samples were collected at three sites, Thicket cave, Sailors Gully,and Bowmanston Pumping Station. The range of vadose water compositions represents increasing effects of limestone dissolution withdepth, where the Thicket cave water sample was the shallowest and Bowmanston Pumping Station was the deepest.

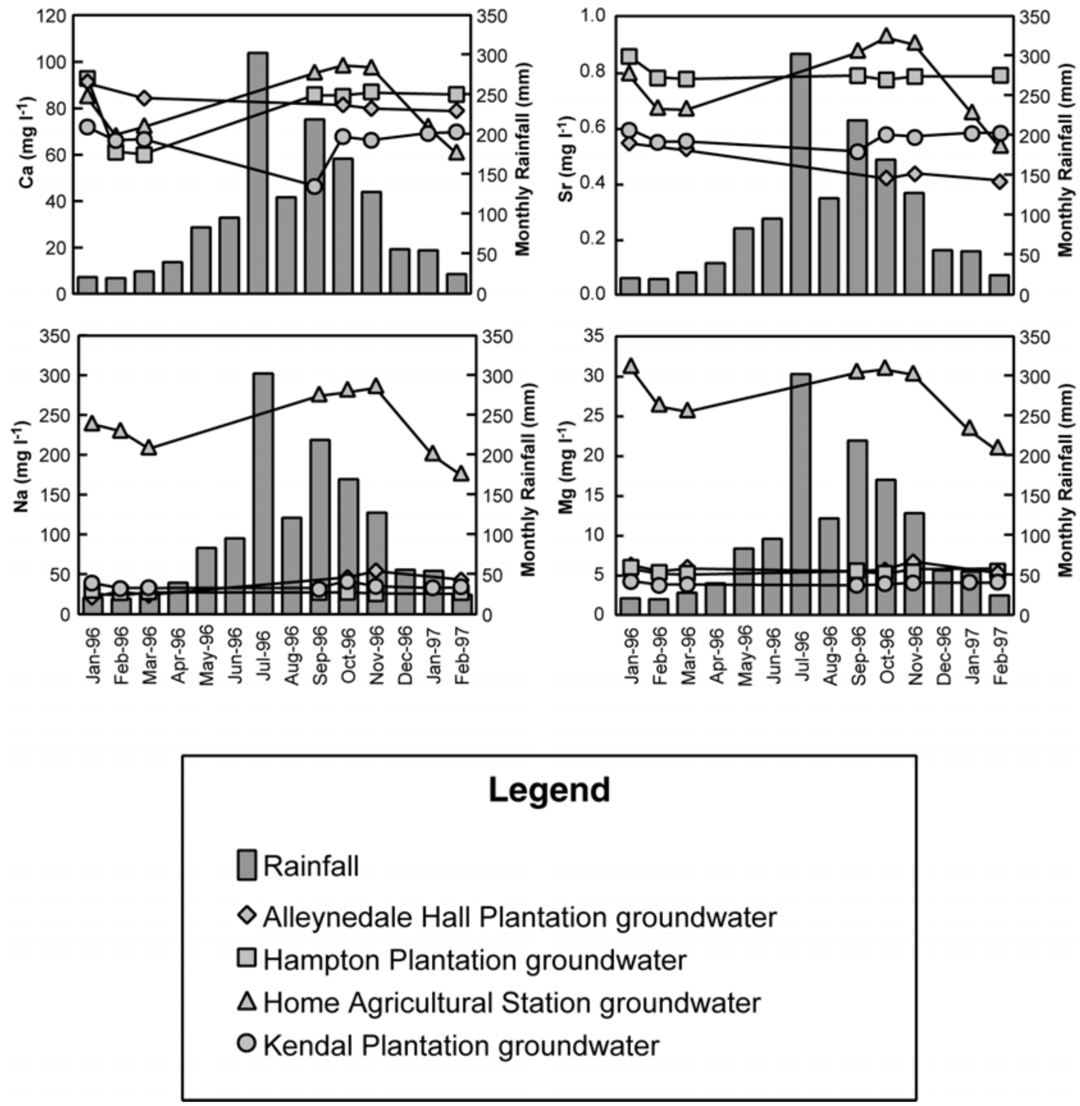

Figure 5-7. Barbados groundwater major and trace element seasonal compositional fluctuations for the period January 1996 through February 1997.

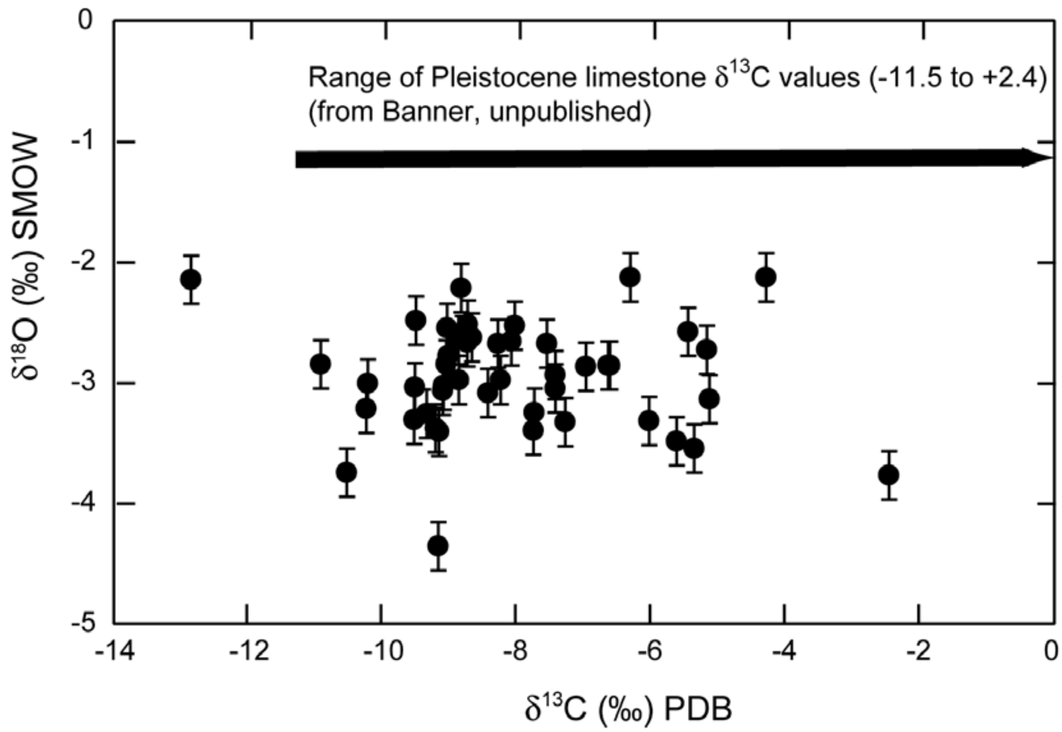

Figure 5-8. Carbon and oxygen isotopic compositions of Barbados groundwater. The range of groundwater carbon isotopic compositions coincides withreflect the range of Pleistocene limestone compositions. The range oflimestone $\delta^{13}C$ values results from vadose and phreatic diagenesis of the limestone (Allan and Matthews, 1977). Vadose diagenesis produces more negative limestone $\delta^{13}C$ values as a result of soil influences on the carbon isotopic composition of the limestone.

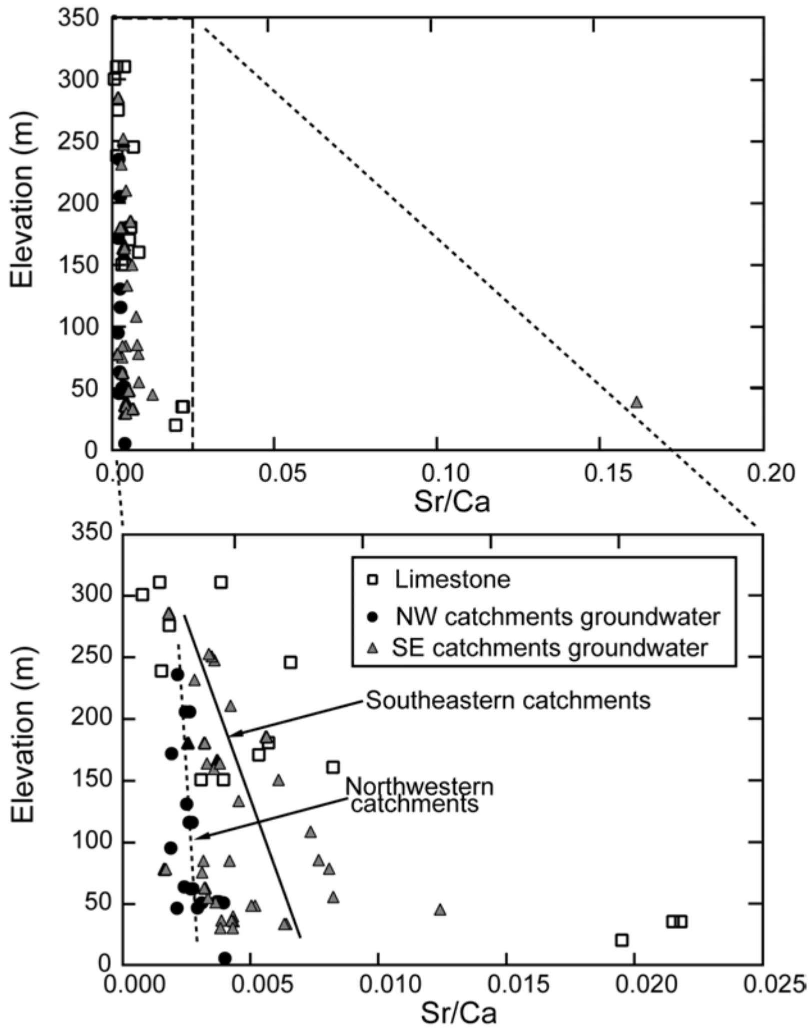

Figure 5-9. Barbados groundwater and Pleistocene limestone aquifer rock display Sr/Ca ratios that generally decrease with increasing elevation. The variation of Pleistocene limestone Sr/Ca ratios is related to increasing effects of diagenetic alteration with elevation (Banner et al., 1994). This diagenetic alteration preferentially removes Sr from the limestone, resulting in decreasing limestone Sr/Ca ratios over time. Groundwater Sr/Ca ratios reflect the compositions of the aquifer rock. In both groundwater catchments, groundwater Sr/Ca ratios decrease with increasing elevation. The more uniform groundwater Sr/Ca ratios in the northwestern catchments reflect the more intense diagenetic alteration of the Pleistocene limestones in that part of Barbados (Matthews, 1968).

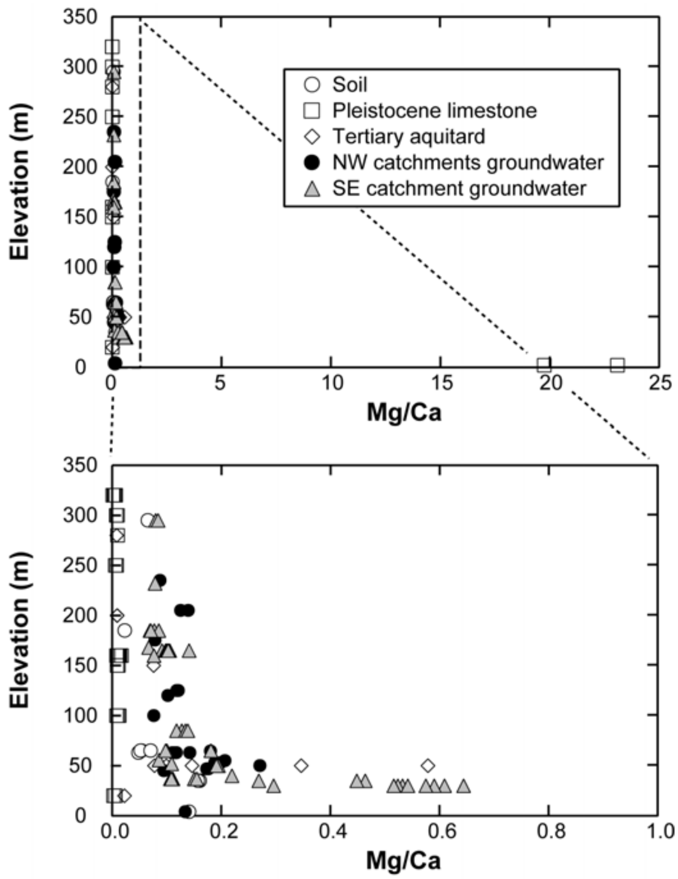

Figure 5-10. In both northwestern and southeastern parts of Barbados, groundwater Mg/Ca ratios decrease withincreasing elevation. The spatial distribution of groundwater Mg/Ca ratios is similar to the Sr/Ca ratios. Groundwaterin the northwest have a narrow range of Mg/Ca ratios relative to groundwater in the southeast. Like the Sr/Ca ratios, groundwater Mg/Ca ratios are a reflection of variations of aquifer rock compositions as a function of elevation. The narrow range in the northwest occurs due to more intense diagenetic alteration of the aquifer that preferentially removes both Sr and Mg from the rock. In most cases, Barbados soils have lower Mg/Ca ratios than groundwater at the same elevation. The soils also display decreasing Mg/Ca ratios with increasing elevation.

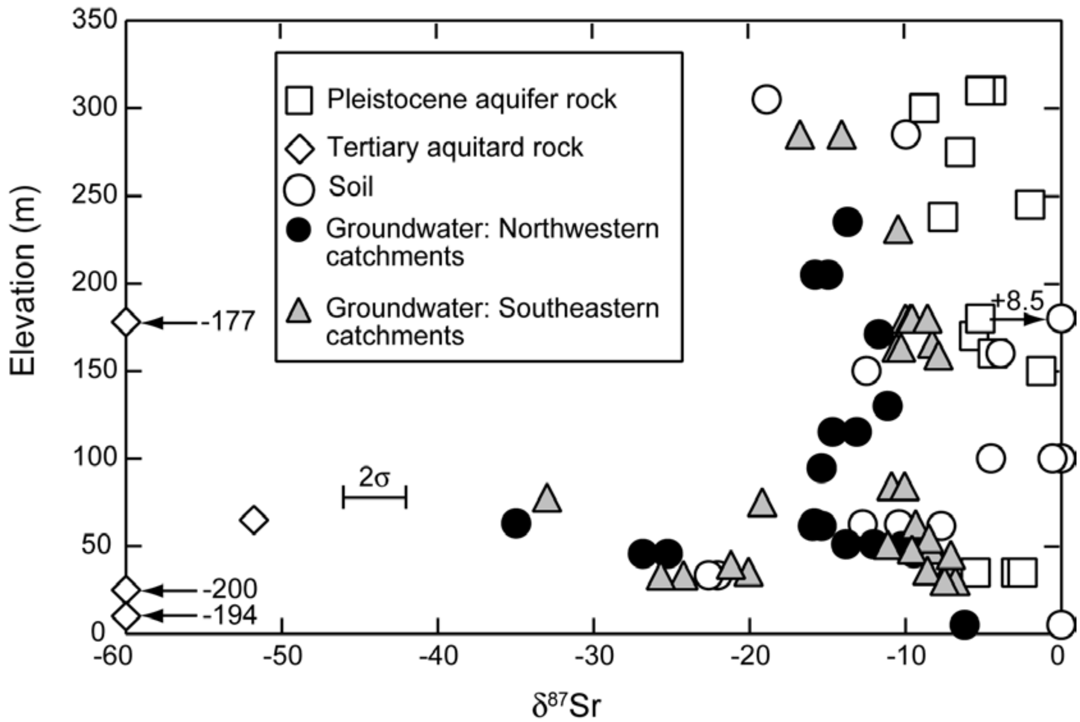

Figure 5-11. The Sr isotopic compositions of Barbados groundwater lie betweenPleistocene limestone aquifer and Tertiary aquitard rock compositions. Most groundwaters on Barbados display Sr isotopic composition that reflect a predominant Pleistocene limestone or soil influence, however, in some parts of the aquifer, groundwater Sr isotopic compositions reflect a greater influence of the Tertiary aquitard on groundwater Sr isotopic compositions. Rock Sr isotopic compositions from Banner et al. (1994) while some soil Sr isotopic compositions from Banner et al. (1994) and Borg and Banner (1996). Bar represents standard deviation (2σ) of Sr analyses.

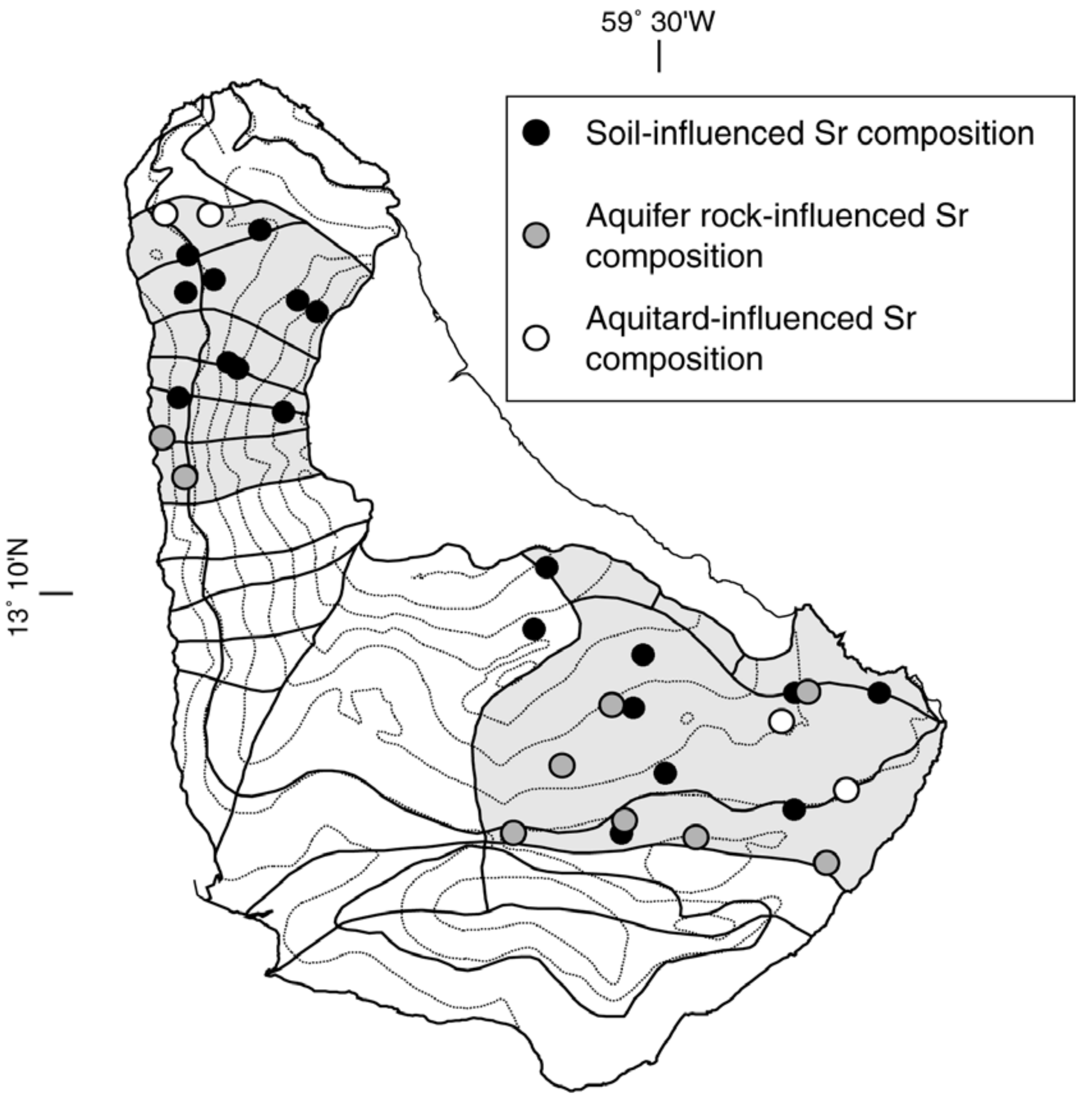

Figure 5-12. Groundwater Sr isotopic compositions display the influence of Pleistocene limestone aquifer rock and Tertiary aquitard rock that increases downgradient.

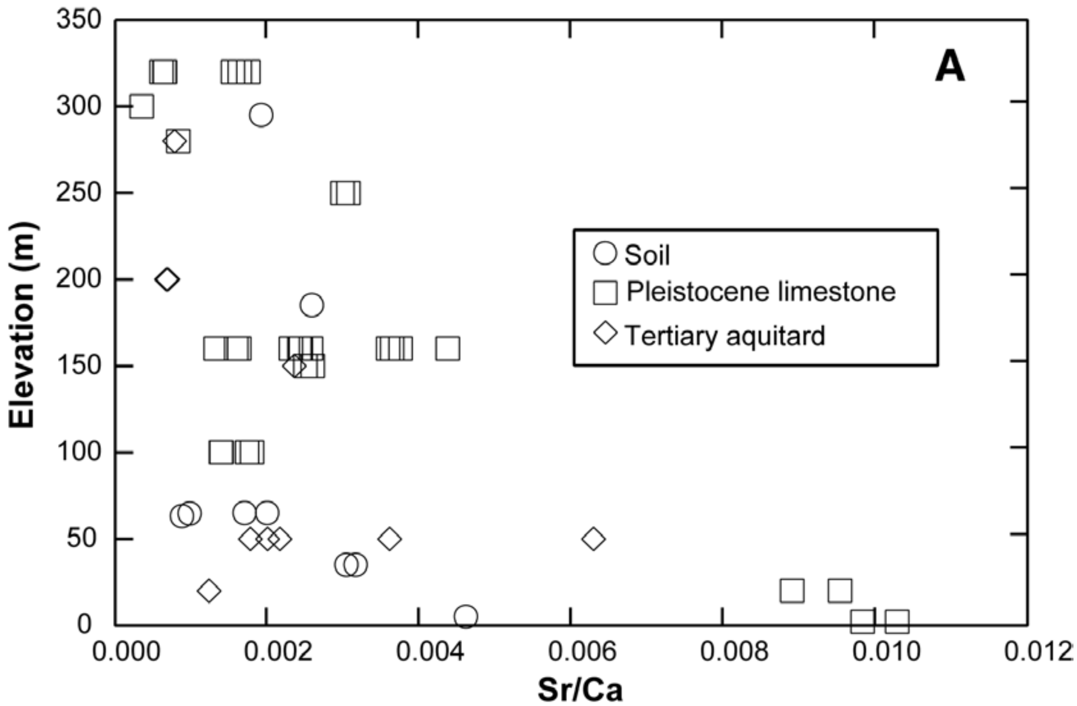

Figure 5-13. Barbados soil leachate, Pleistocene limestone, and Tertiary aquitard Sr/Ca and Mg/Ca ratios generally decrease with increasing elevation. The relationship between elevation and soil and Pleistocene limestone Sr/Ca and Mg/Ca ratios can be attributed to the relative age of the soils and limestones at each elevation. At higher elevations, the soils and limestones are older than at lower elevations. The lower Sr/Ca and Mg/Ca ratios at higher elevations are the result of weathering over a longer period of time that leaches Sr and Mg from the soil and limestone. Rock Sr isotopic compositions from Banner et al. (1994) while some soil Sr isotopic compositions from Banner et al. (1994) and Borg and Banner (1996).

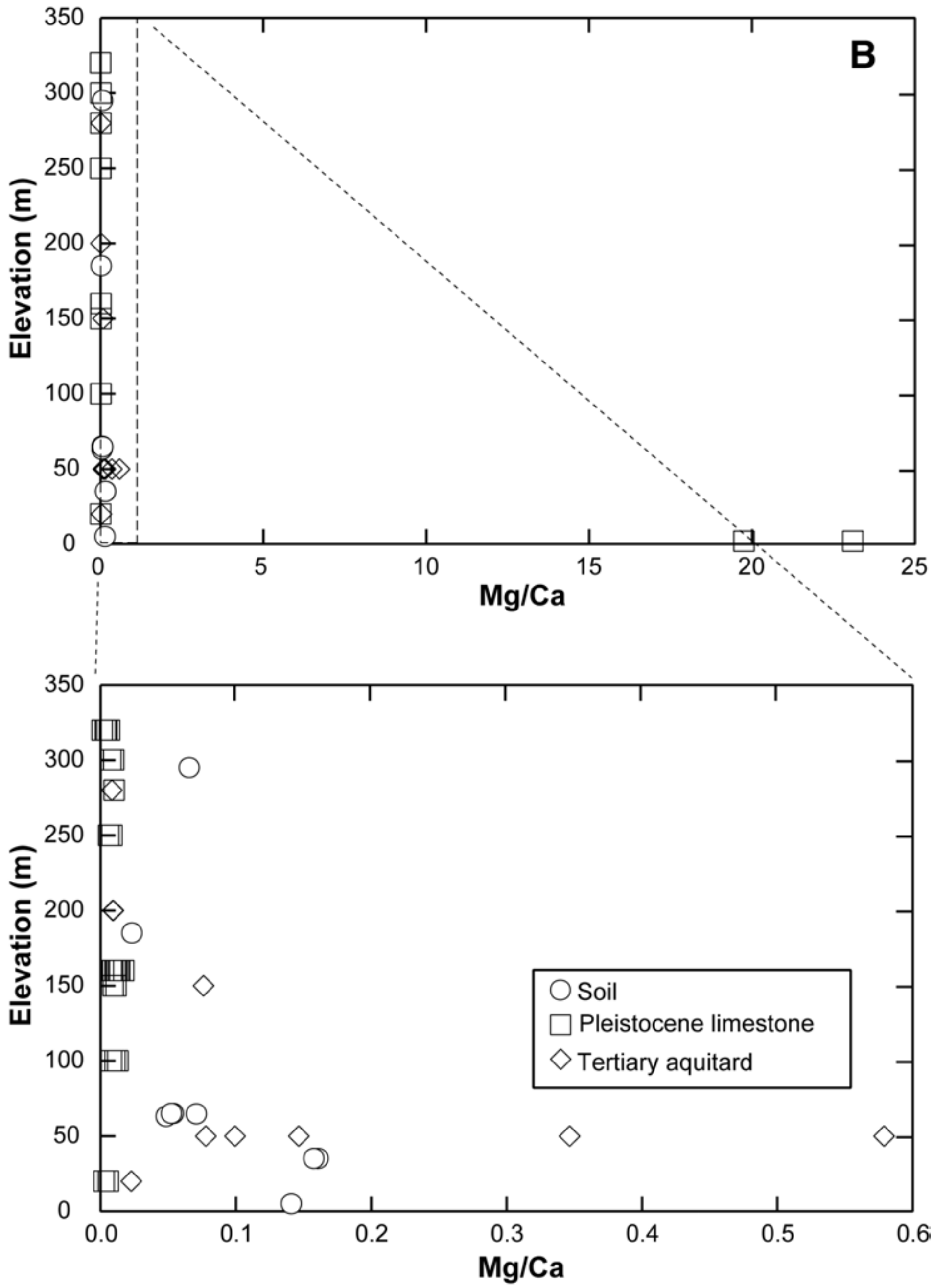

Figure 5-13. (cont.).

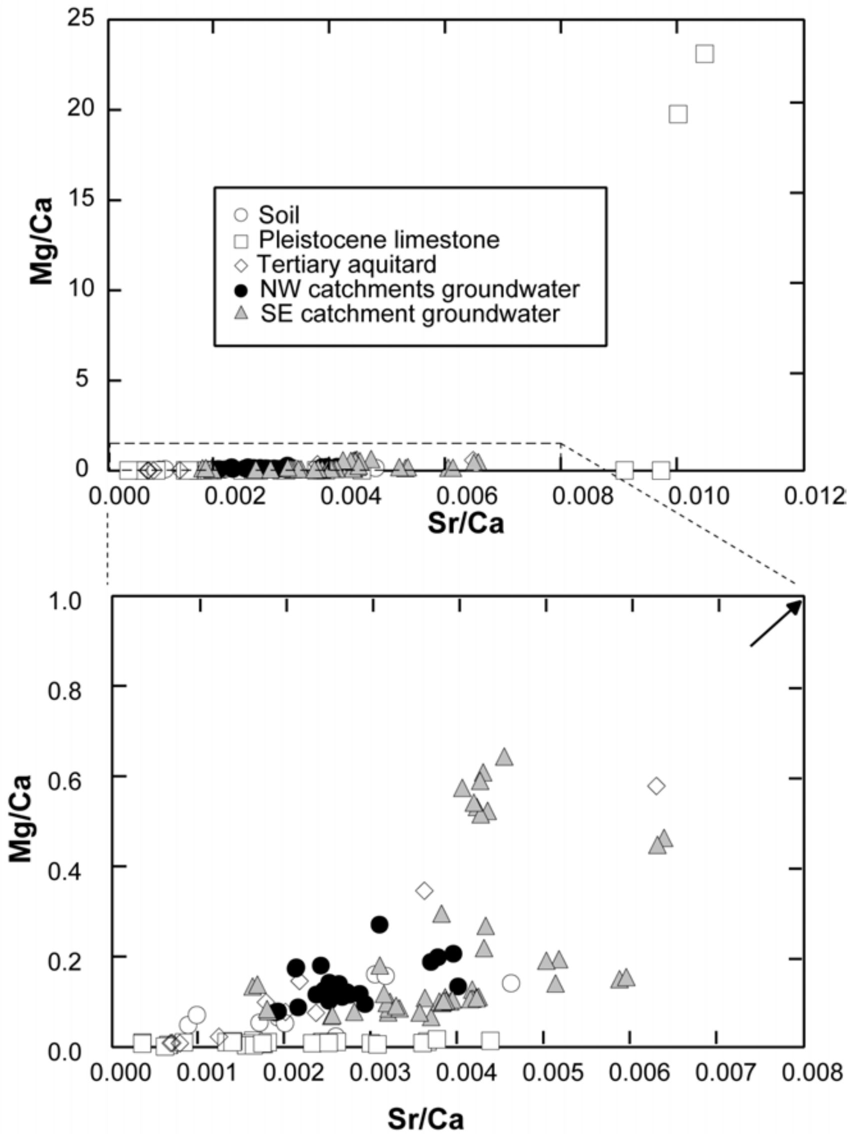

Figure 5-14. Barbados soil, Pleistocene limestone, Tertiary aquitard and groundwater Sr/Ca and Mg/Ca ratios. Tertiary aquitard Mg/Ca ratios increase with Sr/Ca ratios and are generally higher than Pleistocene limestone Mg/Ca ratios. With a few exceptions, soil and groundwater Sr/Ca and Mg/Ca ratios lie between the respective compositions of Tertiary aquitard and Pleistocene limestone aquifer rock compositions. Rock Sr isotopic compositions from Banner et al. (1994) while some soil Sr isotopic compositions from Banner et al. (1994) and Borg and Banner (1996).

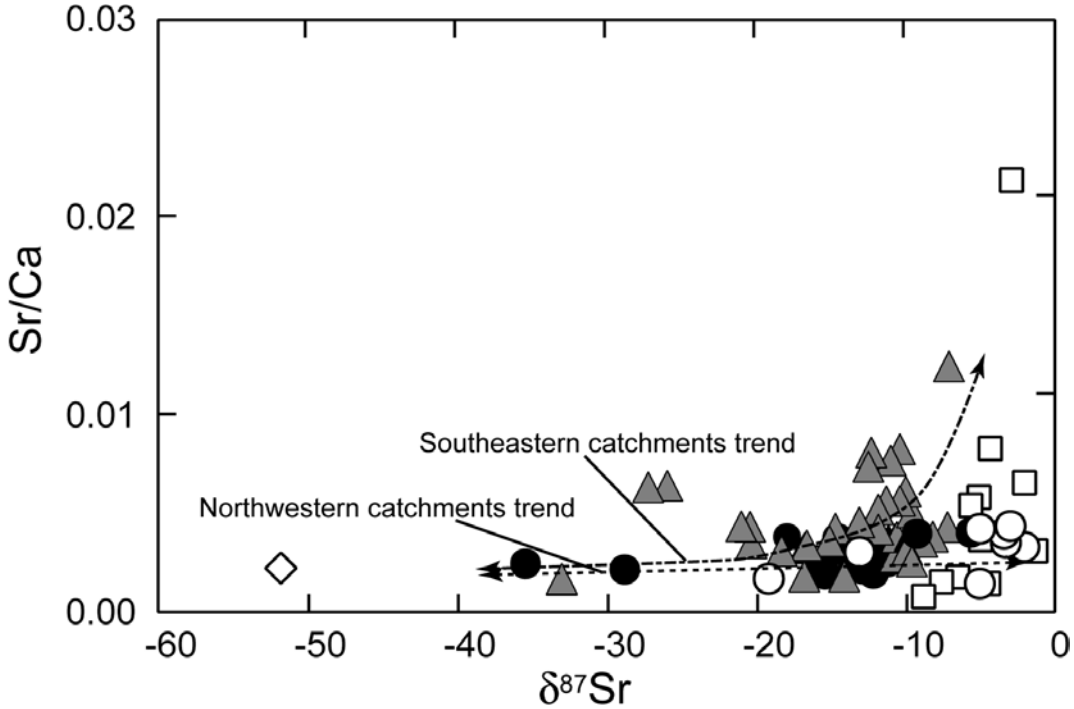

Figure 5-15. Groundwater δ^{87}Sr values and Sr/Ca ratios in northwestern and southeastern Barbados follow different trends. In northwestern Barbados,the groundwater is characterized by uniform Sr/Ca ratios and a wide range of δ^{87}Sr values while in southeastern Barbados, groundwaters arecharacterized by a range of both Sr/Ca ratios and δ^{87}Sr values. The curves represent trends that show groundwater compositional changes that approach aquifer or aquitard rock compositions.

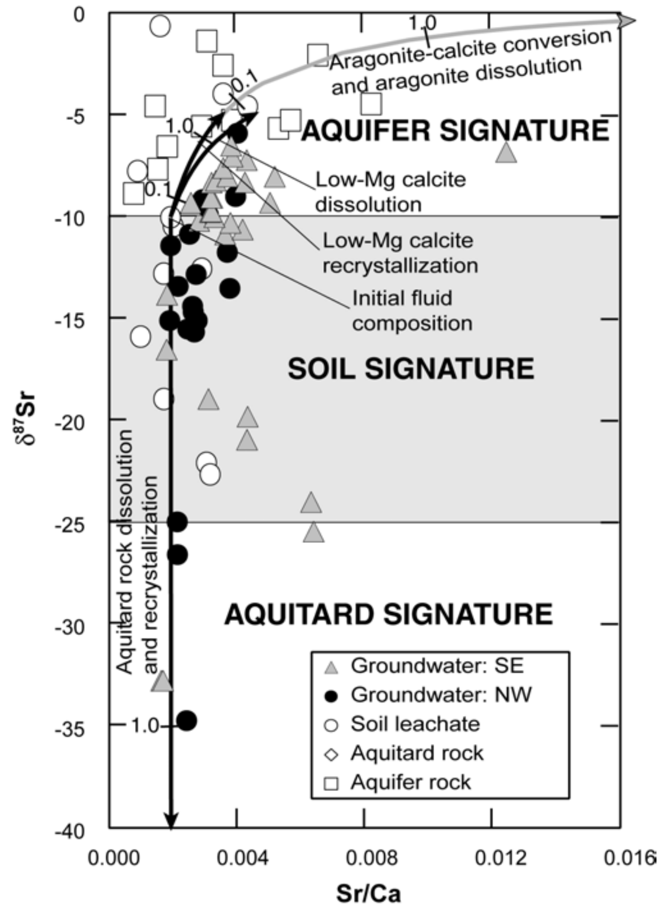

Figure 5-16. Geochemical modeling indicates expected groundwater compositional associated with geochemical processes, such as dissolution and recrystallization of aragonite and calcite in aquifer and aquitard rock. Groundwater compositions can be grouped based on their apparent relationships with aquifer and aquitard rock compositions, and soil compositions that differ from the Pleistocene limestone compositions. This indicates that most groundwater has retained soil Sr isotopic compositions. The numbers on the curves indicate number millimoles of dissolved aragonite or calcite. The arrows on the curves indicate direction of increasing water-rock interaction.

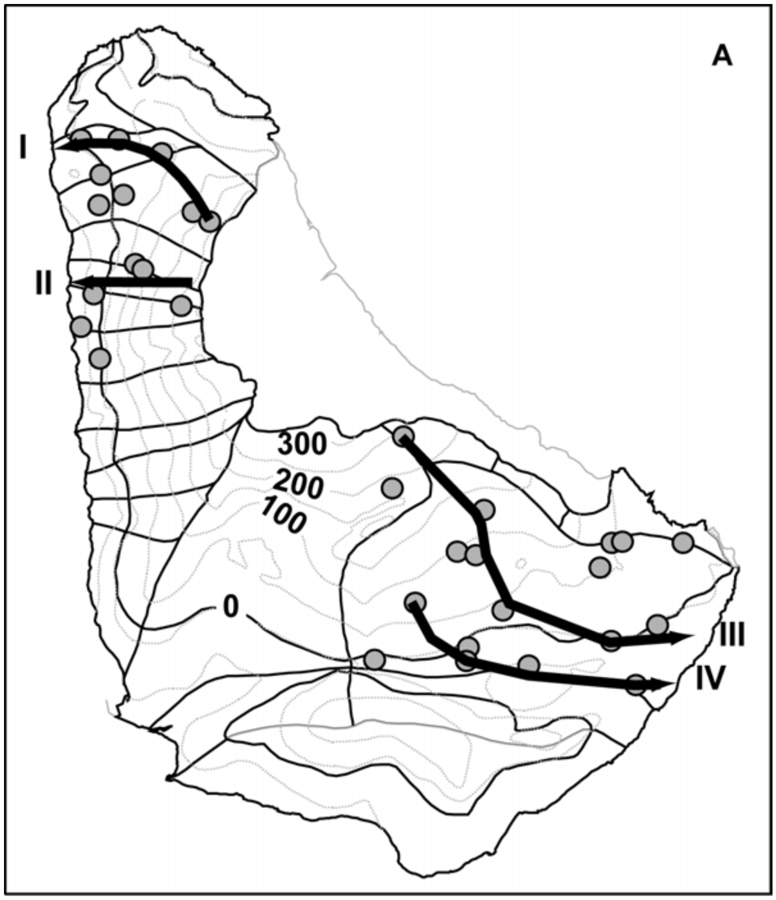

Figure 5-17. A. The variation of groundwater δ^{87}Sr values along selected groundwater flow paths is used to compare results of geochemical modeling with observed groundwater data. These flow paths were determined based on the topography of the aquifer base (Fig. 5-3). B. In northwestern Barbados, groundwaters display soil-influenced δ^{87}Sr values up-gradient and aquitard- and aquifer rock-influences down-gradient on flow paths I and II, respectively. C. On flow path III, groundwater δ^{87}Sr values are mostly aquifer rock-influenced. The exception probably indicates nearby discrete recharge. Groundwater δ^{87}Sr values along flow path IV indicate initial soil influence at the beginning of the flow path changing to aquifer rock-influenced compositions due to interaction with the surrounding Pleistocene limestone. Down-gradient, groundwater reflect increasing aquitard influences due to an influx of groundwater from the underlying aquitard.

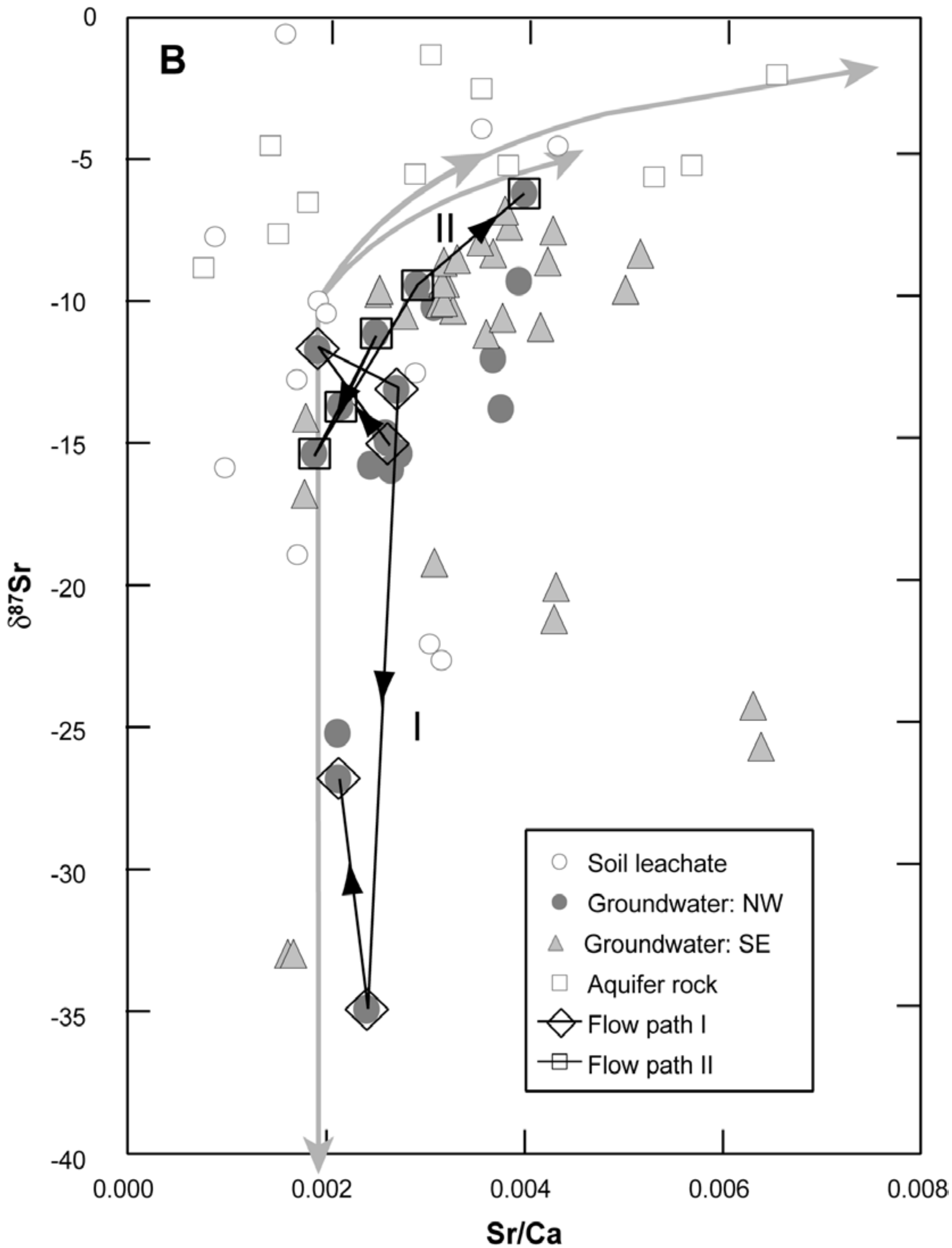

Figure 5-17. (Cont.)

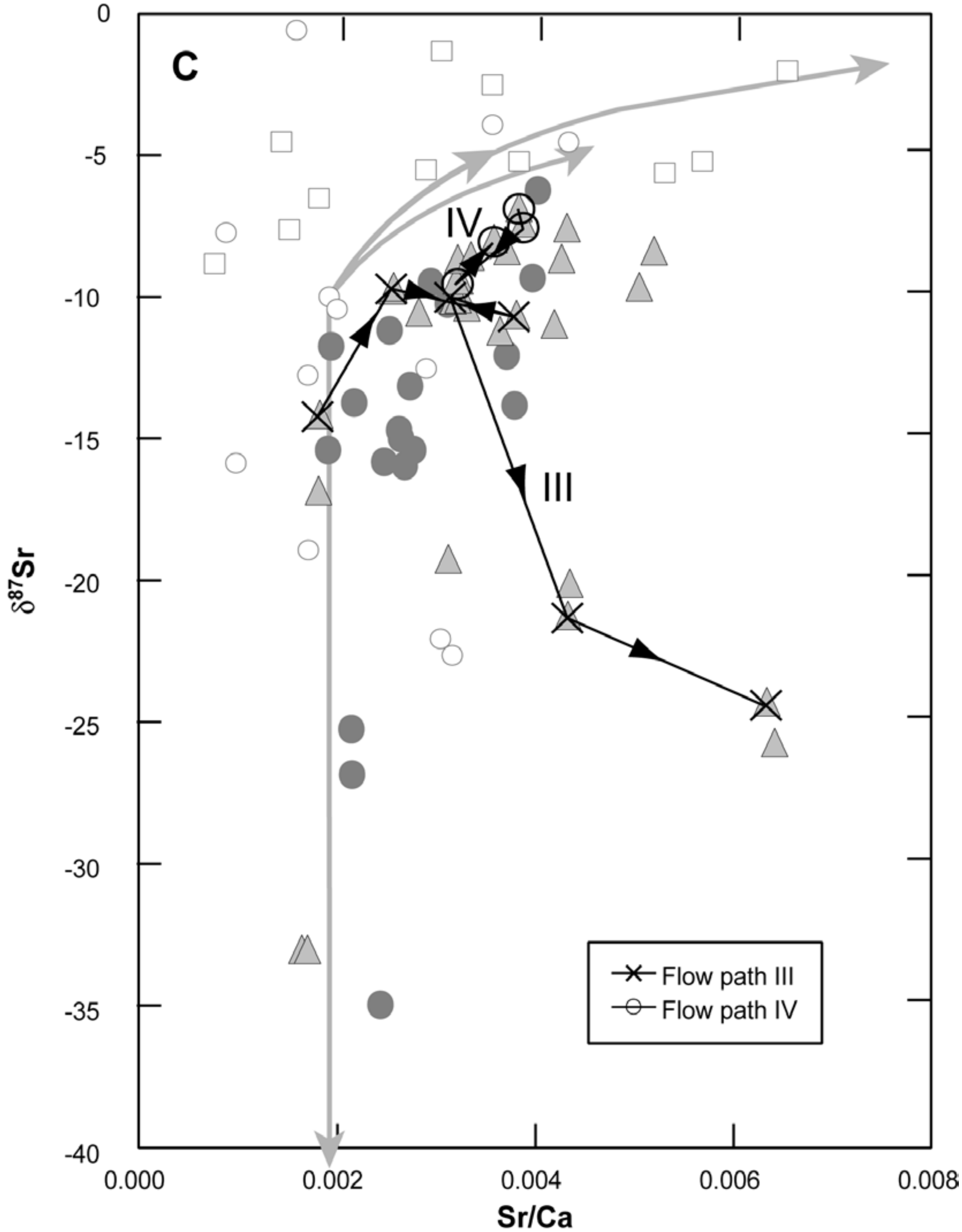

Figure 5-17. (Cont.)

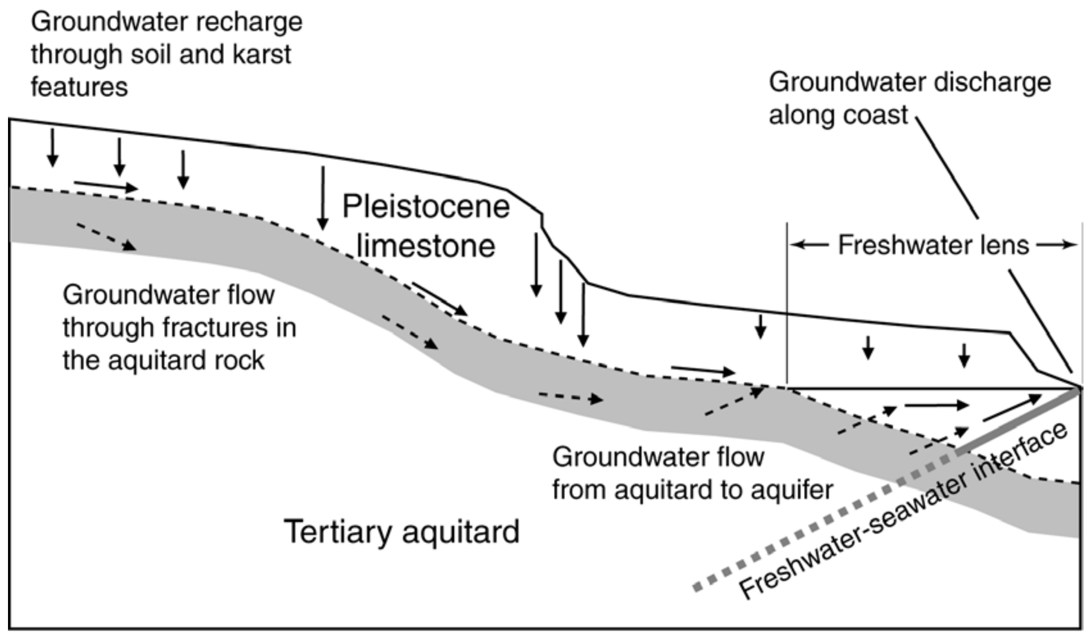

Figure 5-18. Schematic diagram showing grounwater flow through the Pleistocene limestone aquifer. Most groundwater flows along the contact between the highly permeable limestone aquifer rock and the underlying aquitard rock. Aquitard-influenced groundwater Sr isotopic compositions that occur in isolated parts of the aquifer indicate that there is some groundwater flow through the aquitard rocks. This most likely takes the form of limited groundwater flow through fractures. Aquitard-influenced groundwater Sr isotopic compositions occur in the aquifer at relatively low elevations. This spatial distribution can be explained by upward groundwater flow from the aquitard into the aquifer rock as the groundwater encounters the coastal freshwater-seawater interface.

APPENDIX

Table A-1. Rainwater Cl concentration data for Barbados collected at rainwater sample site A (Fig. 2-1). In most cases, rainfall was measured at the same sample site.

Date	Rainfall (mm)	Cl (mg/l)		Date	Rainfall (mm)	Cl (mg/l)
3/23-24/97	2.50*	18.12		11/30/97	0.25	6.19
3/24-26/97	5.25*	7.38		12/3/97	30.99	3.03
4/13-30/97	6.50*	16.04		12/10/97	1.25	28.45
5/1-5/97	3.25*	31.02		12/17/97	5.08	5.91
5/12-15/97	0.00*	26.65		12/20-21/97	7.11	5.28
5/15-20/97	0.25*	11.05		12/31/97	8.89	32.31
6/10-12/97	3.00*	8.18		1/2/98	2.56	10.07
6/22-23/97	14.25*	1.64		1/8/98	3.33	10.65
6/27-29/97	0.50*	28.47		1/15/98	7.18	6.12
7/14/97	15.25*	5.82		1/27/98	2.82	15.96
7/27/97	3.25*	10.79		2/14/98	0.26	21.74
7/27/97	3.25*	11.00		2/17/98	1.54	7.93
7/28/97	17.25*	6.95		2/18/98	1.54	22.31
7/28/97	17.25*	6.95		3/27/98	0.51	14.23
8/22/97	8.25*	1.31		3/28/98	0.76	16.64
8/26/97	22.25*	0.88		4/16/98	1.02	36.45
9/1/97	4.32*	3.82		4/19/98	64.26	4.05
9/6/97	97.28*	1.46		4/20/98	5.00	9.30
11/7/97	0.25	2.62		6/18/98	2.60	16.67
11/12/97	9.91	5.34		6/21/98	9.91	18.79
11/26/97	0.51	10.74		6/22/98	3.81	6.99
11/28/97	9.14	11.60		6/28/98	2.54	9.52
11/29/97	9.91	7.10		7/2/98	20.77	6.95

Asterisks indicate rainfall measured at the airport (rainwater sample site B).

Table A-2. Oxygen and hydrogen isotope data for groundwater samples collected in this study. The oxygen isotope analyses were conducted at Colorado School of Mines while the hydrogen isotope analyses were conducted at University of Arizona. Site locations shown in Fig. 2-1.

	Sample Site Name and Number	Date	$\delta^{18}O$ (‰) (SMOW)	δD (‰) (SMOW)
1	Bowmanston PS (Drip)	1/9/96	-3.05	-15.80
2	Bowmanston PS (Stream)	8/5/94	-3.41	-15.27
2	Bowmanston PS (Stream)	1/9/96	-3.07	-15.36
3	Carmichael Pltn.	1/8/96	-2.53	-16.14
4	Claybury Pltn.	7/23/94	-2.55	
5	Congo Road	8/3/94	-3.40	-18.66
6	Easy Hall Pltn.	7/23/94	-3.75	
6	Easy Hall Pltn.	1/2/96	-2.85	-15.60
7	Edgecumbe Pltn.	1/3/96	-2.78	-16.07
7	Edgecumbe Pltn.	7/22/94	-2.94	
8	Halton Pltn.	7/23/94	-2.52	
8	Halton Pltn.	1/9/96	-2.85	-18.51
9	Hampton Pltn.	7/30/94	-3.31	-16.49
9	Hampton Pltn.	1/3/96	-3.38	-16.32
9	Hampton Pltn.	9/30/96	-3.04	-16.18
9	Hampton Pltn.	10/31/96	-3.14	-16.90
9	Hampton Pltn.	10/31/96	-3.17	-16.90
9	Hampton Pltn.	11/30/96	-3.17	-16.68
9	Hampton Pltn.	11/30/96	-3.20	-16.68
9	Hampton Pltn.	2/28/97	-3.20	-16.32
9	Hampton Pltn.	3/27/97	-3.21	-18.20
10	Henley Pltn.	7/23/94	-2.65	-15.38
11	Home Agri. Stn.	8/4/94	-2.86	
11	Home Agri. Stn.	1/9/96	-2.67	-15.39
12	Kendal Pltn.	8/2/94	-3.32	-14.76
12	Kendal Pltn.	1/3/96	-3.03	-15.22
12	Kendal Pltn.	10/31/96	-3.27	-17.30
12	Kendal Pltn.	1/31/97	-3.22	-16.36
12	Kendal Pltn.	1/31/97	-3.25	-16.36
12	Kendal Pltn.	11/27/97	-3.25	-16.63
13	Little Bentleys	7/21/94	-3.09	-15.22
14	Marshall Trading	8/2/94	-3.33	-9.05
15	Mount Pltn.	7/23/94	-2.68	-15.46

Table A-2. (Cont.)

	Sample Site	Date	$\delta^{18}O$ (‰) (SMOW)	δD (‰) (SMOW)
16	Pollard Mill	8/2/94	-3.25	
16	Pollard Mill	1/8/96	-2.13	-15.93
17	Ruby	8/4/94	-3.22	-20.45
17	Ruby	1/2/96	-4.36	
18	Three Houses Sprg.	7/27/94	-3.14	-15.94
18	Three Houses Sprg.	1/2/96	-2.68	-16.64
19	Alleynedale Hall Pltn.	7/28/94	-2.66	
19	Alleynedale Hall Pltn.	1/5/96	-2.98	-18.49
20	Alleynedale II	1/4/96	-2.63	-16.57
21	Barrows Childrens Home	8/7/94	-3.77	
21	Barrows Childrens Home	1/5/96	-2.86	-19.07
22	Bromefield Pltn.	7/24/94	-3.55	
22	Bromefield Pltn.	1/7/96	-2.87	-20.76
23	Carlton PS	1/3/96	-2.22	-15.57
24	Farm Pltn.	1/4/96	-2.49	-16.95
25	Mount Gay Distillery	7/29/94	-2.98	
25	Mount Gay Distillery	1/8/96	-3.07	-17.58
26	Mullins Bay	1/6/96	-2.15	-15.04
27	Portland Pltn.	1/5/96	-2.13	-17.32
28	Rock Hall Pltn.	1/4/96	-3.04	-17.05
29	Sailor Gully Cave	1/10/96	-3.01	
30	Trents Pltn.	8/7/94	-3.49	-13.36
31	Welchtown Pltn.	8/3/94	-2.73	-14.93
31	Welchtown Pltn.	1/5/96	-2.58	-16.27
32	White Hall	1/4/96	-3.26	-16.54
--	Woodbourne Oilfield	8/4/94	+2.44	-19.84

Table A-3. Recharge estimates based on mean monthly evapotranspiration and rainfall for Barbados. Based on data from Food and Agriculture Organization (1985).

Month	Mean Av. Rainfall (mm)	Evapo-transpiration (mm)	Recharge (mm)
Jan	61	128	0
Feb	47	128	0
Mar	38	167	0
Apr	46	166	0
May	54	166	0
Jun	90	159	0
Jul	129	157	0
Aug	147	159	0
Sep	145	142	3
Oct	167	131	36
Nov	148	118	30
Dec	102	120	0

Table A-4. Recharge estimates at sample site located in southeastern and northwestern Barbados, based on groundwater and rainwater O isotopes and Cl concentrations.

Sample Site		Elevation (m)	1992 Rainfall (mm)	1994 Samples			
				Groundwater		Recharge (%)	
				$\delta^{18}O$ (‰) (SMOW)	Cl (ppm)	^{18}O	Cl
1	Bowmanston PS (Drip)	180	1,520				
2	Bowmanston PS (Stream)	180	1,520	-3.41	34.63	19%	21%
3	Carmichael Pltn	54	1,440				
4	Claybury Pltn	231	1,660	-2.55	29.66	19%	24%
5	Congo Road	39	1,160	-3.40	89.49	24%	8%
6	Easy Hall Pltn	285	1,550	-3.75	35.37	19%	20%
7	Edgecumbe Pltn	62	1,370	-2.94	41.16	19%	17%
8	Halton Pltn	84	1,390	-2.52	49.29	23%	15%
9	Hampton Pltn	36	1,300	-3.31	42.21	21%	17%
10	Henley Pltn	166	1,550	-2.65	32.34	18%	22%
11	Home Agricultural Station	30	1,140	-2.86	412.76	22%	2%
12	Kendal Factory/Pltn	163	1,520	-3.32	38.34	18%	19%
13	Little Bentleys	51	1,360	-3.09	45.50	19%	16%
14	Marshall Trading	35	1,100	-3.33	114.59	25%	6%
15	Mount Pltn	159	1,480	-2.68	31.64	19%	23%
16	Pollard Mill	78	1,200	-3.25	79.56	23%	9%
17	Ruby	33	1,080	-3.22	133.42	25%	5%
18	Three Houses Spring	48	1,160	-3.14	63.68	23%	11%

Table A-4. (Cont.)

Sample Site		Elevation (m)	1992 Rainfall (mm)	1996 Samples			
				Groundwater		Recharge (%)	
				$\delta^{18}O$ (‰) (SMOW)	Cl (ppm)	^{18}O	Cl
19	Alleynedale Hall pltn	62	1,480	-2.98	48.21	17%	15%
20	Alleynedale II	50	1,500	-2.63	358.25	20%	2%
21	Barrow Childrens Home	51	1,400	-2.86	94.16	18%	8%
22	Bromefield Pltn	46	1,290	-2.87	50.71	19%	14%
23	Carlton PS	50	1,780	-2.22	169.30	29%	4%
24	Farm Pltn	46	1,760	-2.49	47.34	23%	15%
25	Mount Gay Distillery	115	1,480	-3.07	50.65	18%	14%
26	Mullins Bay	5	1,770	-2.15	128.58	30%	6%
27	Portland Pltn	171	1,620	-2.13	33.07	34%	22%
28	Rock Hall Pltn	235	1,860	-3.04	30.07	14%	24%
29	Sailor Gully Cave	140	1,750	-3.01	112.42	15%	6%
30	Trents Pltn	63	1,300				
31	Welchtown Pltn	205	1,630	-2.58	134.97	20%	5%
32	White Hall	95	1,700	-3.26	38.52	16%	19%

NOTE:

- 1992 rainfall data for Barbados was obtained from the Caribbean Meteorological Institute database. Rainfall at groundwater sample sites was extrapolated from adjacent rainfall stations less than 4 km away.

Table A-5. Major and trace element compositions of groundwater and vadose water samples collected on Barbados. Note: BDL – Below detection limit.

Site No.	19	19	19	19	19	19	20	21
Well	Alleynedale Hall Plantation	Alleynedale Hall Plantation	Alleynedale Hall Plantation	Alleynedale Hall Plantation	Alleynedale Hall Plantation	Alleynedale Hall Plantation	Alleynedale II	Barrows Childrens Home
Date	7/28/94	1/5/96	3/26/96	10/30/96	11/29/96	2/2/97	1/4/96	8/7/94
Temperature (°C)	27.1	26.9	--	--	--	--	26.0	27.2
SC (µS/cm)	624	616	--	--	--	--	1,480	985
TDS (ppm)	494	492	--	--	--	--	947	741
pH	7.19	7.42	--	--	--	--	7.41	7.01
Eh (mV)	286	306	--	--	--	--	254	283
Ca (ppm)	91.5	91.3	84.3	81.3	79.8	78.8	95.8	129
Mg (ppm)	6.17	6.43	6.03	5.77	6.90	5.57	15.8	14.8
Na (ppm)	26.4	24.3	24.7	44.7	53.3	41.5	159	36.8
K (ppm)	8.90	16.8	7.90	1.95	3.78	2.86	10.3	34.5
Li (ppm)	BDL	0.08	BDL	BDL	0.02	0.02	0.15	BDL
Sr (ppm)	0.534	0.549	0.529	0.424	0.439	0.408	0.649	1.04
Fe (ppm)	BDL	0.06	--	--	--	--	BDL	0.01
Mn (ppm)	BDL	BDL	--	--	--	--	BDL	0.06
HCO_3 (ppm)	237	237	--	--	--	--	210	362
Cl (ppm)	54.0	48.2	--	--	--	--	358	122
SO_4 (ppm)	23.80	20.95	--	--	--	--	54.23	14.58
NH_3 (ppm)	BDL	0.12	--	--	--	--	0.04	1.45
NO_3 (ppm)	32.1	32.0	--	--	--	--	29.4	5.5
SiO2 (ppm)	13.5	14.1	13.7	12.4	11.6	12.1	12.8	17.8
Calcite SI	0.1	0.3	--	--	--	--	0.2	0.2
Aragonite SI	-0.1	0.2	--	--	--	--	0.0	0.0
Charge Balance	1%	4%	--	--	--	--	-6%	2%

Table A-5. (Cont.)

Site No.	21	1	1	2	2	22	22	23
Well	Barrows Childrens Home	Bowmanston Pumping Station (Drip)	Bowmanston Pumping Station (Drip)	Bowmanston Pumping Station (Stream)	Bowmanston Pumping Station (Stream)	Bromefield Plantation	Bromefield Plantation	Carlton Pumping Station
Date	1/5/96	8/5/94	1/9/96	8/5/94	1/9/96	7/24/94	1/7/96	1/3/96
Temperature (°C)	27.0	--	--	--	--	27.5	27.5	27.7
SC (μS/cm)	919	420	--	523	--	670	606	969
TDS (ppm)	679	328	365	395	399	516	483	641
pH	7.08	7.84	7.50	7.81	7.25	7.28	7.30	7.40
Eh (mV)	311	233	--	274	--	209	276	226
Ca (ppm)	116	59.8	67.8	78.2	80.1	86.1	79.5	89.4
Mg (ppm)	14.0	2.81	3.52	3.29	3.45	9.23	8.38	11.2
Na (ppm)	33.8	28.8	25.2	23.5	22.4	38.6	32.5	85.7
K (ppm)	7.10	2.31	10.2	3.73	11.5	12.0	17.6	9.59
Li (ppm)	0.11	BDL	0.20	0.04	0.24	0.05	0.11	0.19
Sr (ppm)	0.957	0.418	0.474	0.434	0.447	0.402	0.370	0.773
Fe (ppm)	BDL	0.01	BDL	0.01	0.06	0.01	BDL	BDL
Mn (ppm)	0.02	BDL	BDL	BDL	BDL	BDL	BDL	BDL
HCO_3 (ppm)	360	119	153	189	184	241	223	196
Cl (ppm)	94.2	44.0	37.2	34.6	31.5	61.5	50.7	169
SO_4 (ppm)	16.82	25.92	25.66	25.86	25.42	25.29	29.55	28.28
NH_3 (ppm)	0.21	0.89	BDL	0.30	BDL	0.39	BDL	0.04
NO_3 (ppm)	16.4	37.1	31.8	28.1	30.2	23.1	22.3	36.0
SiO2 (ppm)	18.4	7.3	9.7	7.6	9.3	17.5	17.9	14.7
Calcite SI	0.2	0.2	0.1	0.5	0.0	0.1	0.1	0.2
Aragonite SI	0.1	0.1	-0.1	0.4	-0.2	0.0	0.0	0.0
Charge Balance	-3%	3%	5%	3%	7%	4%	4%	2%

Table A-5. (Cont.)

Site No.	3	4	5	6	6	7	7	24
Well	Carmichael Plantation	Claybury Plantation	Congo Road	Easy Hall Plantation	Easy Hall Plantation	Edgecumbe Plantation	Edgecumbe Plantation	Farm Plantation
Date	1/8/96	7/23/94	8/3/94	7/23/94	1/2/96	7/22/94	1/3/96	1/4/96
Temperature (°C)	27.2	25.5	27.4	25.3	26.6	26.4	27.1	26.1
SC (µS/cm)	564	472	788	396	377	587	576	467
TDS (ppm)	438	356	580	182	269	456	466	326
pH	7.92	7.61	7.18	7.91	7.84	7.22	7.33	7.47
Eh (mV)	238	294	285	285	286	312	211	299
Ca (ppm)	86.6	74.0	88.2	54.4	53.3	89.9	92.8	62.6
Mg (ppm)	4.52	3.53	11.8	2.64	2.73	5.48	5.53	3.62
Na (ppm)	21.7	15.2	57.5	19.4	16.7	24.3	24.0	25.4
K (ppm)	12.4	3.17	6.58	2.53	0.85	1.62	8.14	1.04
Li (ppm)	0.21	0.03	0.08	0.05	BDL	BDL	0.18	0.11
Sr (ppm)	0.631	0.453	0.831	0.215	0.209	0.633	0.645	0.401
Fe (ppm)	0.05	0.01	0.02	0.01	BDL	0.01	BDL	BDL
Mn (ppm)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
HCO_3 (ppm)	219	158	242	96	97	233	237	127
Cl (ppm)	32.7	29.7	89.5	35.4	29.4	41.2	35.6	47.3
SO_4 (ppm)	23.82	22.88	39.05	28.62	30.42	14.52	17.57	17.31
NH_3 (ppm)	0.21	0.12	0.49	BDL	BDL	0.12	0.34	BDL
NO_3 (ppm)	26.4	41.0	24.8	28.2	30.0	34.0	31.4	29.9
SiO2 (ppm)	9.8	6.6	18.0	6.3	7.6	10.9	12.6	11.4
Calcite SI	0.7	0.2	0.0	0.2	0.1	0.1	0.2	-0.1
Aragonite SI	0.6	0.1	-0.1	0.1	0.0	0.1	0.1	-0.2
Charge Balance	5%	3%	3%	4%	2%	2%	6%	4%

Table A-5. (Cont.)

Site No.	8	8	9	9	9	9	9	9
Well	Halton Plantation	Halton Plantation	Hampton Plantation	Hampton Plantation	Hampton Plantation	Hampton Plantation	Hampton Plantation	Hampton Plantation
Date	7/23/94	1/9/96	7/30/94	1/3/96	2/27/96	3/27/96	9/30/96	10/31/96
Temperature (°C)	25.9	--	27.8	27.1	--	--	--	--
SC (μS/cm)	504	--	600	606	--	--	--	--
TDS (ppm)	374	357	459	484	--	--	--	--
pH	7.65	7.30	7.18	7.07	--	--	--	--
Eh (mV)	277	--	313	270	--	--	--	--
Ca (ppm)	67.2	63.5	80.3	92.7	60.9	59.8	85.7	85.0
Mg (ppm)	5.21	4.55	5.38	6.27	5.57	5.64	5.78	5.56
Na (ppm)	27.6	24.2	24.8	28.6	26.9	26.8	26.8	26.1
K (ppm)	2.66	13.0	2.23	5.48	2.75	2.92	3.17	2.58
Li (ppm)	BDL	0.22	BDL	0.08	0.02	0.02	0.02	BDL
Sr (ppm)	0.613	0.437	0.677	0.860	0.783	0.779	0.791	0.776
Fe (ppm)	0.01	0.03	0.01	BDL	--	--	--	--
Mn (ppm)	BDL	BDL	BDL	BDL	--	--	--	--
HCO_3 (ppm)	165	162	240	242	--	--	--	--
Cl (ppm)	49.3	40.0	49.9	47.9	--	--	--	--
SO_4 (ppm)	13.91	15.25	17.92	18.14	--	--	--	--
NH_3 (ppm)	BDL	BDL	0.12	BDL	--	--	--	--
NO_3 (ppm)	32.0	22.5	25.6	29.8	--	--	--	--
SiO2 (ppm)	10.1	10.7	11.2	11.8	10.3	10.3	11.2	11.0
Calcite SI	0.3	-0.1	0.0	0.0	--	--	--	--
Aragonite SI	0.1	-0.3	-0.1	-0.2	--	--	--	--
Charge Balance	2%	6%	-4%	3%	--	--	--	--

Table A-5. (Cont.)

Site No.	9	9	10	11	11	11	11	11
Well	Hampton Plantation	Hampton Plantation	Henley Plantation	Home Agricultural Station	Home Agricultural Station	Home Agricultural Station	Home Agricultural Station	Home Agricultural Station
Date	11/29/96	2/28/97	7/23/94	8/4/94	1/9/96	2/27/96	3/27/96	9/30/96
Temperature (°C)	--	--	26.3	27.3	--	--	--	--
SC (μS/cm)	--	--	489	1,750	--	--	--	--
TDS (ppm)	--	--	377	1,060	1,170	--	--	--
pH	--	--	7.32	7.35	7.40	--	--	--
Eh (mV)	--	--	284	238	--	--	--	--
Ca (ppm)	86.9	85.8	83.6	111	85.3	68.3	72.4	95.5
Mg (ppm)	5.63	5.67	3.40	20.0	31.6	26.7	26.0	30.9
Na (ppm)	26.5	27.5	14.7	194	239	230	209	276
K (ppm)	2.23	2.42	0.52	6.74	24.9	11.0	10.1	10.2
Li (ppm)	BDL	BDL	BDL	0.04	0.37	0.09	0.08	0.11
Sr (ppm)	0.788	0.792	0.675	0.928	0.801	0.678	0.675	0.882
Fe (ppm)	--	--	0.02	0.04	BDL	--	--	--
Mn (ppm)	--	--	BDL	BDL	BDL	--	--	--
HCO_3 (ppm)	--	--	186	210	184	--	--	--
Cl (ppm)	--	--	31.5	413	479	--	--	--
SO_4 (ppm)	--	--	21.31	58.38	87.93	--	--	--
NH_3 (ppm)	--	--	BDL	0.21	0.17	--	--	--
NO_3 (ppm)	--	--	26.3	30.8	28.8	--	--	--
SiO2 (ppm)	11.1	9.0	8.7	9.4	10.3	8.8	9.0	9.6
Calcite SI	--	--	0.1	0.2	0.0	--	--	--
Aragonite SI	--	--	-0.1	0.0	-0.1	--	--	--
Charge Balance	--	--	4%	-3%	-2%	--	--	--

Table A-5. (Cont.)

Site No.	11	11	11	11	12	12	12	12
Well	Home Agricultural Station	Home Agricultural Station	Home Agricultural Station	Home Agricultural Station	Kendal Plantation	Kendal Plantation	Kendal Plantation	Kendal Plantation
Date	10/29/96	11/28/96	1/31/97	2/28/97	8/2/94	1/3/96	2/27/96	3/27/96
Temperature (°C)	--	--	--	--	26.7	29.7	--	--
SC (μS/cm)	--	--	--	--	522	556	--	--
TDS (ppm)	--	--	--	--	493	426	--	--
pH	--	--	--	--	7.52	7.50	--	--
Eh (mV)	--	--	--	--	391	274	--	--
Ca (ppm)	98.5	97.6	72.2	61.1	75.9	71.8	65.9	66.4
Mg (ppm)	31.3	30.6	23.8	21.3	4.21	4.41	3.92	4.04
Na (ppm)	281	286	201	176	26.9	33.1	29.4	29.4
K (ppm)	10.7	11.2	11.5	10.7	7.69	15.7	7.02	7.01
Li (ppm)	0.13	0.14	0.16	0.12	BDL	0.08	BDL	BDL
Sr (ppm)	0.936	0.911	0.662	0.541	0.546	0.595	0.551	0.556
Fe (ppm)	--	--	--	--	0.02	BDL	--	--
Mn (ppm)	--	--	--	--	0.01	BDL	--	--
HCO_3 (ppm)	--	--	--	--	262	170	--	--
Cl (ppm)	--	--	--	--	44.4	53.7	--	--
SO_4 (ppm)	--	--	--	--	23.46	23.55	--	--
NH_3 (ppm)	--	--	--	--	0.30	0.12	--	--
NO_3 (ppm)	--	--	--	--	38.1	43.4	--	--
SiO2 (ppm)	9.6	9.5	9.3	9.3	8.3	9.9	8.5	8.6
Calcite SI	--	--	--	--	0.4	0.2	--	--
Aragonite SI	--	--	--	--	0.2	0.0	--	--
Charge Balance	--	--	--	--	-9%	4%	--	--

Table A-5. (Cont.)

Site No.	12	12	12	12	12	13	14	25
Well	Kendal Plantation	Kendal Plantation	Kendal Plantation	Kendal Plantation	Kendal Plantation	Little Bentleys	Marshall Trading	Mount Gay Distillery
Date	9/30/96	10/29/96	11/27/96	1/31/97	2/28/97	7/21/94	8/2/94	7/29/94
Temperature (°C)	--	--	--	--	--	28.1	29.0	27.6
SC (μS/cm)	--	--	--	--	--	593	522	637
TDS (ppm)	--	--	--	--	--	461	553	495
pH	--	--	--	--	--	7.78	7.28	7.36
Eh (mV)	--	--	--	--	--	273	265	276
Ca (ppm)	46.1	67.6	66.0	69.0	69.6	89.3	89.0	94.9
Mg (ppm)	3.95	4.15	4.23	4.32	4.34	5.91	14.5	6.84
Na (ppm)	28.9	39.7	31.2	31.7	31.2	26.1	71.8	30.7
K (ppm)	10.2	15.2	10.8	10.7	10.5	2.54	6.80	2.78
Li (ppm)	0.05	0.04	0.04	0.04	0.04	BDL	0.08	BDL
Sr (ppm)	0.518	0.579	0.569	0.583	0.585	0.708	0.842	0.541
Fe (ppm)	--	--	--	--	--	BDL	0.02	0.06
Mn (ppm)	--	--	--	--	--	BDL	BDL	BDL
HCO_3 (ppm)	--	--	--	--	--	228	182	244
Cl (ppm)	--	--	--	--	--	45.5	115	55.5
SO_4 (ppm)	--	--	--	--	--	14.27	47.99	16.74
NH_3 (ppm)	--	--	--	--	--	0.21	0.73	BDL
NO_3 (ppm)	--	--	--	--	--	36.2	3.1	27.0
SiO2 (ppm)	9.3	9.3	9.2	9.4	9.4	11.5	21.0	15.2
Calcite SI	--	--	--	--	--	0.7	0.0	0.1
Aragonite SI	--	--	--	--	--	0.5	-0.1	0.3
Charge Balance	--	--	--	--	--	3%	11%	3%

Table A-5. (Cont.)

Site No.	25	15	26	16	16	27	28	17
Well	Mount Gay Distillery	Mount Plantation, The	Mullins Bay	Pollard Mill	Pollard Mill	Portland Plantation	Rock Hall Plantation	Ruby
Date	1/8/96	7/23/94	1/6/96	8/2/94	1/8/96	1/5/96	1/4/96	8/4/94
Temperature (°C)	26.6	25.9	28.5	27.9	26.5	26.6	26.4	27.6
SC (μS/cm)	628	528	920	790	725	538	740	952
TDS (ppm)	486	417	661	598	544	420	379	685
pH	7.30	7.33	7.13	7.33	7.50	7.37	7.36	7.31
Eh (mV)	259	282	261	307	284	230	264	233
Ca (ppm)	93.0	89.8	112	115	98.3	87.6	74.2	72.0
Mg (ppm)	6.87	4.18	9.11	9.39	8.28	4.19	3.96	20.3
Na (ppm)	27.7	17.0	65.2	45.7	41.2	19.0	19.1	90.8
K (ppm)	8.07	1.81	8.99	0.79	9.66	6.16	8.26	8.70
Li (ppm)	0.14	BDL	0.17	BDL	0.23	0.09	0.09	0.09
Sr (ppm)	0.553	0.699	0.979	0.409	0.362	0.368	0.350	1.01
Fe (ppm)	BDL	BDL	BDL	0.08	BDL	BDL	BDL	0.02
Mn (ppm)	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL
HCO_3 (ppm)	244	218	266	240	218	203	181	248
Cl (ppm)	50.7	31.6	129	77.1	67.0	33.1	30.1	133
SO_4 (ppm)	16.67	16.32	30.22	68.88	63.35	30.64	23.91	52.51
NH_3 (ppm)	0.34	BDL	0.39	0.39	0.58	0.12	0.04	0.21
NO_3 (ppm)	21.9	26.8	26.1	24.1	21.4	24.7	28.0	31.0
SiO2 (ppm)	15.7	9.9	12.8	16.2	15.6	11.3	9.3	25.4
Calcite SI	0.2	0.2	0.1	0.2	0.3	0.2	0.1	0.1
Aragonite SI	0.1	0.0	0.0	0.3	0.2	0.0	-0.1	-0.1
Charge Balance	4%	4%	2%	4%	4%	4%	4%	1%

Table A-5. (Cont.)

Site No.	17	29	18	18	18	30	31	31	32
Well	Ruby	Sailor Gully Cave	Thicket Cave	Three Houses Spring	Three Houses Spring	Trents Plantation	Welchtown Plantation	Welchtown Plantation	White Hall
Date	1/2/96	1/10/96	8/2/94	7/27/94	1/2/96	8/7/94	8/3/94	1/5/96	1/4/96
Temperature (°C)	27.4	--	--	26.8	26.7	27.5	26.8	26.8	26.0
SC (μS/cm)	1,010	--	--	679	675	1,890	853	931	469
TDS (ppm)	718	509	761	515	523	1,230	596	623	348
pH	7.11	--	7.64	7.07	7.16	7.14	7.17	7.32	7.67
Eh (mV)	238	--	--	300	225	281	282	294	270
Ca (ppm)	75.2	80.3	60.3	87.8	88.4	226	98.8	96.5	70.2
Mg (ppm)	20.5	4.99	6.64	10.4	10.3	24.8	7.55	8.18	3.27
Na (ppm)	94.8	56.6	212	40.3	38.5	85.0	52.6	57.9	21.6
K (ppm)	15.6	10.7	13.6	0.64	2.39	35.7	12.5	27.2	2.84
Li (ppm)	0.06	0.31	0.16	BDL	BDL	BDL	0.07	0.10	0.05
Sr (ppm)	1.04	0.441	0.409	0.994	0.972	1.20	0.531	0.554	0.290
Fe (ppm)	BDL	BDL	0.02	0.02	BDL	0.12	0.06	BDL	BDL
Mn (ppm)	BDL	BDL	BDL	BDL	BDL	0.42	0.01	BDL	BDL
HCO_3 (ppm)	262	210	156	247	248	281	213	210	141
Cl (ppm)	135	112	304	63.7	63.4	396	117	135	38.5
SO_4 (ppm)	54.87	11.28	66.48	18.76	22.96	102.8	25.83	23.86	26.82
NH_3 (ppm)	BDL	0.58	--	0.21	BDL	--	0.68	0.21	BDL
NO_3 (ppm)	33.3	4.0	84.5	29.2	33.0	39.1	39.2	38.9	33.0
SiO2 (ppm)	25.4	17.2	11.8	14.1	14.9	30.8	27.4	24.4	10.3
Calcite SI	-0.1	-0.2	0.1	-0.1	0.0	0.4	0.0	0.2	0.2
Aragonite SI	-0.2	-0.4	-0.1	-0.2	-0.1	0.2	-0.1	0.0	0.1
Charge Balance	1%	2%	-2%	3%	2%	-1%	2%	3%	4%

Table A-5. (Cont.)

Ion	Precision (2σ)	Detection Limit (ppm)
Ca	5%	0.005
Mg	2%	0.005
Na	2%	0.01
K	5%	0.01
Li	10%	0.015
Sr	2%	0.005
Fe	2%	0.005
Mn	2%	0.005
Cl	2%	0.01
Br	3%	0.03
SO4	4%	0.05
SiO2	5%	0.1

Table A-6. Strontium and C isotopic compositions of Barbados groundwater, vadose water and soil samples collected as part of this study.

Site No.	Well	Date	$\delta^{13}C$ (‰) (PDB)	$^{87}Sr/^{86}Sr$	$\delta^{87}Sr$
Groundwater and vadose water samples					
19	Alleynedale Hall Plantation	7/28/94	-8.08	0.709084	-12.8
19	Alleynedale Hall Plantation	1/5/96	-8.24	0.709088	-12.3
20	Alleynedale II	1/4/96	-8.67	0.709092	-11.7
21	Barrows Childrens Home	8/7/94	-2.46	0.709100	-10.6
21	Barrows Childrens Home	1/5/96	-6.61	0.709080	-13.4
1	Bowmanston Pumping Station (Drip)	8/5/94		0.709123	-7.3
1	Bowmanston Pumping Station (Drip)	1/9/96	-7.43	0.709113	-8.7
2	Bowmanston Pumping Station (Stream)	8/5/94	-9.16	0.709103	-10.2
2	Bowmanston Pumping Station (Stream)	1/9/96	-9.10	0.709116	-8.3
22	Bromefield Plantation	7/24/94	-5.36	0.709003	-24.3
22	Bromefield Plantation	1/7/96	-6.97	0.709003	-24.3
23	Carlton Pumping Station	1/3/96	-8.83	0.709109	-9.3
3	Carmichael Plantation	1/8/96	-8.03	0.709095	-11.3
4	Claybury Plantation	7/23/94	-9.04	0.709127	-6.8
5	Congo Road	8/3/94	-7.75	0.709029	-20.6
6	Easy Hall Plantation	7/23/94	-10.53	0.709084	-12.8
6	Easy Hall Plantation	1/2/96	-10.92	0.709065	-15.5
7	Edgecumbe Plantation	7/22/94	-9.02	0.709088	-12.3
7	Edgecumbe Plantation	1/3/96	-7.43	0.709101	-10.4
24	Farm Plantation	1/4/96	-9.50	0.709093	-11.6
8	Halton Plantation	7/23/94	-8.73	0.709113	-8.7
8	Halton Plantation	1/9/96	-9.05	0.709133	-5.9
9	Hampton Plantation	7/30/94	-9.53	0.709122	-7.5
9	Hampton Plantation	1/3/96	-9.21	0.709126	-6.9
9	Hampton Plantation	1/3/96		0.709126	-6.9
9	Hampton Plantation	2/27/96		0.709137	-5.4
9	Hampton Plantation	3/27/96		0.709135	-5.7
9	Hampton Plantation	9/30/96		0.709144	-4.4
9	Hampton Plantation	10/31/96		0.709141	-4.8
9	Hampton Plantation	10/31/96			

Table A-6. (Cont.)

Site No.	Well	Date	$\delta^{13}C$ (‰) (PDB)	$^{87}Sr/^{86}Sr$	$\delta^{87}Sr$
9	Hampton Plantation	11/29/96		0.709129	-6.5
9	Hampton Plantation	11/29/96			
9	Hampton Plantation	2/28/97		0.709139	-5.1
9	Hampton Plantation	2/28/97			
10	Henley Plantation	7/23/94	-8.87	0.709127	-6.8
11	Home Agricultural Station	8/4/94	-6.64	0.709133	-5.9
11	Home Agricultural Station	1/9/96	-8.74	0.709140	-4.9
12	Kendal Plantation	8/2/94	-6.03	0.709124	-7.2
12	Kendal Plantation	1/3/96	-9.09	0.709122	-7.5
12	Kendal Plantation	1/3/96		0.709122	-7.5
12	Kendal Plantation	3/27/96		0.709098	-10.9
12	Kendal Plantation	9/30/96		0.709136	-5.5
12	Kendal Plantation	10/29/96		0.709118	-8.0
12	Kendal Plantation	11/27/96			
12	Kendal Plantation	1/31/97			
12	Kendal Plantation	1/31/97			
13	Little Bentleys	7/21/94	-8.43	0.709124	-7.2
14	Marshall Trading	8/2/94	-7.28	0.709025	-21.2
25	Mount Gay Distillery	7/29/94	-8.86	0.709080	-13.4
25	Mount Gay Distillery	1/8/96	-9.10	0.709091	-11.8
15	Mount Plantation, The	7/23/94	-8.28	0.709111	-9.0
26	Mullins Bay	1/6/96	-12.85	0.709134	-5.8
16	Pollard Mill	8/2/94	-7.74	0.708952	-31.4
16	Pollard Mill	1/8/96	-4.29	0.708952	-31.4
27	Portland Plantation	1/5/96	-6.31	0.709117	-8.2
28	Rock Hall Plantation	1/4/96	-9.52	0.709103	-10.2
17	Ruby	8/4/94	-10.24	0.709007	-23.7
17	Ruby	1/2/96	-9.17	0.708998	-25.0
29	Sailor Gully Cave	1/10/96	-10.22	0.709105	-9.9
18	Thicket Cave	8/2/94		0.709044	-18.5
18	Three Houses Spring	7/27/94	-5.13	0.709102	-10.3
18	Three Houses Spring	1/2/96	-7.55	0.709129	-6.5
30	Trents Plantation	8/7/94	-5.62	0.708965	-29.6

Table A-6. (Cont.)

Site No.	Well	Date	$\delta^{13}C$ (‰) (PDB)	$^{87}Sr/^{86}Sr$	$\delta^{87}Sr$
31	Welchtown Plantation	8/3/94	-5.17	0.709085	-12.7
31	Welchtown Plantation	1/5/96	-5.45	0.709091	-11.8
32	White Hall	1/4/96	-9.34	0.709075	-14.1
--	Woodbourne Oilfield	8/4/94	3.73	0.707973	-169.5
Soil samples					
19	Alleynedale Hall Plantation			0.709120	-7.7
2	Bowmanston Plantation			0.709236	8.5
6	Easyhall Plantation			0.709104	-10.0
7	Edgecumbe Plantation			0.709085	-12.7
7	Edgecumbe Plantation			0.709101	-10.4
26	Mullins Bay			0.709185	1.4
17	Ruby			0.709019	-22.0
17	Ruby			0.709015	-22.6
30	Trents Plantation			0.709063	-15.8

Table A-7. Location and contact information for sites visited on Barbados.

Sample Location	Latitude	Longitude	Contact	Address
Alleynedale Hall Plant.	13.2755	59.6276	Mr. Mortley	Alleyndale Hall Pltn, St. Peter
Alleynedale II PS	13.2720	59.6360	B.J. Mwansa	BWA, The Pines
Barrows Childrens Home	13.2825	59.6350	Arthur Smith	Contents, St. Lucy
Bowmanston PS	13.1668	59.5075	B.J. Mwansa	BWA, The Pines
Woodbourne Oilfield	n/a	n/a	Leslie Barker	Energy and Natural Resources Div., Min. Finance and Planning, Bay St., Bridgetown
Bromefield Plant.	13.2945	59.6416	Burton Ward	Haggatt Hall House, St. Michael
Buttals	13.1180	59.5384	Mr. Marshall	Buttals Farm, St. George
Carlton PS	13.2190	59.6360	B.J. Mwansa	BWA, The Pines
Carmichael Plant.	13.1162	59.5445	Mr. Marshall	Buttals Farm, St. George
Claybury Plant.	13.1744	59.5382	Thom. A. Herbert	Claybury Pltn, St. John
Congo Road	13.1220	59.4652	Robin Hunte	Congo Road, St. Philip
Easy Hall Plant.	13.1920	59.5343		
Edgecumbe Plant.	13.1197	59.5131	Ian Weekes	Edgecumbe Pltn., St. Philip
Farm Plant.	13.2420	59.6380		
Halton Plant.	13.1329	59.5015	Robin Watson	Halton Pltn., St. Philip
Hampton Plant.	13.1139	59.4929	Peter Fenty	Sunbury Pltn., St. Philip
Henley Plant.	13.1526	59.5164		
Home Agri. Sta.	13.1068	59.4567		
Kendal Plant.	13.1516	59.5104	William Clark	Kendall Pltn., St. John
Little Bentleys	13.1157	59.5141	H.K. Melville	Little Bentley, Christ Church
Marshall Trading	13.1552	59.4407		
Mount Plant., The	13.1354	59.5306	John A.C. Hutson	Mount Pltn., St. George
Mount Gay Distillery	13.2895	59.6145	Carl Ward	Mount Gay Distillery, St. Lucy

Table A-7. (Cont.)

Sample Location	Latitude	Longitude	Contact	Address
Mullins Bay	13.2310	59.6420	Stan Michelini	Sunset Crest, St.James
Pollard Mill	13.1473	59.4686	John Porter	Pollards Mill, St. Philip
Portland Plant.	13.2868	59.6051	Lennox Ward	Portland Pltn., St. Peter
Rock Hall Plant.	13.2370	59.6080		
Ruby	13.1068	59.4500		
Sailors Gully Cave				
Thicket Cave	13.1554	59.4645		
Three Houses Sprg.	13.1557	59.4613		
Trents Plant.	13.2929	59.6277	Vic Johnson	Trents Pltn., St. Lucy
Welchtown Plant.	13.2660	59.5987		
Windsor Plant.	13.1159	59.5255	Mr. Marshall	Buttals Farm, St. George
White Hall	13.2520	59.6240	Richard Parrish	White Hall, St.Peter

Table A-7. (Cont.)

Sample Location	Tel. #	Fax #	Remarks
Alleynedale Hall Plant.			Irrigation well
Alleynedale II PS	427-3990		Public supply well dug 1994-95
Barrows Childrens Home			Irrigation well (when pump installed), low yield
Bowmanston PS	427-3990		Stream approx. 30' wide, 2' deep
Woodbourne Oilfield	429-5254		Collected from separation tank in the Woodbourne Oilfield, St. Philip
Bromefield Plant.	429-2819		Pumps to artificial wetlands (1994 only)
Buttals	429-2629		No pump, located outside house, not sampled
Carlton PS	427-3990		Public supply well
Carmichael Plant.	429-2629		Irrigation well
Claybury Plant.	425-3900	425-2888	Pumps periodically, timer, located on hill surrounded by fruit trees, very high nitrates
Congo Road			Domestic use, serves a few houses
Easy Hall Plant.			Domestic use, very high nitrates
Edgecumbe Plant.	423-2347		Irrigation well
Farm Plant.			Abandoned site
Halton Plant.	423-2685	423-2233	Irrigation well
Hampton Plant.	423-6281		Drip irrigation, small pump
Henley Plant.			Irrigation well
Home Agri. Sta.			Irrigation well
Kendal Plant.			Irrigation well
Little Bentleys	423-6129	429-7047	Irrigation well, small pump
Marshall Trading			Irrigation well, overgrown
Mount Plant., The	429-0424	429-0423	Irrigation well
Mount Gay Distillery	439-8812		Industrial, very large pump

Table A-7. (Cont.)

Sample Location	Tel. #	Fax #	Remarks
Mullins Bay	432-2622		Newly constructed dug well
Pollard Mill	423-6530		Irrigation well, on timer, bailer sampled
Portland Plant.	422-2122		Abandoned well
Rock Hall Plant.			Abandoned windmill
Ruby			Irrigation well, oil in well, surface pump
Sailors Gully Cave			Small cave on southern side of road through Sailors Gully
Thicket Cave			Sample taken ~30' from cave entrance, drip water
Three Houses Sprg.			Discharges into small pool with fish
Trents Plant.			Abandoned, possibly contaminated, rusty, saline water
Welchtown Plant.			Abandoned well
Windsor Plant.	429-2629		Used for mixing chemicals
White Hall			Well for hydroponic garden

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