GEOCHEMICAL CONSTRAINTS ON RECHARGE AND GROUNDWATER EVOLUTION: THE PLEISTOCENE AQUIFER OF BARBADOS

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ABSTRACT: The Pleistocene limestone aquifer of Barbados is composed of highly permeable reef limestone overlying Tertiary deep-sea strata that act as an aquitard. Groundwater infiltrates through the soil and limestone then flows along the top of the aquitard and into a freshwater lens before discharging along the coast. Discrete recharge takes place through sinkholes, drainage wells and dry valley beds. Soils influence recharge because of varying infiltration rates. Soils occurring at higher elevations are generally more permeable than those at lower elevations. Consequently, there is greater potential for diffuse recharge through soils at higher elevations on the island. Recharge was quantified by comparison of groundwater and rainwater Cl concentrations and oxygen isotopic compositions. The results indicate that recharge (1) is due to rapid infiltration, (2) occurs only during the wettest months of the year, and (3) represents 15-30% of annual rainfall.

Major and trace element and isotopic variations in Barbados groundwaters are used to constrain the relative influences of (1) mineral-solution reactions with aquifer and aquitard rock, (2) ion exchange in soils, (3) seawater mixing, (4) anthropogenic inputs, and (5) variations in recharge. Major element compositions of groundwater reflect the effects of limestone dissolution and fresh groundwater-seawater mixing in coastal areas, whereas elevated nitrate concentrations indicate a widespread anthropogenic impact. Groundwater Sr isotopic variations are used to trace soil and rock sources of dissolved constituents. Aquitard influences appear to be associated with low hydraulic gradients.

KEY TERMS: Barbados; water quality; hydrogeology; karst aquifers; recharge; isotopes

INTRODUCTION

The aim of this research is to use constituents in groundwater to constrain recharge and geochemical processes taking place in a karst aquifer. The geochemical evolution of groundwater in limestone aquifers is influenced by factors that include recharge, aquifer and aquitard rock, soil, groundwater flow paths, and anthropogenic inputs. Constraining recharge is important in constraining groundwater budgets, and water and ion fluxes through an aquifer. Barbados is unique for this research because of the occurrence of contrasting limestone compositions and groundwater flow-path lengths and gradients. This research involved groundwater sampling in groundwater catchments along the west coast of Barbados and the St. Philip North catchment in southeastern Barbados, as well as collection of rainwater samples. Available rainwater data for Barbados from the Global Network for Isotopes in Precipitation (GNIP) database was also utilized.

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GEOLOGY AND HYDROGEOLOGY OF BARBADOS

Barbados is composed of Pleistocene reef deposits up to 100 m thick. These reef deposits are derived from coral reefs that grew outward from the center of the island in response to continuing uplift, forming a series of terraces parallel to the present-day coastline. There are three main terraces, separated by the First and Second High Cliffs, respectively (Fig. 1A). The geochemical composition of the Pleistocene limestones is related to age and therefore elevation. Younger limestones occur at relatively low elevations and have higher Sr/Ca ratios than older limestones due to the impact of diagenetic alteration that increases with age (Matthews, 1968; Banner et al., 1994). The Tertiary rocks that directly underlie the Pleistocene limestone consist of (1) marls with interbedded volcanic ash and (2) terrigenous sediments (Speed, 1981; Ladd et al., 1990).

The Pleistocene limestone aquifer of Barbados is composed of highly porous Pleistocene coral limestone with underlying low-permeability Tertiary sediments acting as an aquitard (Senn, 1946). Recharge to the aquifer takes place by diffuse and discrete infiltration through the soil and overlying limestone. The water table occurs just above the contact between the Pleistocene limestone and the underlying aquitard. Due to the relatively thin saturated thickness of this aquifer, the topography of the Pleistocene-Tertiary contact controls the direction and gradients of groundwater flow within most parts of the aquifer. Groundwater generally flows from the elevated central and southern portions of the island towards the coast. This aquifer is divided into two hydrologic zones: (1) the streamwater zone which is the upland portion of the aquifer characterized by gravity-flow along the base of the Pleistocene limestone, and (2) the sheetwater zone which is the freshwater lens portion of the aquifer that occurs in low-lying parts of the island (Fig. 1B). Discharge from the Pleistocene limestone aquifer primarily takes the form of discharge from the freshwater lens into the sea. Some discharge also takes place from springs that occur along the eastern margin of the aquifer where the Pleistocene-Tertiary contact outcrops and from a few springs that occur where the Pleistocene limestone is thin and consequently the water table intersects land surface.

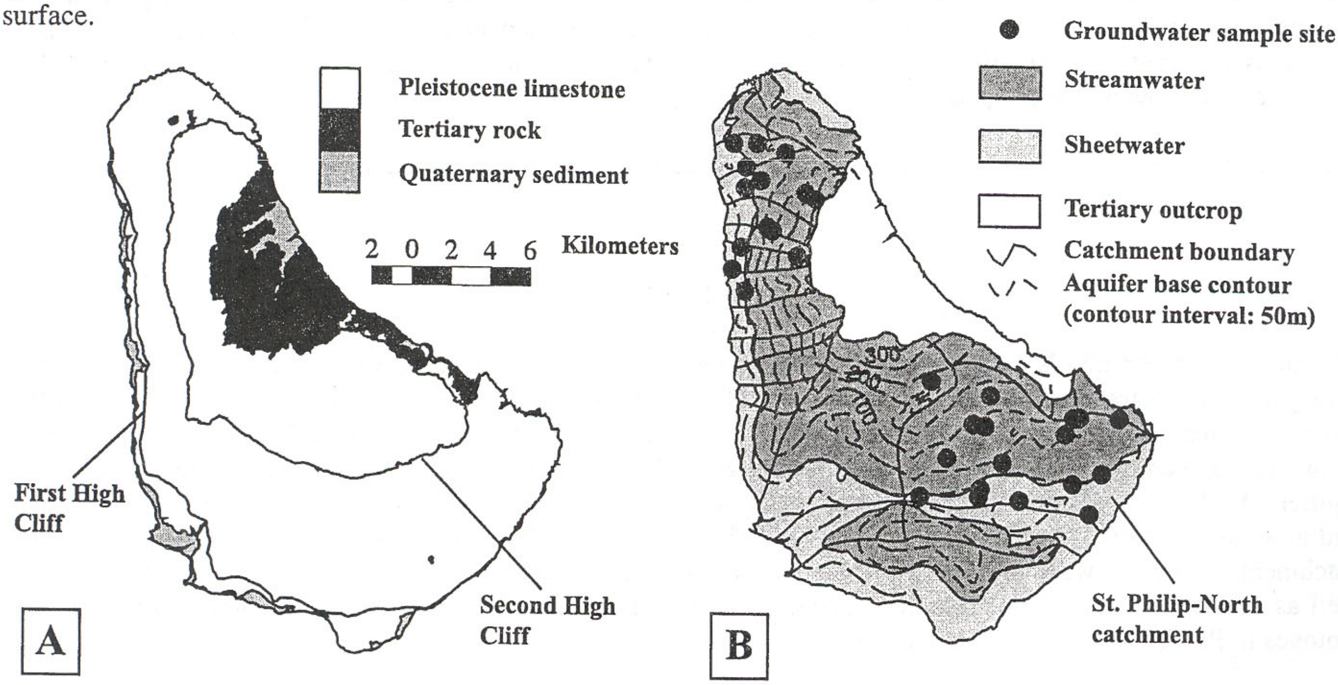

Figure 1. A: Geologic map of Barbados. B: Hydrogeologic map of Barbados. Adapted from 1:50,000 maps by Directorate of Overseas Surveys (1983) and Stanley Associates (1978).

INFILTRATION AND RECHARGE PROCESSES

Surface karst features, such as sinkholes and dry valleys, are potential sites for rapid discrete recharge to limestone aquifers. On Barbados, sinkholes are associated with relatively flat areas, especially immediately above and below the Second High Cliff. Dry valleys are associated with moderate to steep slopes and only flow during periods of intense rainfall. Erosion in dry valleys has exposed the underlying limestone, particularly where these valleys cut through terraces such as the Second High Cliff. The presence of caves and karst depressions in the sides of dry valleys suggests discrete infiltration of water from the dry valleys directly into the limestone. Manmade drainage wells are also means by which discrete recharge to the aquifer may take place.

Soils occurring above the Second High Cliff have infiltration rates of approximately 250 mm/h (Tullstrom, 1964; Fig. 2). 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 are approximately 50 mm/h (Tullstrom, 1964). Soils occurring along topographic valley axes and in some sinkholes are virtually impermeable due to the accumulation of clay sediment (Tullstrom, 1964). Differences in soil infiltration rates can be attributed to differences in age and mineral composition (Vernon and Carroll, 1965). Similar to the underlying limestone, soils occurring at lower elevations are younger, less altered and consequently are composed primarily of smectite clay while older soils at higher elevations are composed primarily of kaolinite (Vernon and Carroll, 1965). Tullstrom (1964) measured an infiltration rate of 1,400 mm/h through limestone at a site in southern Barbados.

Recharge can potentially take place by diffuse infiltration through the soil or by discrete infiltration through drainage wells, sinkholes or dry valleys. Diffuse recharge is most likely to occur through soils characterized by high infiltration rates. These soils occur above the Second High Cliff and at lower elevations in northwestern Barbados. Karst shafts and drainage wells act as 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 produce runoff.

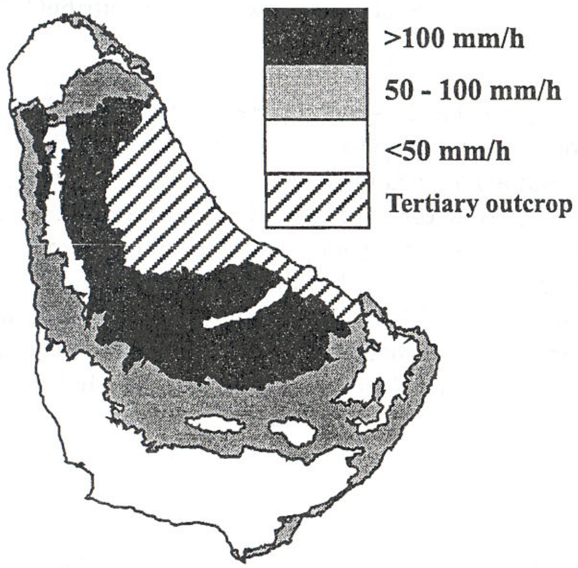

Figure 2. Infiltration rates of Barbados soils. Adapted from Vernon and Carroll (1965) and Tullstrom (1964).

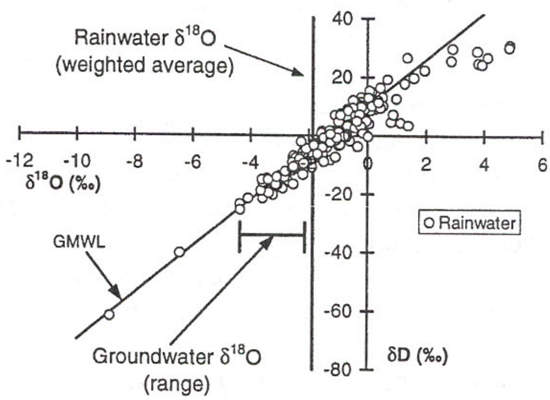

Figure 3. The $\delta^{18}O$-δD compositions of rainwater and groundwater on Barbados. The rainwater data was obtained from the GNIP database (1972-1991) and from this study. Note that the weighted average rainwater $\delta^{18}O$ lies does not coincide with the range of groundwater $\delta^{18}O$ values. (GMWL = Global Meteoric Water Line).

OXYGEN ISOTOPES AND RECHARGE ESTIMATION

The oxygen and hydrogen isotopic compositions of Barbados rainwater mostly lie along the Global Meteoric Water Line (GMWL; Fig. 3). The highest rainwater isotopic compositions deviate from the GMWL due to evaporation effects associated with dry season conditions (Rozanski et al., 1993). High rainwater δD and $\delta^{18}O$ values are associated with relatively light rainfall during the dry season (January - May) while low values occur primarily during the wet season months (June - December) associated with heavy rainfall. This seasonal compositional fluctuation is associated with the "amount effect" in which rainwater becomes progressively more depleted in ^{18}O as rainfall increases (Dansgaard, 1964). The oxygen isotopic composition of groundwater reflects the weighted average of the rainwater that actually infiltrates to the water table. The narrow range of Barbados groundwater $\delta^{18}O$ values relative to rainwater compositions, together with the fact that the weighted average rainwater composition does not coincide with the range of groundwater compositions suggests (1) a limited period of recharge during the wet season, and (2) rapid infiltration with little evaporation prior to recharge.

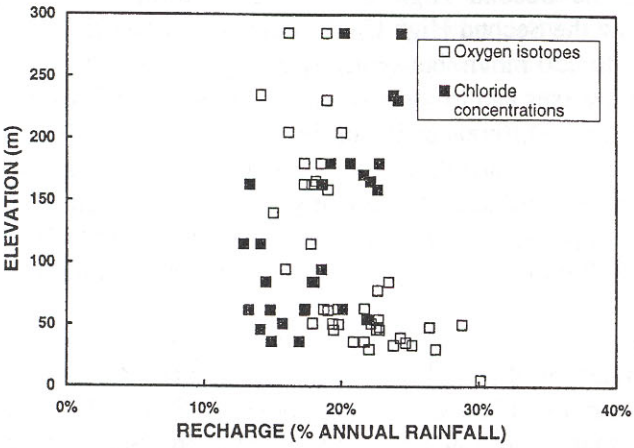

Figure 4. Land surface elevation vs. recharge estimates based on two methods: oxygen isotopes and chloride concentrations, methodology described in the text. Increased recharge at elevations below 100 m is attributed to discrete recharge adjacent to the Second High Cliff.

Recharge estimation based on oxygen isotopes is most applicable to small aquifers, such as Barbados, where groundwater residence times are short and thus groundwater compositions reflect present climatic conditions. Recharge can be estimated by comparing the compositions of groundwater and rainwater. Assuming that only periods of heavy rainfall contribute to recharge, the weighted average of rainwater can be recalculated to be equal to the average composition of groundwater by eliminating isotopic data associated with dry months. The weighted average oxygen isotopic composition of Barbados rainwater is equal to the average composition of the groundwater when data from months with less than 195 mm of rainfall are excluded. One can therefore deduce that (1) only monthly rainfall in excess of 195 mm contributes to recharge on Barbados and (2) recharge occurs during the wettest 1-3 months of the year. This method can be used to estimate recharge at individual sample sites using the following equation:

$$R(\%) = \frac{100 \cdot \sum_{n} P_{month}}{n \cdot P_{Av.Total}} \qquad (1)$$

where:

R = Recharge expressed as a percent of annual rainfall;

ΣP_{month} = Sum of rainfall for all months used to calculate a rainwater weighted average oxygen isotopic composition equal to the groundwater oxygen isotopic composition at a specific location;

n = Number of data points used to calculate the weighted average; and

$P_{Av.\ Total}$ = Annual rainfall for specific location, expressed in millimeters (1992 data used in this study).

Estimated recharge is 15-20% of annual rainfall at elevations higher than 100 m, apparently increasing to 30% or greater below 100 m (Fig. 4). This increase in recharge coincides with the location of the Second High Cliff.

Comparison of Cl concentrations in rainwater and groundwater may also be used to estimate recharge based on the following equation:

$$R(\%) = \frac{100 \cdot C_{Cl_{rw}}}{C_{Cl_{gw}}} \qquad (2)$$

where:

C_{Cl} = The concentration of Cl in rainwater (rw) and groundwater (gw), respectively.

This method assumes conservative behavior for Cl and is therefore not valid in coastal areas where seawater-freshwater mixing adds Cl to the groundwater. Samples from elevations below 25 m are therefore not included in the Cl recharge estimates. Generally, recharge estimates based on Cl concentrations agree with those based on oxygen isotopes (Fig. 4). The advantages of indirect recharge estimation based on groundwater and rainwater constituents over direct measurement of hydrologic parameters are: (1) direct measurement requires extensive and intensive measurement procedures to overcome the spatial and temporal heterogeneity, (2) difficulties in accurately measuring coastal discharge and evaporation, and (3) direct measurement may not provide information on the temporal or spatial distribution of recharge.

FACTORS INFLUENCING GROUNDWATER QUALITY

Major element compositions of groundwater in the Pleistocene limestone aquifer vary from Ca-HCO_3 to Na-Cl reflecting the effects of limestone dissolution during infiltration and along flow paths, and freshwater-seawater mixing in coastal areas, respectively. Ubiquitous elevated nitrate concentrations (0.7 to 10 mg/l-N) indicate a widespread anthropogenic impact, primarily associated with the widespread use of nitrogenous fertilizers for agriculture on Barbados. The Sr/Ca ratios of Barbados groundwater show different trends along their respective flow paths (Fig. 5). In the northwestern catchments, Sr/Ca ratios remain relatively constant between values of 0.002 and 0.004 while in the central and southern catchments, the Sr/Ca ratios increase progressively down-gradient in response to the occurrence of younger, less altered, more Sr-rich limestone at lower elevations. Groundwater Sr isotopic variations are used to trace different sources of Sr because on Barbados, soil, Pleistocene aquifer and Tertiary aquitard rocks have different Sr isotopic compositions (Banner et al., 1994). The Sr isotopic composition is expressed as: $\delta^{87}Sr = [(^{87}Sr/^{86}Sr)_{sample} - (^{87}Sr/^{86}Sr)_{seawater})/(^{87}Sr/^{86}Sr)_{seawater}] \times 10^5$, where $\delta^{87}Sr = 0$ in modern seawater. Groundwater Sr isotopic compositions progressively approach isotopic compositions of the Pleistocene limestone along flow paths. Groundwater influence by Tertiary rock is apparent in parts of the aquifer characterized by low hydraulic gradients (Fig. 6).

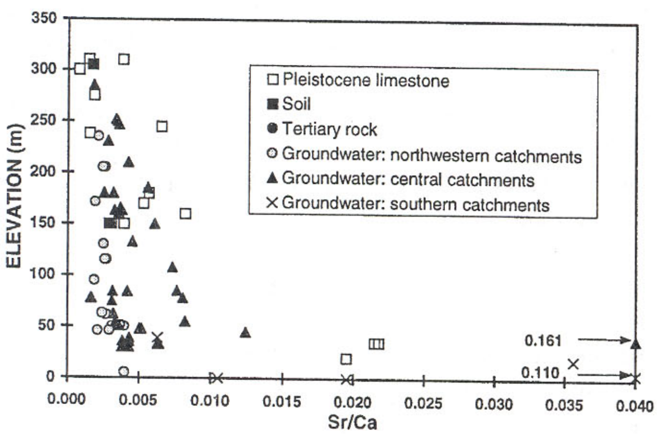

Figure 5. Variation of Sr/Ca ratios for Pleistocene limestones, soils, and groundwaters with elevation. Data from this study and Banner et al. (1994).

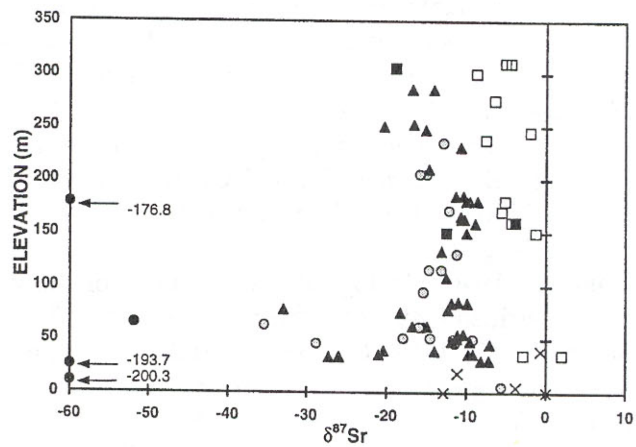

Figure 6. Variation of $\delta^{87}Sr$ of Barbados groundwater, Tertiary rocks, Pleistocene limestone, and soil with elevation (analytical uncertainty ±5.4 $\delta^{87}Sr$ units. Data from this study and Banner et al. (1994).

SUMMARY

1. Recharge to the Pleistocene limestone aquifer takes the form of diffuse infiltration through permeable soils and discrete infiltration through some sinkholes, dry valleys, and drainage wells. Discrete recharge requires intense rainfall, resulting in runoff.

2. Comparison of rainwater and groundwater oxygen isotopic compositions indicate that (1) recharge is restricted to the wettest 1-3 months of the year and (2) there is little evapotranspiration prior to recharge.

3. Recharge estimates based on oxygen isotopes and Cl in rainwater and groundwater indicate that (1) recharge is 15-30% of annual rainfall and (2) enhanced recharge occurs near the Second High Cliff.

4. Pleistocene limestone aquifer groundwater compositions reflect the contributions of (1) rainwater that actually recharges the aquifer; (2) interaction with soil, Pleistocene limestone of different compositions, and Tertiary aquitard rock; and (3) the widespread use and leaching of nitrogenous fertilizer. The Sr/Ca ratios of Barbados groundwater indicate interaction between the groundwater and progressively younger, less altered limestone along flow paths.

ACKNOWLEDGEMENTS

This work was made possible by grants from the Geology Foundation at the University of Texas at Austin, Geological Society of America and Sigma Xi, assistance from MaryLynn Musgrove, Beverley Wood, Pedro Welch IV, the Barbados Water Authority, and numerous landowners on Barbados, as well as helpful comments by Joe Troester.

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