

Estimating recharge in a tropical karst aquifer

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

1. 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

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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 landmass (~430 km²), a well characterized hydrogeology and hydrogeochemistry [Senn, 1946; Harris, 1971], and relatively long records of rainwater oxygen isotope (1961–1992) and rainfall data (International Atomic Energy Agency and World Meteorological Organization, Global Network Isotopes in Precipitation, the GNIP database, release May 2, 1998, URL: <http://www.iaea.org/programs/ri/gnip/gnipmain.htm>, 1998) (hereinafter referred to as 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 Engineering Ltd., 1978; Vacher and Ayers, 1980]. Oxygen isotopes in groundwater are typically used as tracers to

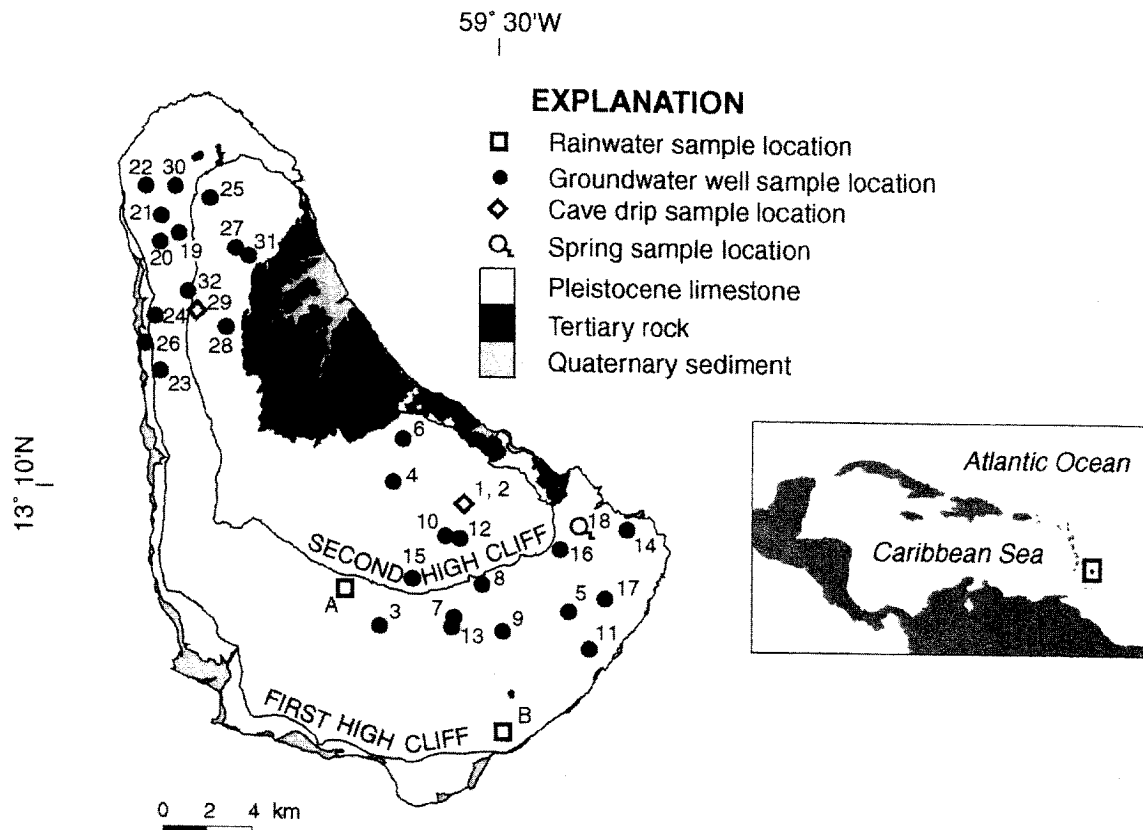


Figure 1. Location and geologic map of Barbados. The Pleistocene limestone that composes the aquifer occurs in the northern, western, and southern portions of Barbados (adapted from *Directorate of Overseas Surveys* [1983]).

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 recharge versus paleorecharge [Smith et al., 1992; Dutton, 1995]; and (4) the relative contribution of recharge waters from different sources, for example, surface water and interaquifer flow [Muir and Copley, 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.

2. Study Area

The Pleistocene limestone aquifer of Barbados is composed of Pleistocene-age coral reef limestones and is underlain by Tertiary-age deep-sea sedimentary rocks that act as an aquitard (Figure 1). Owing to continuous uplift the reef limestone was deposited outward 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 (Figure 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 (Figure 2). Groundwater generally flows from the elevated central portion of the island outward toward the coast following the contours of the top of the aquitard (Figure 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 to 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 Intertropical Convergence Zone (ITCZ) [Falkland, 1991; Reading et al., 1995].

3. Sampling and Analytical Procedures

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

Monthly composite rainwater $\delta^{18}\text{O}$ 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 sam-

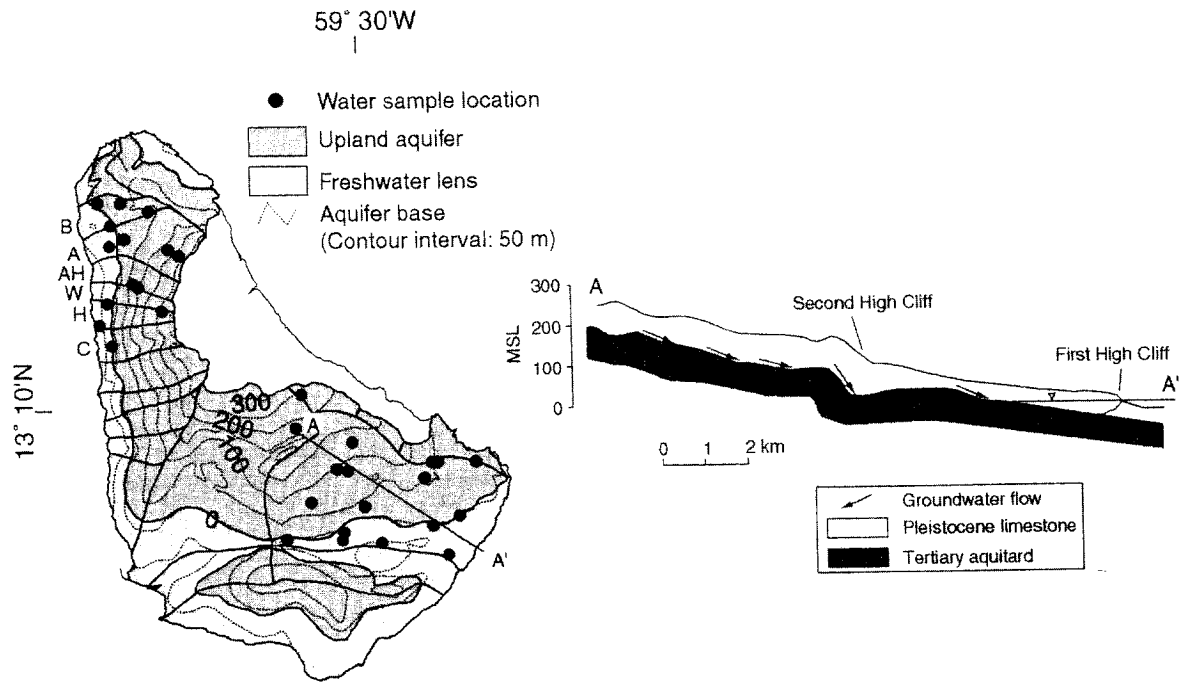


Figure 2. Hydrogeologic map of Barbados. The Pleistocene limestone aquifer is divided into several groundwater catchments because of the topography of the Pleistocene-Tertiary contact. West coast catchments are C, Carlton; H, Haymans; W, The Whim; AH, Ashton Hall; A, Alleyndale; and B, Bourbon (adapted from *Stanley Associates Engineering Ltd.* [1978] and cross section by *Barbados Ministry of Health et al.* [1991]).

ples 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 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 airtight bottles. The rainwater sampling procedure is similar to that used by GNIP except that the rainwater composite sam-

ples 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 (Figure 3b).

Groundwater and rainwater samples were analyzed for their oxygen isotopic compositions at the Colorado School of Mines by a modification of the CO₂ equilibration technique [Epstein and Mayeda, 1953] as described by 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 that of Bigeleisen et al. [1952]. Analytical precision based on standard runs is ±1.4‰.

Table 1. Stable Isotope Data for Rainwater Samples Collected in This Study (Relative to Standard Mean Ocean Water)

Dates	δ ¹⁸ O, ‰	δD, ‰
March 23–24, 1997	-0.34	-3.8
March 24–26, 1997	0.45	9.3
March 24–26, 1997	0.38	11.2
March 30–31, 1997	-0.16	0.7
April 13–30, 1997	-0.27	7.1
April 23–24, 1997	-0.36	4.9
May 12–15, 1997	0.02	-0.4
June 10–12, 1997	-2.25	-2.3
June 22–23, 1997	-2.52	-16.7
June 27–29, 1997	-1.26	0.3
July 14, 1997	-1.89	-10.9

The dates indicate the periods of time over which the rainwater samples were collected. For groundwater stable isotope data from this study, see Table B in electronic supplement.

4. Conventional Methods of Estimating Recharge

Recharge estimates have previously been made by (1) direct measurement methods using water balance based on potential evapotranspiration (PET) or groundwater discharge; (2) indirect measurements 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.

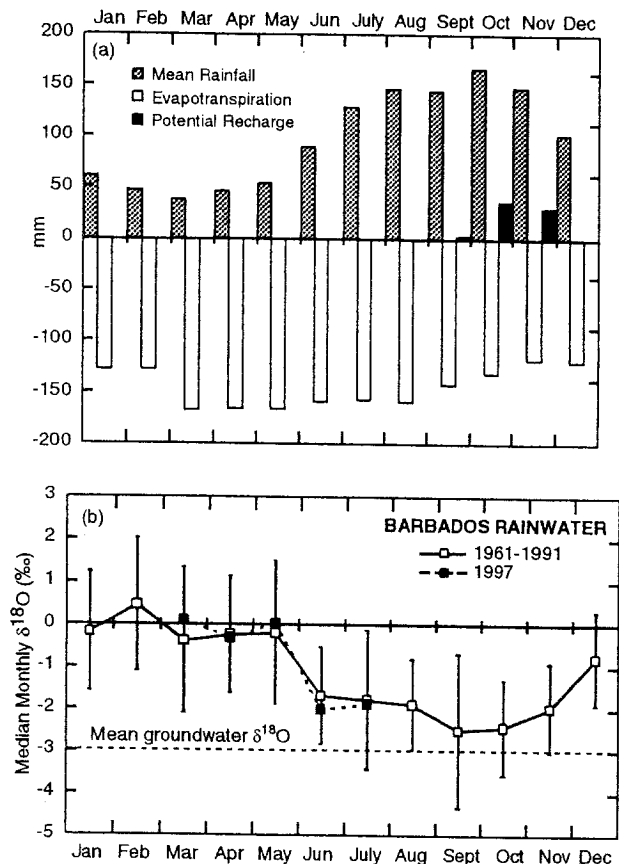


Figure 3. (a) Mean monthly rainfall and potential evapotranspiration for Barbados (1951–1980) from *Food and Agriculture Organization* [1985]. Potential recharge is the difference between mean monthly rainfall and evapotranspiration when rainfall exceeds potential evapotranspiration. Potential recharge is a conservative recharge estimate that indicates recharge only during the peak of the wet season. (b) Seasonal fluctuation of Barbados rainwater $\delta^{18}\text{O}$ values. The open symbols represent median monthly $\delta^{18}\text{O}$ values based on 1961–1992 rainwater data from the Global Network of Isotopes in Precipitation (GNIP) database (IAEA/WMO, 1998), and the closed symbols represent median monthly $\delta^{18}\text{O}$ values from this study (1997). The bars represent the standard deviation (1σ) for the GNIP data.

Comparison of mean monthly rainfall and PET data for Barbados from the *Food and Agriculture Organization* [1985] suggests that the potential for recharge only exists when rainfall exceeds PET (Figure 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 as follows: (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

$$R = (100 \times Q)/(P \times A), \quad (1)$$

where

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

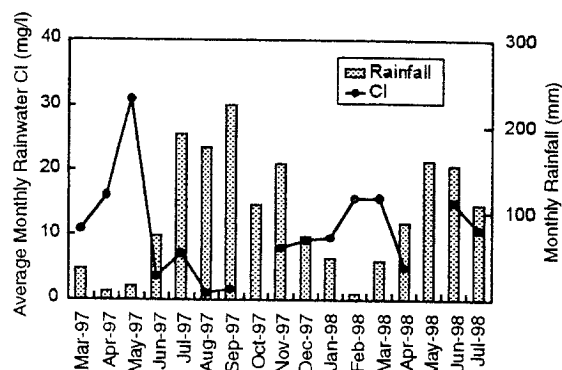


Figure 4. Seasonal fluctuation of Barbados rainwater chloride. These rainwater chloride data represent average monthly concentrations weighted based on associated rainfall amounts. The apparent inverse relationship between chloride concentrations and rainfall is due to dilution, especially during the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

- Q average coastal discharge (m^3/yr) [from *Proctor and Redfern International Ltd.*, 1983; from *Lewis*, 1987];
- P average annual rainfall in the catchment (m/yr) (based on 1992 rainfall data from the Caribbean Meteorological Institute);
- 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) is the weighted-average concentration based on 46 rainwater samples collected at site A and thus takes into account seasonal fluctuations in rainwater composition (Figures 1 and 4). (For additional rainwater chloride data, see Table A in electronic supplement.¹) Recharge can be estimated using the following equation:

$$R = 100 \times C_{\text{Cl}_{\text{rainwater}}}/C_{\text{Cl}_{\text{groundwater}}} \quad (2)$$

where R is recharge (percentage of annual rainfall) and C_{Cl} is chloride concentration (mg/L).

5. Oxygen Isotope Method of Estimating Recharge

Recharge can be estimated using oxygen isotopic compositions of groundwater and rainwater and associated rainfall

¹Supporting data tables are available on diskette or via Anonymous FTP from kosmos.agu.org, directory APEND (Username = anonymous, Password = guest). Diskette may be ordered from American Geophysical Union, 2000 Florida Avenue, N.W., Washington, DC 20009 or by phone at 800-966-2481; \$15.00. Payment must accompany order.

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 (Figure 5a) is used to determine monthly weighted-average rainwater $\delta^{18}\text{O}$ values over the period of record. These monthly values are used to determine those months that when combined are equivalent to the groundwater $\delta^{18}\text{O}$ value thereby satisfying the above assumption. This is done using the following equation:

$$\left[\sum_n (\delta^{18}\text{O}_{\text{rainwater}} \times P_{\text{month}}) \right] / \sum_n P_{\text{month}} = \delta^{18}\text{O}_{\text{groundwater}} \quad (3)$$

where

- n number of individual months taken from the entire 1961–1992 database used in weighted average;
- $\delta^{18}\text{O}_{\text{groundwater}}$ oxygen isotopic composition of groundwater (measured in this study);
- $\delta^{18}\text{O}_{\text{rainwater}}$ composite oxygen isotopic composition of rainwater for month n (i.e., individual GNIP analyses);
- P_{month} monthly rainfall for month n (mm).

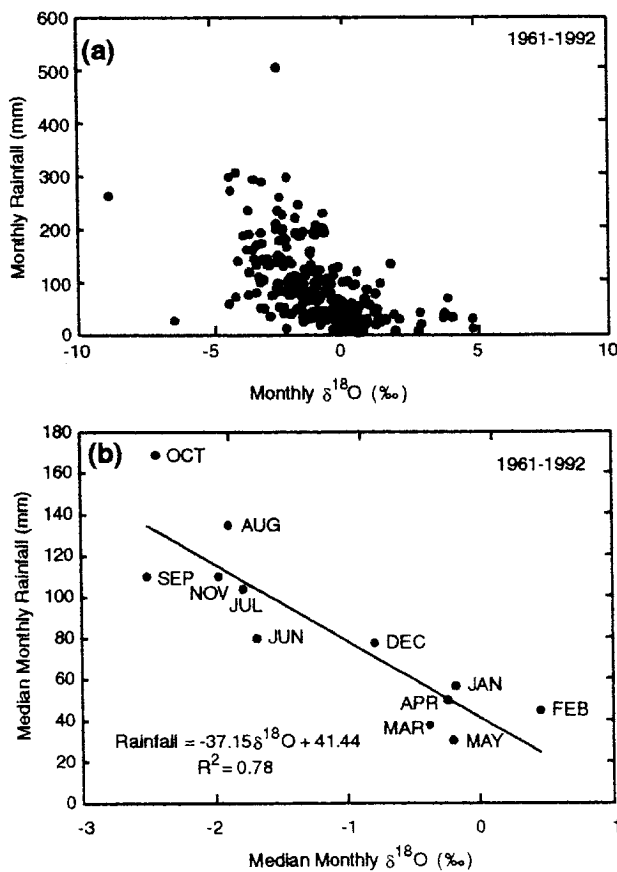


Figure 5. (a) Relationship between monthly $\delta^{18}\text{O}$ values of Barbados rainwater and the monthly rainfall. (b) Relationship between median monthly $\delta^{18}\text{O}$ values of Barbados rainwater and the median monthly rainfall from 1961 to 1997. Figure 5 is based on data obtained from GNIP database (IAEA/WMO, 1998).

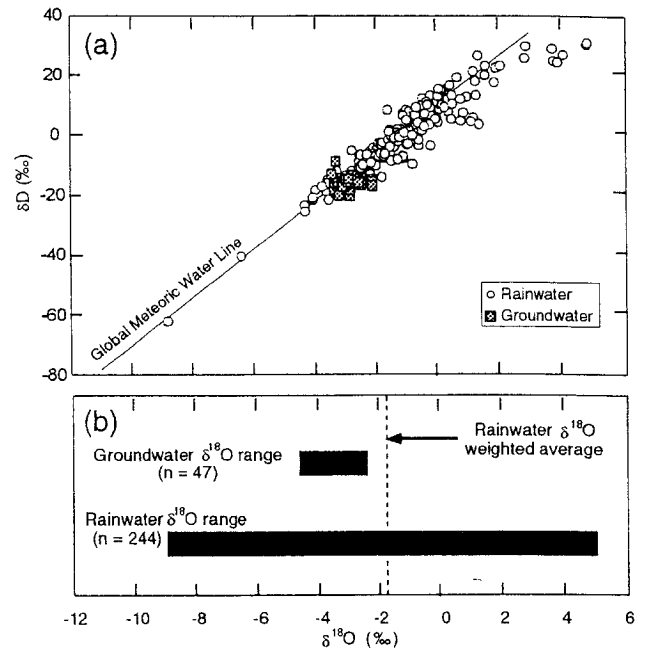


Figure 6. (a) The $\delta^{18}\text{O}$ - δD compositions of rainwater and groundwater on Barbados. The rainwater data are from this study and the GNIP database (IAEA/WMO, 1998), and the groundwater data are from this study and *Banner et al.* [1991]. (b) The ranges of $\delta^{18}\text{O}$ values for Barbados groundwater and rainwater: $\delta^{18}\text{O}_{\text{rainwater (weighted av)}} = \sum_n (\delta^{18}\text{O}_{\text{rainwater}} \times P_{\text{month}}) / \sum_n P_{\text{month}}$.

In equation (3) the term on the left represents the weighted-average $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values are not equal to the weighted-average rainwater composition (Figure 6b). Therefore, in order for (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, (3) determines the months that together produce a weighted-average rainwater $\delta^{18}\text{O}$ value that is equivalent to the groundwater composition. Because the average groundwater $\delta^{18}\text{O}$ value is lower than the weighted-average monthly rainwater $\delta^{18}\text{O}$ value, months with below average $\delta^{18}\text{O}$ values are those that satisfy (3) (Figure 6). Second, the rainfall amounts for those months used to balance (3) are averaged to determine the amount of annual rainfall that actually contributes to recharge. This method can be applied to estimate (1) interannual variations of recharge or (2) spatial variations of recharge. For application 1 the average groundwater $\delta^{18}\text{O}$ value for the island ($\delta^{18}\text{O} = -3.0\text{‰}$) (Figure 6) is used in (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 $\delta^{18}\text{O}$ values in (3) in order to determine spatial variations in recharge.

6. Analytical Results

6.1. Barbados Rainwater Compositions

Oxygen and hydrogen isotopic compositions of Barbados rainwater mostly lie along the GMWL (Figure 6a and Table 1)

Table 2. Factors Affecting Oxygen Isotope Variations in Barbados Groundwater

Isotope Effect	Variation on Barbados	Corresponding $\delta^{18}\text{O}$ 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	$<+0.1\text{‰}$
Fluid-rock interaction	<17 mmol CaCO_3/L , based on $^{87}\text{Sr}/^{86}\text{Sr}$	$<+0.001\text{‰}$ [Banner et al., 1994]

[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 1). The deviation of the highest rainwater $\delta^{18}\text{O}$ 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).

6.2. Barbados Groundwater Compositions

The $\delta^{18}\text{O}$ values of Barbados groundwater and vadose zone water lie within a narrow range compared to those of rainwater (Figure 6b). There is no apparent relationship between Barbados groundwater $\delta^{18}\text{O}$ values and land surface elevation, although there is a tendency for groundwater at lower elevations to have higher $\delta^{18}\text{O}$ values. The narrow range of groundwater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 [Banner et al., 1994]. This degree of water-rock interaction would produce an insignificant shift ($<0.001\text{‰}$) in the oxygen isotopic composition of the groundwater (Table 2).

7. Recharge Estimation Results

7.1. Conventional Recharge Estimates

Annual potential recharge, the difference between monthly rainfall and PET, is approximately 6% of average annual rainfall on Barbados. Potential recharge also indicates that recharge on Barbados is most likely to occur during September, October, and November (Figure 3a). Water-balance recharge estimates based on coastal discharge data from Proctor and Redfern International Ltd. [1983] and Lewis [1987] and water-balance calculations by Stanley Associates Engineering Ltd. [1978] and Delcan [1995] for the same groundwater catchments vary dramatically in some cases (Table 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 (equation (2) and Figure 7). (Tabulated data are available in Table D of electronic supplement.)

7.2. Oxygen Isotope Recharge Estimates

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

Table 3. Results of Different Water-Balance Calculations of Recharge Relative to Annual Rainfall on Barbados

Catchment	Potential Recharge Estimate FAO Data*	Lewis [1987] Data†	Proctor and Redfern International Ltd. [1983] Data‡	Stanley Associates Engineering Ltd. [1978] (Dry Year)§	Stanley Associates Engineering Ltd. [1978] (Average 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
Alleyndale	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	...

Values are expressed as percent of annual rainfall in the respective catchments. Catchments are shown on Figure 2.

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

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

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

§Water-balance calculations are given by Stanley Associates Engineering Ltd. [1978]. In dry and average years it is assumed that Barbados receives average annual rainfall of 1000 mm/yr and 1500 mm/yr, respectively.

||Water-balance calculations are given by DELCAN [1995].

$$R_{\text{year}} = 100 \times \left[\sum_n (P_{\text{month}} - \text{AET}_{\text{month}}) \right] / P_{\text{total}} \quad (4)$$

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 $P_{\text{month}} > 195$ mm;
- $\text{AET}_{\text{month}}$ actual evapotranspiration for month n (mm);
- P_{total} average annual rainfall (mm).

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

Using (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 (1500 mm), generally increasing with annual rainfall. This range of recharge estimates reflects interannual variations of rainfall that over the past 40 years have ranged from 700 mm/yr to 1800 mm/yr at site B.

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

$$R_{\text{site}} = 100 \times \left[\sum_n (P_{\text{month}} - \text{AET}_{\text{month}}/n) \right] / P_{\text{total}} \quad (5)$$

where R_{site} is recharge at a groundwater sample site, P_{month} is rainfall for months n included in (3), and n is number of data points used in (3).

From (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 $\delta^{18}\text{O}$ 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 (Figure 7). This increase in estimated recharge coincides with the location of the Second High Cliff (Figure 1).

8. Discussion

8.1. Controls on Rainwater Oxygen Isotope Variations

There is an inverse relationship between $\delta^{18}\text{O}$ 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].

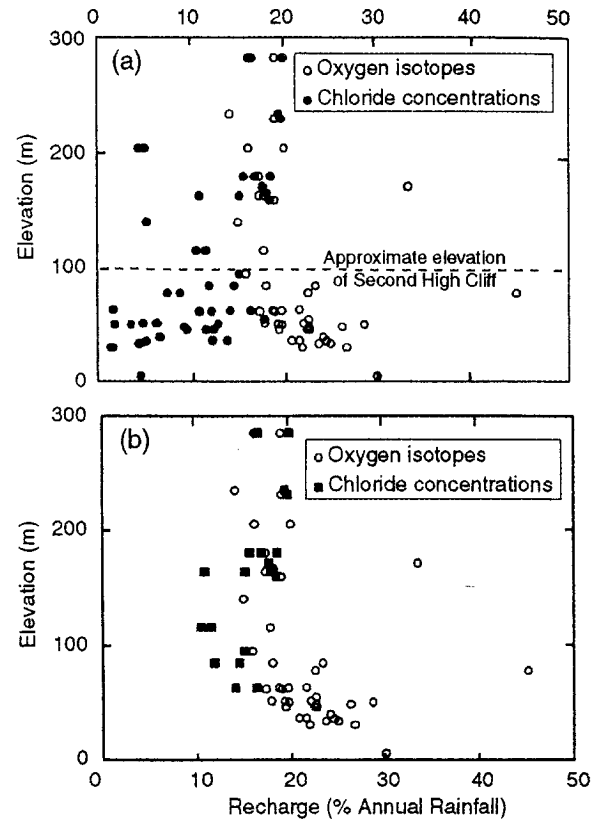


Figure 7. (a) The variation of estimated recharge based on oxygen isotopes (equation (5)) and chloride concentrations of groundwater and rainwater, with surface elevation. These data are tabulated in Table D of the supporting material. (b) The variation of recharge estimates based on oxygen isotopes and chloride concentrations, with land surface elevation. This is similar to Figure 7a except for the omission of low chloride-based recharge estimates that underestimate recharge as a result of elevated chloride concentrations due to freshwater-seawater mixing in coastal areas or evapotranspiration.

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 $\delta^{18}\text{O}$ values is apparent during the dry season and thus weakens any linear correlation that may exist between rainfall amounts and rainwater $\delta^{18}\text{O}$ values (Figures 5a and 6). The influence of altitude and continental effects on rainwater isotopic compositions is negligible on small islands like Barbados because of their low altitudes (i.e., $\sim -0.2\text{‰}$ per 100 m) and small landmasses [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] (Figure 5b).

The range of Barbados rainwater $\delta^{18}\text{O}$ 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) because of the amount effect (Figure 3b). This occurs because

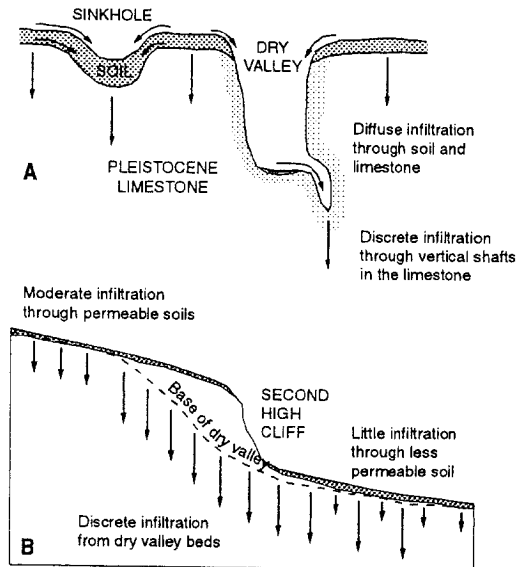


Figure 8. Schematic diagrams showing different pathways by which infiltrating water recharges the limestone aquifer of Barbados: (a) oriented perpendicular and (b) parallel to a hypothetical dry valley.

rainwater associated with heavy rainfall has lower $\delta^{18}\text{O}$ values than rainwater from small rainfall events (Figures 3b and 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 ITCZ is located approximately 8°N of the equator, relatively close to Barbados (approximately 13°N). The proximity of the ITCZ results in increased rainfall and consequently in rainwater with lower $\delta^{18}\text{O}$ values because of 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.

8.2. Relationship Between Groundwater and Rainwater Oxygen Isotopic Compositions

Research conducted in Israel and Brazil indicates 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 $\delta^{18}\text{O}$ values associated with recharge of local runoff have higher $\delta^{18}\text{O}$ values than the average rainwater composition, while groundwater associated with heavy floods has lower $\delta^{18}\text{O}$ values. In both cases the groundwater deviated from the Meteoric Water Line (MWL) because of evaporation. On Barbados the relationship between groundwater and rainwater $\delta^{18}\text{O}$ 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 nonrecharge periods will be included in the weighted-average rainwater composition but not in the average groundwater composition. Similar relationships between rainwater and groundwater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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).

8.3. Factors Affecting Infiltration

The narrow range of groundwater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 [Tullstrom, 1964]. Below the Second High Cliff, at elevations less than 100 m, infiltration rates through the soils range from 12.5 mm/h to 250 mm/h, but typically, they are approximately 50 mm/h [Tullstrom, 1964]. The Pleistocene limestone is much more permeable than the overlying soils with measured infiltration rates of 700–70,000 mm/h [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 (Figure 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 occur along the sides of these dry valleys act as vertical conduits for water to infiltrate directly into the limestone and rapidly recharge the aquifer (Figure 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/d will generate runoff on Barbados [Tullstrom, 1964]. Rainfall rates of this magnitude typically only occur once per year.

The narrow range of groundwater $\delta^{18}\text{O}$ 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, which results 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 because of 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 suggests that this may be the case on Barbados.

8.4. Determining the Seasonal Distribution of Recharge

The average groundwater $\delta^{18}\text{O}$ value (-3.0‰) on Barbados is lower than the weighted average of rainwater (-1.9‰), weighted based on corresponding monthly rainfall data (Figure 6). Moreover, the range of groundwater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values due to the amount effect.

The relationship between the average Barbados groundwater $\delta^{18}\text{O}$ value and rainwater $\delta^{18}\text{O}$ values suggests that significant recharge only takes place during months with more than 195 mm of rainfall, as discussed in section 7.2.1. 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 3 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.

8.5. 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 ($\sim 6\%$) is much lower than those obtained using oxygen isotopes (15–45%). This occurs because the use of PET in recharge estimation overestimates 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 because of 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

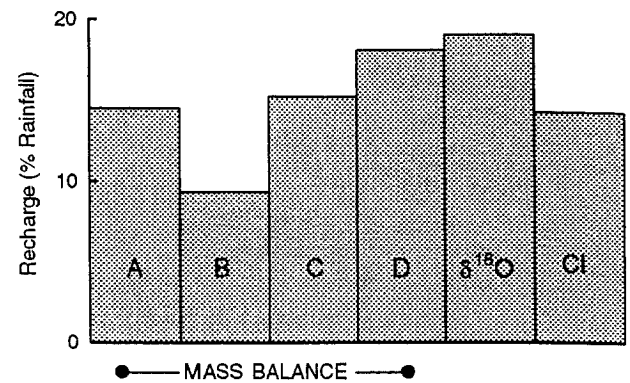


Figure 9. Graph showing recharge estimates for combined west coast catchments obtained by using different water-balance calculations, oxygen isotopes, and chloride concentrations. Water-balance calculations A and B are based on coastal discharge data from Proctor and Redfern International Ltd. [1983] and Lewis [1987], respectively, while C and D are water-balance calculations by Stanley Associates Engineering Ltd. [1978] and Delcan [1995], respectively.

for individual catchments may underestimate or overestimate 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 International Ltd., 1983; Stanley Associates Engineering Ltd., 1978; Delcan, 1995] for individual west coast catchments are highly variable and do not consistently agree with each other (Table 3). However, the results of models A, C, and D, shown in Figure 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 (Figure 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 $\delta^{18}\text{O}$ 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 to >100 mg/L. Freshwater-seawater mixing should result in a $\delta^{18}\text{O}$ value shift of $<0.02\text{‰}$; that is less than the analytical uncertainty and much smaller than the range of groundwater $\delta^{18}\text{O}$ values ($\sim 2\text{‰}$). 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 overestimation of evaporation and would therefore underestimate 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) where abandoned, low-yield, large-diameter dug wells are located at the highest elevations; (2) where the water table is close to land surface; and (3) where a slow cave drip occurs. 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 $\delta^{18}\text{O}$ values. However, groundwater $\delta^{18}\text{O}$ values show no apparent effects of fractionation due to evaporation (see section 6.2). 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 underestimate recharge and are excluded from Figure 7b. Figure 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 (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 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.

8.6. Implications for 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 $\delta^{18}\text{O}$ 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. However, 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 $\delta^{18}\text{O}$ values of rainwater and groundwater and the relationships between $\delta^{18}\text{O}$ values of contemporaneous rainwater and groundwater. Un-

derstanding 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.

9. Conclusions

Seasonal fluctuations of Barbados rainwater $\delta^{18}\text{O}$ values are related to the amount of rainfall, with lower $\delta^{18}\text{O}$ values associated with wet season months (June to December) and higher $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values on Barbados indicate that most recharge is rapid and takes place only during the wettest 1–3 months of the year.

On the basis of evaluation of different potential sites for infiltration the potential for recharge is greatest with 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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