Use of tritium and helium to define groundwater flow conditions in Everglades National Park

René M. Price

Department of Earth Sciences and Southeast Environmental Research Center, Florida International University, Miami, Florida, USA

Zafer Top and James D. Happell

Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Florida, USA

Peter K. Swart

Marine Geology and Geophysics, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Florida, USA

Received 19 December 2002; revised 3 July 2003; accepted 9 July 2003; published 24 September 2003.

[1] The concentrations of tritium (³H) and helium isotopes (³He and ⁴He) were used as tracers of groundwater flow in the surficial aquifer system (SAS) beneath Everglades National Park (ENP), south Florida. From ages determined by ³H/³He dating techniques, groundwater within the upper 28 m originated within the last 30 years. Below 28 m, waters originated prior to 30 years before present with evidence of mixing at the interface. Interannual variation of the 3 H/ 3 He ages within the upper 28 m was significant throughout the 3 year investigation, corresponding with varying hydrologic conditions. In the region of Taylor Slough Bridge, younger groundwater was consistently detected below older groundwater in the Biscayne Aquifer, suggesting preferential flow to the lower part of the aquifer. An increase in ⁴He with depth in the SAS indicated that radiogenic ⁴He produced in the underlying Hawthorn Group migrates into the SAS by diffusion. Higher Δ^4 He values in brackish groundwaters compared to fresh waters from similar depths suggested a possible enhanced vertical transport of ⁴He in the seawater mixing zone. Groundwater salinity measurements indicated the presence of a wide (6-28 km) seawater mixing zone. Comparison of groundwater levels with surface water levels in this zone indicated the potential for brackish groundwater discharge to the overlying Everglades INDEX TERMS: 1829 Hydrology: Groundwater hydrology; 1832 Hydrology: surface water. Groundwater transport; 1040 Geochemistry: Isotopic composition/chemistry; 1890 Hydrology: Wetlands; KEYWORDS: tritium, helium, groundwater, isotopes, Everglades, South Florida

Citation: Price, R. M., Z. Top, J. D. Happell, and P. K. Swart, Use of tritium and helium to define groundwater flow conditions in Everglades National Park, *Water Resour. Res.*, 39(9), 1267, doi:10.1029/2002WR001929, 2003.

1. Introduction

[2] Both tritium and helium isotopes have been used as environmental tracers of groundwater flow in a variety of hydrogeologic settings. The ³H/³He ratio has been used successfully in dating groundwaters less than 50 years old [*Poreda et al.*, 1988; *Schlosser et al.*, 1988; *Ekwurzel et al.*, 1994; *Szabo et al.*, 1996; *Plummer et al.*, 1998b], while ⁴He has been used to quantify groundwater flow rates at both long $(10^4 - 10^8 \text{ yr})$ [*Mazor and Bosch*, 1992] and intermediate (10^2 yr) travel times [*Solomon et al.*, 1996]. These studies focused either on the use of the ³H/³He ratio or on the use of ⁴He in their investigations. Although ⁴He must be measured along with ³He in order to determine the nontritogenic amount of ³He [*Schlosser et al.*, 1998; *Solomon and Cook*, 2000], the concentration of ⁴He tends not to be used in the interpretation of groundwater flow patterns.

Copyright 2003 by the American Geophysical Union. 0043-1397/03/2002WR001929\$09.00

[3] This paper also presents a novel use of ⁴He as a tracer of groundwater flow associated with seawater intrusion into coastal aquifers. Previous studies have used ¹⁴C and temperature as tracers of the seawater intrusion into coastal aquifers [*Back et al.*, 1970; *Kohout*, 1965]. While others have used ²²⁶Ra, ²²²Rn, and CH₄ as tracers of groundwater discharge from coastal aquifers to adjacent marine surface waters [*Moore*, 1996; *Cable et al.*, 1996; *Corbett et al.*, 1999]. The results of the present study suggest that ⁴He can be an additional tool to investigate groundwater flow paths associated with seawater intrusion.

[4] Water flow is an important component of the Everglades ecosystem, and although surface water flow has been extensively monitored within Everglades National Park (ENP), until recently, little attention has been given to understanding groundwater flow. A few studies have focused on groundwater-surface water interactions along canals that border ENP to the east [Genereux and Slater, 1999; Genereux and Guardiario, 1998; Nemeth et al.,

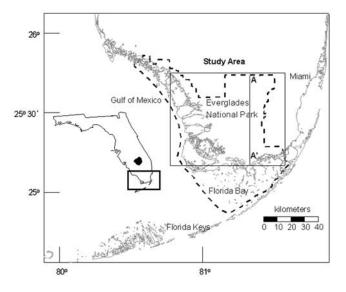


Figure 1. Site map showing boundaries of Everglades National Park and the study area. Line A-A' shown as a cross section in Figure 2.

2000]. Portions of ENP have been included in more regional hydrogeologic studies [Fish and Stewart, 1991; Reese and Cunningham, 2000; Sonntag, 1987]. This is the first widescale study aimed at investigating groundwater flow in ENP. The mainland portion of ENP is extremely flat with elevations ranging from approximately 9 m above sea level along the northern boundary (approximately 70 km inland) to sea level at the coastline. Quantifying water flow components within ENP are difficult due to a low hydraulic gradient (0.00001 to 0.00005) and poorly defined watershed boundaries. Seawater intrusion along the entire coastline of ENP [Fitterman et al., 1999] adds another layer of complexity to understanding the hydrologic system. To overcome the problems associated with the low relief of the region, geochemical tracers (³H, ³He, and ⁴He) were employed to trace water flow indirectly.

2. Hydrogeology

[5] Everglades National Park (ENP) occupies most of the South Florida peninsula and Florida Bay (Figure 1). Groundwater flow in the mainland portion of ENP occurs within the unconfined Surficial Aquifer System (SAS) (Figure 2). The lithologic and hydrologic characterizations of the SAS are described in detail by Fish and Stewart [1991] and Reese and Cunningham [2000]. The SAS consists of Miocene to Holocene age siliciclastic and carbonate sediments and varies in thickness from 50 m to 82 m. It contains two named carbonate aquifers (Gray Limestone Aquifer and Biscayne Aquifer) and two layers of siliciclastic sediments (Figure 2). The Hawthorn Group forms the base of the SAS. The 167 to 243 m thick sequence of low permeable sediments of the Hawthorn Group make it an effective confining unit for the underlying Floridan Aquifer System. In South Florida, the Floridan Aquifer occurs between depths of 250 and 1000 m below the land surface and is artesian with a potentiometric surface of about 12 m above the land surface [Miller, 1986].

[6] The Biscayne Aquifer forms the top of the SAS, and is the principle source of water supply for South Florida. It is one of the most productive aquifers in the world with measured transmissivities in excess of $3.4 \times 10^7 \text{ m}^2 \text{ yr}^{-1}$ and estimated hydraulic conductivity between 1.64×10^6 and 4.45×10^6 m yr⁻¹ [*Fish and Stewart*, 1991]. The Biscayne Aquifer is an unconfined karst aquifer dominantly composed of highly porous units of the Fort Thompson and Miami Limestone Formations with the Key Largo formation interfingering in some areas. Low permeability layers representing sub-aerial exposure surfaces have been identified in the Biscayne Aquifer [Guardiario, 1996; Wilcox, 2000] however their effect on the overall water flow in the Biscayne Aquifer is unclear. The Biscayne Aquifer forms an eastward thickening wedge from a featheredge to over 65 m thick along the southeastern coastline. In many portions of ENP, the Biscayne Aquifer is overlain by marl and peat deposits.

[7] The dominant topographic feature in ENP is an area referred to as the Rocky Glades, which ranges in elevation from 1.5 to 2.5 m. The Rocky Glades is a karst area of pinnacle rock and solution holes and separates the two main waterways, Shark Slough and Taylor Slough (Figure 3). Shark Slough is the larger of the two sloughs (slow moving body of water) and flows southwest toward the Gulf of Mexico. Taylor Slough flows south and discharges into Florida Bay. The Sloughs are dominated by expanses of saw

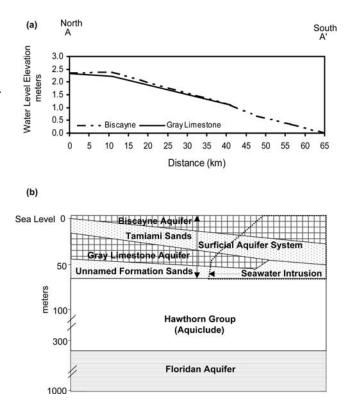


Figure 2. Hydrologic cross sections along line A-A' shown on Figure 1. (a) Average water levels measured in this study of the Biscayne and Gray Limestone Aquifers. (b) Hydrogeologic framework beneath Everglades National Park adapted from *Fish and Stewart* [1991] and *Reese and Cunningham* [2000] showing the approximate extent of seawater intrusion in the SAS.

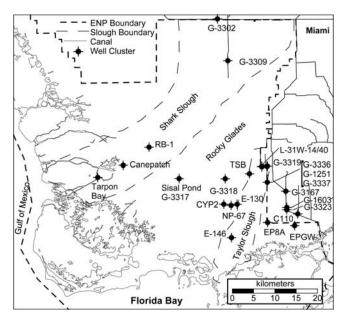


Figure 3. Site map showing sampling locations. Circles with cross represent a cluster of one to four groundwater wells screened within the SAS with depths varying from 1.5 to 53.3 m. The deepest well located at G-3319 is finished at the top of the Hawthorn Group at a depth of 73 m.

grass marshes and tree islands in what was called "The River of Grass". The boundaries of the Sloughs are poorly defined and vary in lateral extent with water level conditions. During high water level conditions, water levels rise above the land surface in the Rocky Glades thereby obscuring the boundaries between Shark Slough and Taylor Slough.

[8] South Florida experiences a subtropical monsoontype climate, with most rainfall occurring in the summer months from mid-May through mid-October. Water levels within ENP vary seasonally with the highest water levels typically recorded in September during the wet season, and the lowest water levels recorded in April near the end of the dry season. The total difference in the seasonal water level varies between 0.1 and 1.5 m [*Fish and Stewart*, 1991]. Water flows mainly toward the south (Figure 4). Groundwater and surface water levels are hydraulically connected and often equate.

[9] Seawater intrusion into the Biscayne Aquifer in eastern and south Dade was first documented in 1940 by Parker et al. [1955]. The onset of seawater intrusion was attributed to lowering of groundwater levels in the Biscayne Aquifer as a result of construction of an extensive system of canals in the 1920s and 1930s designed to drain surface water from Lake Okeechobee and the Everglades to the ocean. Construction of additional canals combined with periodic drought conditions resulted in increasing the extent of seawater intrusion from 1940 to 1990 [Parker et al., 1955; Klein and Waller, 1985; Sonenshein and Koszalka, 1996]. Sonenshein [1997] has documented no significant increase in seawater intrusion in the Biscayne Aquifer in South Dade between 1990 and 1995. More recently, Fitterman et al. [1999] has documented through a series of aerial resistivity surveys that seawater intrudes 10

to 20 km inland into the Biscayne Aquifer along the entire coastline of ENP.

3. Methods

3.1. Sampling and Analysis

[10] Samples for this study were collected over a period of 3 years: (1) between 25 August and 2 October 1997, (2) 15–28 July 1998, and (3) 11–24 June 1999. The 1997 sampling event occurred late in the wet season (between August and October), after the water levels were high for some time (since June). The July 1998 sampling event was preceded by higher than average water levels during the dry

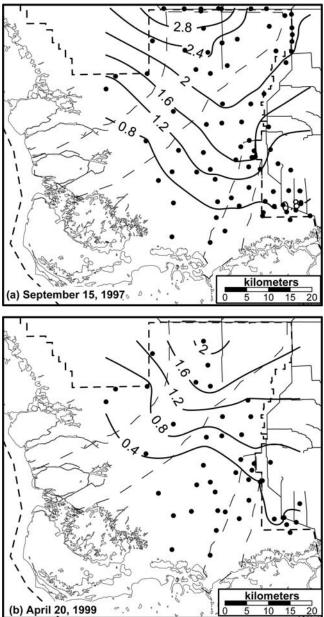


Figure 4. Potentiometric contours in meters measured in Everglades National park during the (a) wet season and (b) dry season. Circles represent water level monitoring stations monitored by ENP and the USGS. Data provided courtesy of ENP and USGS.

season months as a result of a strong El Niño. The June 1999 sampling occurred following the lowest water levels of the 3-year period.

[11] A total of 47 groundwater wells were sampled (Figure 2), although not all wells were sampled at each sampling event [Price, 2001]. The wells sampled in this investigation were organized in clusters of 1 to 4 wells with finished depths ranging from 2 m to 73 m. Most of the wells were screened within the SAS, with the deepest well (73 m) screened at the top of the Hawthorn Group. Prior to sampling, each well was purged of at least three well volumes with a gas-powered pump. Samples were collected using either a submersible pump equipped with Teflon lined polyethylene tubing or a peristaltic pump equipped with Viton tubing. Samples for noble gases were collected in copper tubes fitted with clamps in the field to prevent contact with the atmosphere. Tritium samples were collected in 1-Liter amber glass bottles that were pre-filled with dry argon or nitrogen gas. Temperature, specific conductance and salinity of groundwater and determined at the time of sampling with an Orion S/C/T meter.

[12] Groundwater samples were also collected for determinations for CFC-11 and CFC-12. Age dating obtained from the CFC results was in poor agreement with the ³H/³He ages and suggested that the CFCs may not be conserved in the Everglades environment [*Happell et al.*, 2003; *Price*, 2001]. Tritium was determined either by electrolytic enrichment followed by gas proportional counting, or by mass-spectrometric helium ingrowth method [*Clarke et al.*, 1976]. Helium isotopes were measured in a MAP 215-50 noble gas mass-spectrometer. Neon was measured on an Ametek 100 quadrupole gas analyzer.

3.2. Age Determinations

[13] The ages of the groundwaters were determined according to established ³H/³He techniques [Schlosser et al., 1998; Solomon and Cook, 2000]. In this investigation, the mantle-derived sources of helium were assumed to be insignificant. The assumption is valid given that the Florida Platform is not a tectonically active region. Lithium containing minerals that could be a source for in situ ³He and tritium are most common in granitic and other igneous rocks [Mamyrin and Tolstikhin, 1984] and not present within the upper 5 km of the Florida Platform sediments. Therefore nucleogenic sources of ³He were also considered insignificant, and the observed ³He/⁴He ratios supported this assumption. The ${}^{3}\text{He}/{}^{4}\text{He}$ ratios varied from 0.38×10^{-6} to 1.91×10^{-6} , values which were much larger than the typical crustal ³He/⁴He ratio of 2×10^{-8} [*Mamyrin and* Tolstikhin, 1984]. One method of correcting for the nucleogenic sources of ³He is by the relationship of ³He_{nuc} = ${}^{4}\text{He}_{rad} \cdot R_{rad}$, where ${}^{3}\text{He}_{nuc}$ refers to the nucleogenic sources of ³He, ⁴He_{rad} refers to the radiogenic sources of ⁴He_{rad} and R_{rad} is the crustal ${}^{3}\text{He}/{}^{4}\text{He}$ ratio of 2 \times 10⁻⁸ [Schlosser et al., 1989]. Large ⁴He excesses between 100% and 550% were measured in this investigation. The largest result of ³He_{nuc} using the above equation was 4.5×10^{-15} which is about 7% in excess of solubility. A 10% excess of ³He due to a nucleogenic component would translate to 0.8 to 1.7 year effect on the ${}^{3}\text{H}/{}^{3}\text{He}$ age estimate. This effect was within the analytical uncertainty of 0.5 to 2 years.

[14] Dissolved neon concentrations were used to correct for any excess air that could result from air bubbles trapped

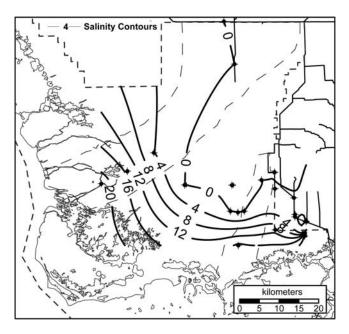


Figure 5. Salinity contours of shallow groundwater (<28 m), indicating that the extent of seawater intrusion in the shallow portion of the SAS ranges from 6 m in the eastern panhandle region to 28 m in Shark Slough.

within the aquifer or introduced during sampling. The atmosphere was considered the sole source of dissolved neon. Neon concentrations measured in the present study varied within 0 to 30% of saturation, with a few samples as high as 70%. The correction using neon may be made by (1) the total dissolution model, in which the trapped air bubbles were assumed to dissolve entirely [Aeschbach-Hertig et al., 1999], (2) the partial diffusive re-equilibration model, in which a fraction of the bubble was assumed to dissolve [Stute et al., 1995], or (3) the constant hydrostatic model, in which solubility was attained in a closed system of initially air saturated water and finite volume of entrapped air under a constant hydrostatic pressure [Aeschbach-Hertig et al., 2000]. Among these the total dissolution model fit best the observed Ne/He ratios, and was used to correct for the helium concentrations.

[15] In order to calculate the solubility of helium, the temperature of the recharge water must be known. While the recharge temperature could be determined from the noble gas concentrations, this process required the measurements of at least four gases [Stute et al., 1995; Wilson and McNeill, 1997]. This arose from the need to resolve solubility from excess air components and the degree of fractionation of the excess air. In addition, helium could not be used as one because of its radiogenic source in SAS groundwaters. As the complete suite of noble gases was not measured in this study, the following means were used. Some studies indicate that recharge temperature was similar to the mean annual air temperature, particularly in areas of deep unsaturated zones [Mazor, 1972; Busenberg and Plummer, 1992]. In Miami, the mean annual air temperature was 24.4 °C. A deep unsaturated zone was not present throughout much of the SAS in ENP, and oxygen and hydrogen stable isotope data suggest that most shallow groundwater

in ENP was recharged by the overlying surface water [*Price*, 2001]. A recharge temperature of 26°C was used for this study as it represented the average air, surface water, and shallow groundwater temperatures measured in the area. Changing the recharge temperature by 2°C resulted in a 1 to 2.5 year change in the ³H/³He age, on the order of the analytical uncertainties.

3.3. Water Levels

[16] The depth to the top of the groundwater was determined in each well using a Solinst depth-to-water meter. Groundwater level was compared to the level of surface water outside of the well casing if present. Water levels measured in wells completed within the seawater mixing zone were converted to equivalent freshwater heads (h_f) using the relationship $h_f = (\rho_s/\rho_f)h_s$, where h_s is the measured length of the saltwater column in the well casing

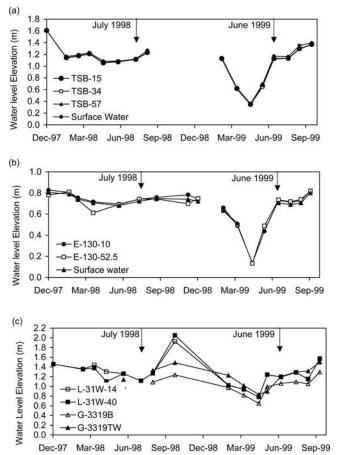
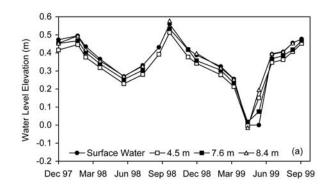


Figure 6. Water levels in well clusters (a) TSB, (b) E-130, and (c) G-3319 and L-31W. Dates depicted by the arrows correspond to the times of groundwater sampling. Groundwater levels often equate with surface water levels at sites TSB and E-130 (a and b) confirming their hydraulic connection. Water levels in the deepest well often are higher than nearby shallower wells (c) confirming the potential for upward groundwater flow from the Hawthorn Group to the SAS. Well depths are TSB-15 (4.6 m); TSB-34 (10.3 m); TSB-57 (17.3 m); E130-10 (3.0 m); E130-52.5 (16 m); L-31W-14 (4.3 m); L31W-40 (13.4 m); G3319B (23.5 m); G3319TW (68 m).



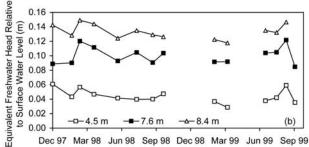


Figure 7. (a) Measured water levels of surface water and groundwater at E-146 and (b) water levels in the same wells corrected for equivalent freshwater heads and compared to the surface water level confirm the potential for brackish groundwater discharge to the surface water of the southern ENP.

above the top of the screen interval, and ρ_s and ρ_f are the densities of the saltwater and freshwater, respectively. Both ρ_s and ρ_f were determined for the groundwater and surface water, respectively, from the field measured values of salinity and temperature according to *Fofonoff and Millard* [1983].

4. Results and Discussion

4.1. Seawater Intrusion

[17] The salinity of groundwaters sampled in this investigation indicates the presence of a wide seawater mixing zone in the SAS (Figure 5). In the shallow portion of the SAS (0 to 28 m), brackish groundwater with salinities of 0.7 to 24 is detected inland of the coastline at distances of 28 km in Shark Slough, 10 to 14 km in Taylor Slough and 6 to 10 km in the C-111 basin. At depths greater than 28 m, brackish groundwater with salinities of 1.4 to 3.5 is detected further inland at distances of up to 20 km in Taylor Slough, and 28 to 30 km in Shark Slough and the C-111 basin. The results on Figure 5 are similar to those reported by Fitterman et al. [1999], who used detailed Time domain Electromagnetic Soundings to define the lateral extent of seawater intrusion in the Biscayne Aquifer. Unlike the results of Fitterman et al. [1999], who reported a near sharp seawater interface, particularly in the region of Taylor Slough, salinity values measured in this investigation suggest a wide mixing zone ranging in width from 6 to 30 km. Since the salinity of the groundwaters sampled in

this investigation do not approach those of seawater, then the exact width of the seawater mixing zone can not be ascertained.

4.2. Water Levels

[18] Shallow groundwater levels equate to surface water levels in many areas of ENP, confirming their hydraulic connection (Figures 6a and 6b). Furthermore, there is little or no measurable difference in groundwater levels between adjacent wells completed in the Miami Limestone and underlying Fort Thompson Formations of the Biscayne Aquifer (Figure 6b). These results are similar to those observed by [Guardiario, 1996]. Despite the presence of a low permeable layer between the formations, the extremely low hydraulic gradient and fast horizontal groundwater flow rates $(500-1200 \text{ m yr}^{-1} [Price, 2001])$ most likely make it difficult to measure differences in the water levels between the two formations. During the present study, groundwater levels are at their highest in December 1997 and in September 1999, and at their lowest in April 1999. Water levels are relatively high between December 1997 and March 1998 during what are typically dry season months, due to excess rainfall associated with a strong El Niño.

[19] A potential for upward groundwater flow is observed between the deepest well completed in the Hawthorn Group and its neighboring shallow wells (Figure 6c). These findings are consistent with *Reese and Cunningham* [2000] whom report that the upper units of the Hawthorn Group are semiconfining to confining. The

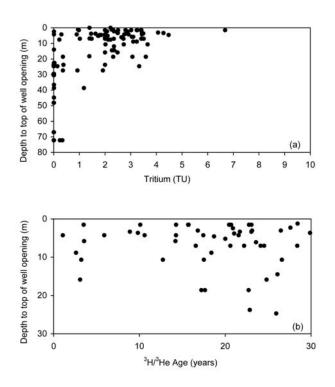


Figure 8. (a) Tritium concentrations (TU) in groundwaters with sampling depth. (b) The ${}^{3}\text{H}/{}^{3}\text{He}$ age (years) of groundwaters with sampling depth in the upper 28 m of the SAS.

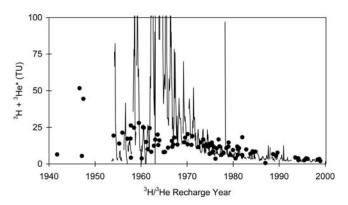


Figure 9. The sum of ³H and radiogenic ³He in groundwaters samples as a function of recharge year. Line represents the tritium concentrations measured in Miami rainfall from 1964 through 1999 and scaled from Ottawa data from 1954 to 1963. Recharge year of groundwaters prior to 1950 is not representative of actual recharge year but is an artifact of mixing. Groundwater recharge years match the tritium in rainfall line between 1970 and 1999. Groundwaters determined to be recharged prior to 1970 do not match the rainfall line most likely due to dispersion and mixing processes.

potential for upward groundwater flow is also observed at all well clusters located within the seawater mixing zone (Figures 7a and 7b).

4.3. ${}^{3}\text{H}/{}^{3}\text{He}$

[20] Tritium concentrations in the groundwater samples varied from <0.01 TU (1 TU = $1 {}^{3}$ H/10¹⁸¹H) to about 4 TU (Figure 8a). In one well 6 TU was encountered, however, this result was not replicated in later samplings. Tritium concentrations greater than 1 TU were concentrated in the upper 28 m of the SAS. Below a depth of 38 m tritium concentrations were less than 1 TU.

[21] Groundwater ages determined by the ³H/³He dating technique are considered apparent ages, which are not necessarily the true age of the groundwater. Uncertainty in the groundwater ages stems from a number of factors including a lack of helium confinement, mixing of waters of different ages as well as dispersive processes. A loss of ³He across the water table can result in an underestimation of the true groundwater age, and is most significant in areas with low infiltration rates [Schlosser et al., 1988, 1989]. Although not quantified in this investigation, infiltration of recharge water to the groundwater table is expected to be relatively fast through the karst Biscayne Aquifer. Furthermore, throughout many areas of the Everglades the aquifer is recharged by overlying surface water, the presence of which is expected to provide an added barrier against the loss of ³He from across the groundwater table.

[22] Hydrodynamic dispersion increases the uncertainty in ${}^{3}H/{}^{3}He$ ages, particularly during the 1960s when the tritium concentration in the atmosphere and subsequently rainfall was relatively high [Solomon and Sudicky, 1991; *Plummer et al.*, 1993]. Dispersion of high tritium concentrations associated with the tritium bomb peak in 1963 into older groundwaters would result in an underestimation in the age of the pre-1963 groundwater. The reverse occurs for waters recharged after 1964.

[23] Finally, mixing of waters of different ages can produce a variety of effects on the ³H/³He age of the groundwater. Mixing of young groundwater containing detectable concentrations of ³H and ³He with older groundwater that contains undetectable concentrations of these constituents results in a ³H/³He groundwater age of the mixture equal to the age of the young groundwater component, regardless of the proportions of each water mass in the mixture. To illustrate the effect of mixing one can consider the extreme case of equal mixing of newly recharged water (zero age) with pre-nuclear era (zero tritium) water. Apparent tritium concentration would be half of the rain and yet the age equation would yield zero age. However a case like this is readily distinguishable by a ⁴He concentration of the mixture that is significantly elevated (>10%) above atmospheric equilibrium. Mixing of two post-1960 water samples of different ages results in an ${}^{3}\hat{H}/{}^{3}He$ age in-between the ages of the two end-members. In this investigation, mixing of groundwaters with different ages is expected in wells completed within the seawater mixing zone.

[24] The consistency of the estimated apparent ${}^{3}\text{H}/{}^{3}\text{He}$ ages was checked against the rain tritium history. The procedure consists of summing the observed ³H and tritiogenic ³He for each sample, in tritium units, and plotting these against the recharge year (observation year minus the ${}^{3}\text{H}/{}^{3}\text{He}$ age). The results are then compared with the rain tritium history. Rain tritium record exists for Miami since 1964. The longest running record is for Ottawa, and this can be scaled for Miami to extend the Miami rain tritium record back to 1954. The comparison shown in Figure 9 indicates a reasonable agreement between estimated tritium in the recharge rain and actual rain measurements (except for four samples) between 1970 and 1999. However, for groundwaters recharged prior to 1970, the estimated tritium recharge values are lower than the observed rain values. This discrepancy in groundwater older than 30y is commonly reported by others using the tritium-helium technique [Ekwurzel et al., 1994; Dunkel et al., 1993; Shapiro et al., 1998] and is attributed to dispersion of the 1963 tritium over time, as well as mixing of waters with different ages.

[25] Low levels of tritium prevented reliable age dating for most of the groundwater samples below 28 m. Above 28 m, 3 H/ 3 He ages of the groundwaters ranged from near zero to 30 years with no discernable trend in 3 H/ 3 He age with depth. The lack of a discernable trend with depth may be related to the large vertical distance between the wells sampled in this investigation. The use of closely spaced (1.5 to 2.0 m), multilevel monitoring wells has proven useful in other studies for identifying a relationship of increasing groundwater age with depth, particularly in well-characterized recharge zones [*Schlosser et al.*, 1988, 1989]. Characterizing the hydrologic conditions over an area as wide as ENP required the use of available wells with vertical distances between wells in a single cluster varying between 2.5 to over 20 m.

[26] The future use of ³H/³He age dating is moving toward complex hydrologic conditions with pre-existing wells [*Plummer et al.*, 1998b]. Although the sampling and results of such investigations may not be ideal for determination of groundwater flow paths and rates, useful hydrologic information can still be obtained. For instance, the results of this investigation indicate that the upper 28 m of

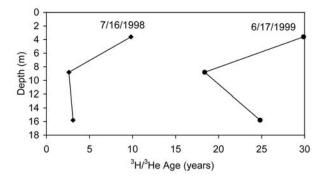


Figure 10. The ${}^{3}\text{H}/{}^{3}\text{He}$ age (years) of groundwater with sampling depth at Taylor Slough Bridge for samples collected in July 1998 and June 1999. The consistent decrease in ${}^{3}\text{H}/{}^{3}\text{He}$ age of the groundwater between the shallow and intermediate wells indicate a preferential flow path to the intermediate well. The large variability in groundwater ages obtained between the 1998 and 1999 sampling events suggest varying hydrologic conditions.

the Surficial Aquifer System has groundwater ages of 30 years or less. This is important in terms of understanding the susceptibility of this aquifer to contamination from anthropogenic sources. The lack of detectable tritium at depths greater than 38 m in the Surficial Aquifer System indicates that the deeper groundwater has not received inputs of groundwater younger than 60 years old. Knowledge of longer travel times within the Gray Limestone Aquifer and the underlying sands may make these units a valuable alternate water supply for South Florida if the upper units were to become contaminated.

[27] The 28 to 38 m depths of detectable tritium concentrations in the groundwater may be representative of a hydrologic barrier to vertical flow. The upper 28 m to 38 m of the Surficial Aquifer System beneath ENP consists of the Biscayne Aquifer and the Tamiami Sands. The karst nature of the Biscayne Aquifer most likely allows for rapid vertical infiltration of groundwater through sinkholes and other conduits. Units of the Tamiami Sands are reported to have hydraulic conductivities that are one to two orders of magnitude less than the overlying Biscayne Aquifer [*Fish and Stewart*, 1991].

[28] Alternatively, the 28 to 38 m depth of detectable tritium in groundwater may represent an average 30-year penetration depth for an unconfined aquifer. This depth and age range for the surficial aquifer system that is a combination of karst and siliciclastic sediments is very similar to other studies using ³H/³He age dating of groundwater in unconfined aquifers in a variety of geologic settings. For instance, in the Coastal Plain sediments of New Jersey, Szabo et al. [1996] determined ³H/³He groundwater ages between 30 and 40 years for wells screened between 24 and 26 m below the water table. While Ekwurzel et al. [1994] obtained a ³H/³He age of 20.9 years for a groundwater sample from a depth of 31.1 m in the Coastal Plain of the Delmarva Peninsula. This depth compares with results reported by Schlosser et al. [1998, 1989] for an unconfined sand aguifer in Germany in which detectable tritium concentrations decrease significantly between depths of 30 and 40 m. In addition, [*Shapiro et al.*, 1998] report 3 H/ 3 He groundwater ages between 10 and 40 years to a depth of 40 m in a glacial fill valley in Ohio. Conversely, *Plummer et al.* [1998a, 1998b] detected relatively young groundwater between the ages of 20 and 35 years in deep wells screened between 50 to 100 m in a confined portion of the Upper Floridan Aquifer in Georgia and concluded that the young water was penetrating to deeper depths via sink holes.

[29] In this investigation, there was considerable interannual variability in groundwater ages of wells sampled in successive years. For instance, the ³H/³He age of groundwater from CYP2-10 varied from 3 years in 1997 to 0 years in 1998 and then 15 years in 1999. In many of the shallow, fresh groundwater wells there was an increase in ${}^{3}\text{H}/{}^{3}\text{He}$ age of groundwater, between 5 to 21 years, from the July 1998 to the June 1999 sampling (Figure 10). This large inter-annual variation in ³H/³He age suggested varying hydrologic conditions within the 11 months of sampling. Water level elevations measured throughout ENP during the July 1998 and June 1999 sampling events were similar and considered moderately high (Figures 6a and 6b). In addition, hydrologic gradients in Taylor Slough between sites TSB and E-130 were similar for both sampling periods (0.000051 and 0.000059). What varied between the sampling periods were the antecedent water level conditions (Figures 6a and 6b). For the three months prior to the July 1998 sampling, water level elevations across ENP were unseasonably high due to excess rainfall associated with the El Niño. Conversely, during the three months prior to the June 1999 sampling, water level elevations were at their lowest, typical for the end of the dry season. During this time, groundwater levels dropped to below the ground surface in many regions of ENP, resulting in the absence of surface water. Stable isotopes of oxygen and hydrogen suggest that both rainfall and surface water recharge the shallow (<28 m) groundwater flow system of the SAS [Price, 2001]. For the months prior to the July 1998 sampling, there was significant rainfall and surface water available for recharge producing the younger observed ³H/³He ages. A lack of groundwater recharge during the dry season of 1999 resulted in older groundwater reaching the wells.

[30] A comparison of potentiometric maps between high water level and low water level conditions provides further evidence of the varying hydrologic conditions (Figures 4a and 4b) particularly in the region of Taylor Slough. During high water level conditions the dominant direction of groundwater flow in Taylor Slough is southeast. Alternatively, during low water table conditions, the direction of flow in Taylor Slough is southwest. Artificially elevated water levels in the canals that border ENP to the east may be responsible for the southwesterly flow in Taylor Slough during the dry season.

[31] Exceptions to the above mentioned trend include wells located next to canals in the C-111 basin (G-1251, G-3336, and G-3323A). In these wells, the groundwater age decreases by 4 to 15 years between the July 1998 and July 1999 sampling events. A hydraulic connection between the canals and the Biscayne Aquifer has been documented, with a dominant recharge of canal water to the aquifer during the dry season [*Genereux and Slater*, 1999]. Recharge of the

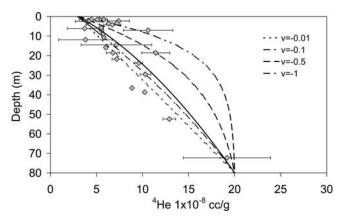


Figure 11. Mean ⁴He concentrations in fresh groundwaters with sampling depth. Error bars represent ± 1 standard error. Solid line is the best fit second order polynomial of the data. Dashed lines are modeled ⁴He concentration profiles for varying vertical velocities (mm y⁻¹) as determined by equation (2), assuming a constant porosity of 0.3. Modeled velocities shown in the figure legend are negative in the upward direction and range from -0.01 to -1 mm y⁻¹.

aquifer by water in the canals during the dry season of 1999 is most likely responsible for producing the younger ${}^{3}\text{H}/{}^{3}\text{He}$ ages observed in these wells in June 1999.

[32] Using the stable oxygen and hydrogen isotopic composition of groundwaters, *Meyers et al.* [1993] suggested a rapid flushing of the upper 20 m of the SAS, on the order of 90 days. This short time cycle is consistent with changes in water levels and the direction of the hydraulic gradient observed in this investigation (Figures 7 and 8). The youngest groundwater ages obtained in this study are near zero and 2.4 yr. With uncertainties in the age calculations of 0.5 to 2 years, these young ages are consistent with a residence time of less than a year. However, the average ³H/³He groundwater age for the upper 28 m is 17 ± 9 years, suggesting that most of the shallow groundwater has a residence time significantly greater than the 90 days.

[33] In the well cluster at Taylor Slough Bridge (TSB), the groundwater age consistently decreases with depth between 3.6 m and 8.8 m (Figure 10), suggesting a faster flow path to the deeper well. The shallow well is completed within the Miami Limestone, while the deeper well is completed within the Fort Thompson formation, below the low permeable layer that separates these two formations. The Biscayne aquifer is a karst aquifer with numerous solution holes that are not only observed at the ground surface but at depth from geophysical surveys [Cunningham and Aviantara, 2001] and from sudden drops in drill rods [Wilcox, 2000]. Solutions holes can provide a fast route for surface water and rainwater to recharge the aquifer. In one nearby study, stable isotope data were used to identify fast groundwater recharge (one to three days following a major rainfall event) from the ground surface to a well completed in a cavern near the bottom of the Biscayne Aquifer [Wilcox, 2000]. Similarly fast groundwater recharge into the Fort Thompson via vertical solution holes combined with separation from the overlying Miami Limestone by the

(a) 0

(≟ 30 40

10

20 30

low permeable layer can adequately explain the differences in the ${}^{3}\text{H}/{}^{3}\text{He}$ ages between wells TSB-15 and TSB-34.

4.4. ⁴He

[34] A comparison of the concentrations of neon with ⁴He suggests that most of the observed ⁴He is of radiogenic origin, with an excess air fraction less than 10% in most of the samples. Air corrected ⁴He excess (Δ^4 He%) is the amount above solubility equilibrium at the temperature of recharge and is $({}^{4}\text{He}_{conr}/{}^{4}\text{He}_{eq} -1) \times 100$. Values of $\Delta^{4}\text{He}$ range from -1.05 to 550%. The common trend for radiogenic ⁴He is increasing concentration with depth in a given aquifer [Shapiro et al., 1998; Solomon et al., 1996; Stute et al., 1992]. Accordingly, ⁴He increases with depth in the fresh groundwater samples collected in ENP, with the highest levels in the deepest well (Figure 11). The Δ^4 He values in this well ranged from 140.2 to 549.5%. This deep well is completed in Miocene age units at the top of the Hawthorn Group that contain up to 40 percent phosphorite grains [Reese and Cunningham, 2000]. Phosphorites in Florida typically contain between 0.012 and 0.015% uranium [Sweeney and Windham, 1979]. Over the time period of the Miocene, from 5 and 25 Ma, it is estimated that 2.8×10^{-5} cm³ STP g⁻¹ to 1.7×10^{-4} cm³ STP g^{-1} of ⁴He would be produced from the radioactive decay of U alone. These estimates are two to three orders of magnitude greater than the highest observed ⁴He concentration (2.2×10^{-7} cm³ g⁻¹), and suggest that an upward flux of ⁴He from the Hawthorn Group could be the source of ⁴He observed in the SAS.

[35] Water levels in the Hawthorn Group well were often higher than those measured in nearby wells completed at shallower depths in the SAS (Figure 6c), suggesting the potential for upward flow from the Hawthorn Formation to the SAS. To test this hypothesis, the observed distribution of ⁴He within the freshwater portion of the SAS was modeled using a one-dimensional, steady state advectiondiffusion equation:

$$De\frac{\partial^2 C}{\partial z^2} - V\frac{\partial C}{\partial z} = 0, \qquad (1)$$

where, *C* is the concentration of ⁴He in the groundwater as a function of depth (*z*), *V* is the vertical groundwater flow velocity, and D_e is the vertical diffusion coefficient. Two boundary conditions were applied to the model. At the top of the aquifer, $C = C_0$ and z = 0, and at the bottom of the aquifer, $z = z_1$ (80 m) and $C = C_1$. The concentrations of ⁴He at the top (C_0) and bottom (C_1) of the aquifer were determined as 3×10^{-8} cc/g and 20×10^{-8} cc/g, respectively, based upon the best fit of the data using the parabolic function: ⁴He (1×10^{-8} cc/g) = $0.0015z^2 + 0.0767z + 5.5389$ (R² = 0.76). In this model, the direction of z was considered positive downward from the top of the aquifer so that groundwater velocities (*V*) directed upward were negative. Based upon these boundary conditions, the solution to equation (1) is:

$$C = [(C_1 - C_0 e^P) + (C_0 - C_1) e^{\left(\frac{Pz}{z_1}\right)}] / (1 - e^P), \qquad (2)$$

where P is analogous to the dimensionless Peclet number defined by $P = Vz_I/D_e$. For a complete description of

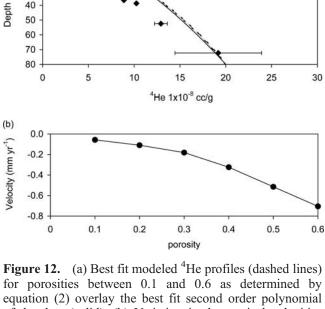


Figure 12. (a) Best fit modeled 'He profiles (dashed lines) for porosities between 0.1 and 0.6 as determined by equation (2) overlay the best fit second order polynomial of the data (solid). (b) Variation in the vertical velocities (mm y^{-1}) of groundwater flow with porosity as determined by the best fit lines shown in Figure 12a vary between -0.02 and -0.7 mm y^{-1} .

derivation of equation (2), see Stephenson et al. [1994]. The term D_e describes the effected diffusion coefficient in the aquifer and is defined as $De = Dn^2$ [Cornett et al., 1989], where D is the diffusion coefficient of He in water at 25° C $(7.22 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ [Jähne et al., 1987]})$ and n was the porosity of the SAS. The relationship of P in terms of De is valid for small values of P(<1) where chemical transport is transverse to the dominant direction of groundwater flow and is diffusion dominated [Fetter, 1999]. This assumption is considered valid for this effort since the vertical transport of ⁴He is modeled in a groundwater flow system dominated by horizontal flow. Porosity values for the SAS vary from 0.2 to 0.55 [Schmoker and Halley, 1982]. In this model, both vertical groundwater velocity and diffusion were considered to be uniform throughout the thickness of the aquifer. There are two unknowns in equation (2), P and V, therefore the model was solved iteratively, making first an assumption of V and then solving for P until there was a close fit of the model to the observed data. Modeled ⁴He concentration profiles are compared to the observed ⁴He concentrations with depth in the SAS for an intermediate porosity value of 0.3 and variable velocities (Figure 11). A best fit of the model for porosities between 0.1 and 0.6 result in vertical groundwater flow velocities between 0.02 and 0.7 mm yr⁻¹ (Figures 12a and 12b). The resultant P numbers were less than 1 and varied from 0.8 to 0.97. The low velocities and corresponding low P numbers suggest that the transport of ⁴He from the Hawthorn Group through the freshwater portion of the SAS is dominated by diffusive processes.

[36] In brackish samples, mean values of Δ^4 He are often higher than freshwater samples collected from similar

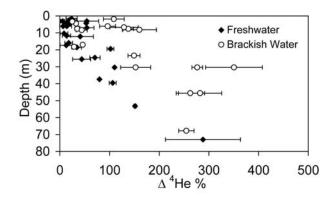


Figure 13. Mean ⁴He excess (%) of brackish groundwaters is often higher than fresh groundwaters collected from a similar depth. Error bars represent ± 1 standard error.

depths by as much as 240%, but typically between 40 and 150% (Figure 13). There are several potential mechanisms that can produce the high Δ^4 He values in the brackish groundwater samples. These include, but are not limited to, the potential for higher vertical velocities in the seawater mixing zone or enhanced calcium carbonate dissolution in the seawater mixing zone. Vertical velocities in the seawater mixing zone may be higher than those estimated in the freshwater area, and may be advection dominated. A series of benchmark papers [Cooper, 1959; Kohout, 1960, 1964] clearly illustrated the dynamics of seawater intrusion into the Biscayne Aquifer along the Atlantic Coastline of South Florida. The dynamics of groundwater flow associated with seawater intrusion can be used to explain the high Δ^4 He values observed in the brackish samples (Figure 14). As both fresh groundwater and intruding seawater flow along the bottom of the SAS, they entrain high concentrations of ⁴He found there due to diffusive upward fluxes from the Hawthorn Group. Where the two water types meet the dominant direction of groundwater flow is vertically upward, transporting the ⁴He toward the surface of the SAS most likely at a rate faster than the diffusive transport rate calculated in the freshwater portion of the aquifer. Measured water levels in well clusters located within the seawater mixing zone indicate the potential for groundwater discharge (Figure 7b).

[37] If brackish groundwater were discharging to the overlying surface water, then elevated concentrations of ⁴He would be expected in the surface water. Helium isotopes were not measured in the surface water in this investigation; however, Top et al. [2001] identified high levels of Δ^4 He in surface water along the northern coastline of Florida Bay. Their results, combined with the landward extent of shallow seawater intrusion observed in this study, suggest that brackish groundwater maybe discharging along a 6 to 28 km wide strip that parallels the coastline of ENP. This distance is comparable to the 20 km strip representative of the inner shelf off of the South Atlantic Bight where Moore [1996] attributed high concentrations of ²²⁶Ra to submarine groundwater discharge. The groundwater discharging along this zone is expected to be brackish along the inland side of the strip and become progressively more saline toward the coastline and into Florida Bay and the Gulf of Mexico. The dynamics of seawater intrusion may also explain the elevated concentrations of ²²²Rn observed in Florida Bay [*Corbett et al.*, 1999].

[38] Another potential mechanism for the observed elevated concentrations of ⁴He in the brackish groundwaters is carbonate mineral dissolution. The mixing of freshwater and seawater in carbonate aquifers has been hypothesized to enhance carbonate mineral reactions, in particular calcite dissolution and aragonite neomorphism [Plummer, 1975; Back et al., 1979, 1986]. Dissolution of uranium containing carbonate minerals would result in a release of trapped ⁴He to the surrounding groundwater. Linear regression analysis resulted in an insignificant correlation between ⁴He and salinity (slope = 0.0221; R² = 0.0006). However, the mixing of calcite saturated freshwater with calcite supersaturated seawater produces a nonlinear relationship in the saturation index of calcite [Plummer, 1975]. The two dominant carbonate units in the SAS include the shallow Biscayne Aquifer, which is Pleistocene to Holocene in age, and the Pliocene age Gray Limestone Aquifer (Figure 2). Assuming an average uranium concentration of 3 ppm as typical of marine carbonates [Milliman, 1974], then the amount of helium produced from these materials assuming a maximum age of 1 My for the Biscayne Aquifer and an average age of 4 My for the Pliocene age Gray Limestone Aquifer would be 3.5×10^{-7} cm³ STP g⁻¹ and 1.4×10^{-6} cm³ STP g⁻¹ of ⁴He per gram of rock for the two aquifers, respectively. These estimates demonstrate the availability of helium in the rock. Relating these figures to expected groundwater concentrations is more complex due to many factors over the geologic history of the rock such as the extent of seawater intrusion, carbonate mineral dissolution rate, and groundwater flow rate. The concentrations of ⁴He measured in groundwaters of the SAS ranged from 0.4×10^{-7} cm³ g^{-1} to 2.2 \times $10^{-7}~cm^3~g^{-1},$ and therefore dissolution of carbonate minerals from within these aquifers, particularly

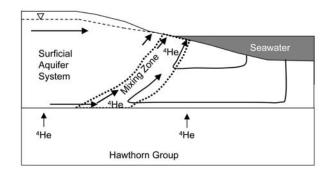


Figure 14. Seawater intrusion into the SAS along the coastline of ENP. Both seawater and the freshwater flowing along the bottom of the aquifer entrain high concentrations of ⁴He that diffuses upward from the Hawthorn Group. Within the mixing zone, the ⁴He is transported upward with the groundwater flow. The landward extent of seawater intrusion, combined with observed high concentrations of ⁴He within surface waters along the northern coastline of Florida Bay [*Top et al.*, 2001] indicate that brackish to saline groundwater discharges to the overlying surface waters of the Everglades and Florida Bay within a 6 to 28 km wide strip that parallels the coastline.

from the Gray Limestone Aquifer, may be an additional source of 4 He to the brackish groundwater of the SAS.

5. Conclusions

[39] Groundwater within the upper 28 m of the SAS in ENP originated within the last 30 yr, and below 28 m before then with evidence of some mixing at the interface. There is considerable inter-annual variability in groundwater ages of wells sampled in successive years, corresponding with varying hydrologic conditions. For instance, ³H/³He ages of groundwater in Taylor Slough tend to be younger following a period of high water level and a dominantly south to southeast flow direction. Significantly older ³H/³He ages of groundwater are observed in Taylor Slough following about 3 months of low water level and a dominantly southwest groundwater flow direction. Near the canals, groundwater ages tend to be younger following the 3 months of low water levels, most likely due a greater contribution of canal water recharging the surrounding aquifer. Young groundwater beneath older age groundwater in a well cluster at the Taylor Slough Bridge indicate the potential for a preferential pathway of groundwater recharge to the lower portion of the Biscayne Aquifer.

[40] Modeling the increase in ⁴He with depth suggests diffusive transport of radiogenic ⁴He from the underlying Hawthorn Group into the SAS. Higher values of Δ^4 He are found in brackish groundwaters compared to fresh waters from similar depths. Potential sources for the elevated ⁴He concentrations in the mixing zone groundwaters include advective vertical transport or enhanced dissolution of carbonate. The results of this investigation suggest that seawater intrusion enhances the vertical transport of ⁴He within the SAS, and that ⁴He may be used as a tracer of groundwater flow associated with seawater intrusion into coastal aquifers.

[41] Acknowledgments. Funding for the project was provided by the South Florida Water Management District with additional assistance from Everglades National Park. We thank Gene Shinn, Christopher Reich and Don Hickey of the USGS for the difficult drilling and installation of groundwater wells in Taylor Slough and Shark Slough, as well as Mike Byrne, Jud Harvey and Bob Mooney for their assistance in the field. We also thank Bob Zepp, James Nelson, and Lucy Given of ENP for providing access to the more remote locations of ENP. Discussions with Bill Nuttle and David Fitterman motivated this research, while James Fourqurean and Neil Plummer provided comments on this manuscript. This is SERC contribution number 203.

References

- Aeschbach-Hertig, W., F. Peeters, U. Beyerle, and R. Kipfer, Interpretation of dissolved atmospheric noble gases in natural waters, *Water Resour*. *Res.*, 35, 2779–2792, 1999.
- Aeschbach-Hertig, W., F. Peeters, U. Beyerle, and R. Kipfer, Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air, *Nature*, 405, 1040–1044, 2000.
- Back, W., B. B. Hanshaw, and M. Rubin, Carbon-14 ages related to occurrence of salt water, *Hydraul. Div. Am. Soc. Civ. Eng.*, 90, 2235–2336, 1970.
- Back, W., B. B. Hanshaw, T. E. Pyle, L. N. Plummer, and A. E. Weidie, Geochemical significance of groundwater discharge and carbonate dissolution to the formation of Caleta Xel Ha, quintana Roo, Mexico, *Water Resour. Res.*, 15, 1521–1535, 1979.
- Back, W., B. B. Hanshaw, J. S. Herman, and J. N. Van Driel, Differential dissolution of a Pleistocene reef in the ground-water mixing zone of coastal Yucatan, Mexico, *Geology*, 14, 137–140, 1986.
- Busenberg, E., and L. N. Plummer, Use of chlorofluoromethanes (CCl₃F and CCl₂F₂) as hydrologic tracers and age-dating tools: The alluvium and terrace system of central Oklahoma, *Water Resour. Res.*, *28*, 2257–2283, 1992.

- Cable, J., G. Bugna, W. Burnett, and J. Chanton, Application of ²²²Rn and CH₄ for assessment of groundwater discharge to the coastal ocean, *Linmol. Oceanogr.*, 41, 1347–1353, 1996.
- Clarke, W. B., W. J. Jenkins, and Z. Top, Determination of tritium by mass spectrometric measurement of ³H, *Int. J. Appl. Radiat. Isot.*, 27, 515–522, 1976.
- Cooper, H. H., Jr., A hypothesis concerning the dynamic balance of fresh water and salt water in a coastal aquifer, J. Geophys. Research, 64, 461– 467, 1959.
- Corbett, D. R., J. Chanton, W. Burnett, K. Dillon, C. Rutkowski, and J. W. Fourqurean, Patterns of groundwater discharge into Florida Bay, *Limnol. Oceanogr.*, 44, 1045–1055, 1999.
- Cornett, R. J., B. A. Risto, and D. R. Lee, Measuring groundwater transport through lake sediments by advection and diffusion, *Water Resour. Res.*, 25, 1815–1823, 1989.
- Cunningham, K. J., and A. Aviantara, Characterization of the karst Biscayne aquifer in southeastern Florida using ground-penetrating radar, digital optical borehole images and cores, Karst Interest Group Proceedings, 134 pp., U.S. Geological Surv., St. Petersburg, Fla., 2001.
- Dunkel, S. A., L. N. Plummer, E. Busenberg, P. J. Phillips, J. M. Denver, P. A. Hamilton, R. L. Michel, and T. B. Coplen, Chlorofluorocarbons (CCl₃F and CCl₂F₂) as dating tools and hydrologic tracers in shallow ground water of the Delmarva Peninsula, Atlantic Coastal Plain, United States, *Water Resour. Res.*, 29, 3837–3860, 1993.
- Ekwurzel, B., P. Schlosser, W. M. Smethie, L. N. Plummer, E. Busenberg, R. L. Michel, R. Weppernig, and M. Stute, Dating of shallow groundwater: Comparison of the transient tracers ³H/³He, chloroflourocarbons, and ⁸⁵Kr, *Water Resour. Res.*, 30, 1693–1708, 1994.
- Fetter, C. W., Contaminant Hydrogeology, 2nd ed., 500 pp., Prentice-Hall, Old Tappan, N. J., 1999.
- Fish, J. E., and M. Stewart, Hydrogeology of the surficial aquifer system, Dade County, Florida, U.S. Geol. Surv. Water Resour. Invest. Rep., 90-4108, 1991.
- Fitterman, D. V., M. Deszcz-Pan, and C. E. Stoddard, Results of timedomain electromagnetic soundings in Everglades National Park, Florida, U.S. Geol. Surv. Open File Rep., 99-426, 1999.
- Fofonoff, N. P., and R. C. Millard Jr., Algorithms for computation of fundamental properties of seawater, *Tech. Pap. Mar. Sci.* 44, 53 pp., United Nations Educ., Sci., and Cultural Organ., Paris, 1983.
- Genereux, D., and J. D. Guardiario, A canal drawdown experiment for determination of aquifer parameters, *J. Hydrol. Eng.*, *3*, 292–302, 1998.
- Genereux, D., and E. Slater, Water exchange between canals and surrounding aquifer and wetlands in the southern Everglades, USA, J. Hydrol., 219, 153–168, 1999.
- Guardiario, J. D. A., Jr., Determination of hydraulic conductivity and dispersivity in the Biscayne Aquifer, Taylor Slough, Everglades National Park, M.S. thesis, Fla. Int. Univ., Miami, Fla., 1996.
- Happell, J. D., R. M. Price, Z. Top, and P. K. Swart, Evidence for the removal of CFC-11, CFC-12, and CFC-113 at the ground water-surface water interface in the Everglades, *J. Hydrol.*, 279, 94–105, 2003.
- Jähne, B., G. Heinz, and W. Dietrich, Measurement of the diffusion coefficients of sparingly soluble gases in water, J. Geophys. Res., 92, 10,767– 10,776, 1987.
- Klein, H., and B. G. Waller, Synopsis of saltwater intrusion in Dade County, Florida, through 1984, U.S. Geol. Surv. Water Resour. Invest. Rep., 85-4101, 1985.
- Kohout, F. A., Cyclic flow of salt water in the Biscayne aquifer of southeastern Florida, J. Geophys. Res, 65, 2133-3141, 1960.
- Kohout, F. A., Flow of freshwater and saltwater in the Biscayne aquifer of the Miami area, Florida, U.S. Geol. Surv. Water Supply Pap., 1613-C, C12-C32, 1964.
- Kohout, F. A., A hypothesis concerning cyclic flow of salt water related to geothermal heating in the Floridan aquifer, *Trans. N. Y. Acad. Sci., Ser. II*, 28, 249–271, 1965.
- Mamyrin, B. A., and I. N. Tolstikhin, *Helium Isotopes in Nature*, Dev. Geochem., vol. 3, 273 pp., Elsevier Sci., New York, 1984.
- Mazor, E., Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in groundwaters: Jordan Rift Valley, Israel, *Geochim. Cosmochim. Acta*, 36, 1321–1336, 1972.
- Mazor, E., and A. Bosch, Helium as a semi-quantitative tool for groundwater dating in the range of 10^4 to 10^8 years, in *Isotopes of Noble Gases as Tracers in Environmental Studies*, pp. 163–178, Int. Atomic Energy Agency, Vienna, 1992.
- Meyers, J. G., P. K. Swart, and J. L. Meyers, Geochemical evidence for groundwater behavior in an unconfined aquifer, south Florida, *J. Hydrol.*, 148, 249–272, 1993.

Miller, J. A., Hydrogeologic framework of the Floridan aquifer system in Florida and parts of Georgia, Alabama and South Carolina, U.S. Geol. Surv. Prof. Pap., 1403-B, 91 pp., 1986.

Milliman, J. D., Marine Carbonates, Recent Sedimentary Carbonates Part 1, 375 pp., Springer-Verlag, New York, 1974.

- Moore, W. S., Large groundwater inputs to coastal waters revealed by ²²⁶Ra enrichments, *Nature*, 380, 612–614, 1996.
- Nemeth, M. S., W. M. Wilcox, and H. M. Solo-Gabriele, Evaluation of the use of transmissivity to quantify leakage beneath levee 31N, Miami-Dade County, Florida, U.S. Geol. Surv. Water Resour. Invest. Rep., 00-4066, 80 pp., 2000.
- Parker, G. G., et al., Water resources of southeastern Florida with special reference to geology and groundwater of the Miami areas, U.S. Geol. Surv. Water Supply Pap., 1255, 965 pp., 1955.
- Plummer, L. N., Mixing of sea water with calcium carbonate ground water, in *Quantitative Studies in the Geological Sciences*, edited by E. H. T. Whitten, *Mem. Geol. Soc. Am.*, 142, 219–238, 1975.
- Plummer, L. N., R. L. Michel, E. M. Thurman, and P. D. Glynn, Environmental tracers for age-dating young ground water, in *Regional Ground-Water Quality*, edited by W. M. Alley, pp. 255–294, Van Nostrand Reinhold, New York, 1993.
- Plummer, L. N., E. Busenberg, J. B. McConnell, S. Drenkard, P. Scholosser, and R. L. Michel, Flow of river water into a karstic limestone aquifer. 1. Tracing the young fraction in groundwater mixtures in the upper Floridan aquifer near Valdosta, Georgia, *Appl. Geochem.*, 8, 995– 1015, 1998a.
- Plummer, L. N., E. Busenberg, S. Drenkard, P. Scholosser, B. Ekwurzel, R. Weppirnig, J. B. McConnell, and R. L. Michel, Flow of river water into a karstic limestone aquifer. 2. Dating the young fraction in groundwater mixtures in the upper Floridan aquifer near Valdosta, Georgia, *Appl. Geochem.*, 8, 1017–1043, 1998b.
- Poreda, R. J., T. E. Cerling, and D. K. Salomon, Tritium and helium isotopes as hydrologic tracers in a shallow unconfined aquifer, *J. Hydrol.*, 103, 1–9, 1988.
- Price, R. M., Geochemical determinations of groundwater flow in Everglades National Park, Ph.D. dissertation, 307 pp., Univ. of Miami, Coral Gables, Fla., 2001.
- Reese, R. S., and K. J. Cunningham, Hydrogeology of the Gray Limestone Aquifer in south Florida, U.S. Geol. Surv. Water Resour. Invest. Rep., 99-4213, 244 pp., 2000.
- Schlosser, P., M. Stute, H. Dörr, C. Sonntag, and K. O. Münnich, Tritium/³He dating of shallow groundwater, *Earth Planet. Sci. Lett.*, 89, 353–362, 1988.
- Schlosser, P., M. Stute, C. Sonntag, and K. O. Münnich, Tritogenic ³He in shallow groundwater, *Earth Planet. Sci. Lett.*, 94, 245–256, 1989.
- Schlosser, P., S. D. Shapiro, M. Stute, W. Aeschbach-Herig, L. N. Plummer, and E. Busenberg, Tritium/³He measurements in young groundwater; chronologies for environmental records, in *Isotope Techniques in the Study of Environmental Change Proceedings*, pp. 165–189, Int. Atomic Energy Agency, Vienna, 1998.
- Schmoker, J. W., and R. B. Halley, Carbonate porosity versus depth: A predictable relation for south Florida, AAPG Bull., 66, 2561–2570, 1982.
- Shapiro, S. D., G. Rowe, P. Schlosser, A. Ludin, and M. Stute, Utilization of the ³H-³He dating technique under complex conditions to evaluated hydraulically stressed areas of a buried-valley aquifer, *Water Resour*. *Res.*, 34, 1165–1180, 1998.

- Solomon, D. K., and P. G. Cook, ³H and ³He, in *Environmental Tracers in Subsurface Hydrology*, edited by P. Cook and A. L. Herczeg, pp. 397–424, Kluwer Acad., Norwell, Mass., 2000.
- Solomon, D. K., and E. A. Sudicky, Tritium and helium 3 isotope ratios for direct estimation of spatial variations in groundwater recharge, *Water Resour. Res.*, 27, 2309–2319, 1991. (Correction, *Water Resour. Res.*, 28, 1197, 1992.)
- Solomon, D. K., H. Hunt, and R. J. Poreda, Source of radiogenic helium 4 in shallow aquifers: Implications for dating young ground-water, *Water Resour. Res.*, 32, 1805–1813, 1996.
- Sonenshein, R. S., Delineation and extent of saltwater intrusion in the Biscayne Aquifer, eastern Dade County, Florida, U.S. Geol. Surv. Water Resour. Invest. Rep., 96-4285, 1997.
- Sonenshein, R. S., and E. J. Koszalka, Trends in water-table altitude (1984–93) and saltwater intrusion (1974–93) in the Biscayne aquifer, Dade County, Florida, U.S. Geol. Surv. Open File Rep., 95-705, 2 sheets, 1996.
- Sonntag, W. H., Chemical characteristics of water in the surficial aquifer system, Dade County, Florida, U.S. Geol. Surv. Water Resour. Invest. Rep., 87-4080, 42 pp., 1987.
- Stephenson, M., W. J. Schwartz, T. W. Melnyk, and M. F. Motycka, Measurement of advective water velocity in lake sediment using natural helium gradients, J. Hydrol., 154, 63–84, 1994.
- Stute, M., C. Sonntag, J. Deak, and P. Schlosser, Helium in deep circulating groundwater in the Great Hungarian Plain: Flow dynamics and crustal and mantel helium fluxes, *Geochim. Cosmochim. Acta*, 56, 2051–2067, 1992.
- Stute, M., M. Forster, H. Frischkorn, A. Serejo, J. F. Clark, P. Sshlosser, W. S. Broecker, and G. Bonani, Cooling of tropical Brazil (5°C) during the Last Glacial Maximum, *Science*, 269, 379–383, 1995.
- Sweeney, J. W., and S. R. Windham, Florida: The new uranium producer, Spec. Publ. Fla. Bur. Geol., 22, 13 pp., 1979.
- Szabo, A., D. E. Rice, L. N. Plummer, E. Busenberg, S. Drenkard, and P. Schlosser, Age dating of ground water using chlorofluorocarbons, tritium/helium 3, and flow path analysis in an unconfined aquifer of the New Jersey coastal plain, *Water Resour. Res.*, 32, 1023–1038, 1996.
- Top, Z., L. W. Brand, R. D. Corbett, W. Burnett, and J. Chanton, Helium and radon as tracers of groundwater input into Florida Bay, J. Coastal Res., 17, 859–868, 2001.
- Wilcox, W. M., A hydrological and stable isotope study of east Everglades National Park and the west well field of Miami-Dade County, Florida, M.S. thesis, 176 pp., Univ. of Miami, Coral Gables, Fla., 2000.
- Wilson, G. B., and G. W. McNeill, Noble gas recharge temperatures and the excess air component, *Appl. Geochem.*, 12, 747–762, 1997.

J. D. Happell and Z. Top, Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA. (jhappell@ rsmas.miami.edu; ztop@rsmas.miami.edu)

R. M. Price, Department of Earth Sciences and Southeast Environmental Research Center, Florida International University, University Park, PC-344, 11200 S.W. 8th Street, Miami, FL 33199, USA. (pricer@fiu.edu)

P. K. Swart, Marine Geology and Geophysics, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA. (pswart@rsmas.miami.edu)