Estuaries and Coasts (2009) 32:694–708
DOI 10.1007/s12237-009-9155-y

Determining Spatial and Temporal Inputs of Freshwater, Including Submarine Groundwater Discharge, to a Subtropical Estuary Using Geochemical Tracers, Biscayne Bay, South Florida

Jeremy C. Stalker · René M. Price · Peter K. Swart

Received: 16 June 2008 / Revised: 16 February 2009 / Accepted: 16 March 2009 / Published online: 30 April 2009

Abstract Geochemical mixing models were used to decipher the dominant source of freshwater (rainfall, canal discharge, or groundwater discharge) to Biscayne Bay, an estuary in south Florida. Discrete samples of precipitation, canal water, groundwater, and bay surface water were collected monthly for 2 years and analyzed for salinity, stable isotopes of oxygen and hydrogen, and Sr^{2+}/Ca^{2+} concentrations. These geochemical tracers were used in three separate mixing models and then combined to trace the magnitude and timing of the freshwater inputs to the estuary. Fresh groundwater had an isotopic signature ($\delta^{18}O$=−2.66‰, δD −7.60‰) similar to rainfall ($\delta^{18}O$= −2.86‰, δD=−4.78‰). Canal water had a heavy isotopic signature ($\delta^{18}O$=−0.46‰, δD=−2.48‰) due to evaporation. This made it possible to use stable isotopes of oxygen and hydrogen to separate canal water from precipitation and groundwater as a source of freshwater into the bay. A second model using Sr^{2+}/Ca^{2+} ratios was developed to discern fresh groundwater inputs from precipitation inputs. Groundwater had a Sr^{2+}/Ca^{2+} ratio of 0.07, while precipitation had a dissimilar ratio of 0.89. When combined, these models showed a freshwater input ratio of canal/precipitation/groundwater of 37%:53%:10% in the wet season and 40%:55%:5% in the dry season with an error of ±25%. For a bay-wide water budget that includes saltwater and freshwater mixing, fresh groundwater accounts for 1–2% of the total fresh and saline water input.

Keywords Groundwater · Isotopes · Trace metals · Geochemistry · Florida · Submarine groundwater discharge

J. C. Stalker (✉) · R. M. Price
Department of Earth Sciences, Florida International University,
PC 344, 11200 SW 8th St,
Miami, FL 33199, USA
e-mail: jstal001@fiu.edu

R. M. Price
Department of Earth Sciences and the Southeast Environmental Research Center, Florida International University,
Miami, USA

P. K. Swart
Division of Marine Geology and Geophysics,
Rosenstiel School of Marine and Atmospheric Sciences,
University of Miami,
Miami, USA

Introduction

The timing and sources of freshwater delivery into an estuarine system affects not only the water quality (Caccia and Boyer 2007; Caccia and Boyer 2005; Younger 1996), but also the health, diversity, and distribution of estuarine species such as seagrasses, juvenile fish, and other benthic organisms (Uchiyama et al. 2000; Rutkowski et al. 1999). Fresh surface water and precipitation are suggested to be the dominant sources of freshwater for most estuarine systems while submarine groundwater discharge (SGD) has largely been ignored due, in part, as a result of the difficulty in quantifying its flux (Slomp and Van Cappellen 2004). Global studies using a variety of methods report a range of SGD from 0.01% to 41% of local surface water inputs or 0.1–10% of total fresh water flux (Taniguchi et al. 2002). Examples from estuaries yield SGD estimates of 10% of total water flux in the Chesapeake Bay (Hussain et al. 1999) and 20% of the total water flux in the Great South Bay of New York (Bokuniewicz 1980). Although SGD input can be small when compared to precipitation or surface water inputs, it cannot be wholly dismissed.

Groundwater generally contains higher concentrations of nutrients, most notably nitrogen and phosphorous, compared to surface water and thus is an important source of chemical constituents to a coastal system (Gonzalez et al. 2007; Kroger et al. 2007; Swarsenski et al. 2007; Price et al. 2006, Slomp and Van Cappellen 2004; Li et al. 1999).

Estimating inputs of SGD has proven difficult. Unlike stream discharge, which can be precisely gauged, groundwater discharge can occur diffusely over a wide area, as a point discharge associated with faults, fractures, and solution holes, or most likely a combination of both processes (Burnett et al. 2003). The results of variable density groundwater flow models based on Darcy's law with calibration to groundwater heads and chloride content tend to give SGD values eight to ten times lower than field based estimates using either seepage meters or geochemical tracers (Smith and Zawadski 2003). Furthermore, these models can have large errors due to the necessity of applying assumptions of hydraulic conductivity in a heterogeneous aquifer. Direct measurement from seepage meters can also be complicated by heterogeneity, making it difficult to extrapolate data from one meter to another, and leading to an over or under estimation on SGD. In addition, seepage meters are labor-intensive and subject to tidal pumping, wave action, poor sediment/bedrock contact, and other physical disturbances (Shinn et al. 2002; Cable et al. 1996). Alternative methods to numerical modeling and seepage meters include the use of geochemical tracers to estimate SGD. Geochemical tracers used to quantify SGD have included radon (Burnett and Dulaiova 2003; Cable et al. 1996), radium isotopes (Moore and Church 1996), methane (Corbett et al. 1999), and helium (Top et al. 2001). The concentrations of these constituents are most often measured in the surface waters of the coastal ocean or bay receiving the SGD (Moore 1999; Moore and Church 1996), and less frequently in combination with measurements from seepage meters (Swarsenski et al. 2007; Cable et al. 1996).

This study used a series of naturally occurring geochemical tracers to identify, differentiate, and quantify the sources of freshwater (precipitation, canal discharge, and groundwater discharge) into an estuarine system. The geochemical tracers used were the stable isotopes of oxygen and hydrogen along with ratio of Sr^{2+}/Ca^{2+}. Swart and Price (2002) developed the use of stable isotopes of oxygen and hydrogen to differentiate freshwater inputs of precipitation from surface water runoff to the estuary of Florida Bay. A limitation of the stable isotope method in Biscayne Bay is the inability to differentiate the precipitation signature from the fresh groundwater. The novel contribution of this study is the addition of a Sr^{2+}/Ca^{2+} tracer to identify and separate the groundwater component from precipitation.

Biscayne Bay

Biscayne Bay is a coastal estuary located in southeastern Florida (Fig. 1). Salinities are seasonally lower than the adjacent open ocean as a result of the mixing of terrestrial and atmospheric sources of freshwater with marine water. Biscayne Bay receives freshwater from three principal sources, surface water canal discharge, precipitation, and SGD. Both precipitation and canal discharge can be directly measured; however, while SGD has been identified as a source (Kohout 1960), the magnitude and spatial distribution remain unknown, as does the relative importance of each of these inputs to the salinity variation in Biscayne Bay.

In the past, small creeks fed fresh water from the Everglades system through the Atlantic coastal ridge to Biscayne Bay (Wanless et al. 1994). Historical information suggests that the magnitude of the groundwater discharge was significantly greater prior to human influences with large portions of the Bay essentially being fresh (salinity <1) or near fresh for significant periods of time (Stone et al. 2000). Nautical reports and coastal surveys during the turn of the twentieth century described large quantities of groundwater discharged into Biscayne Bay by way of underground channels within the karst limestone bedrock (Parker et al. 1955). Groundwater levels were lowered as canals (Fig. 2), which were constructed to drain swampland and mitigate flooding. Since this anthropogenic modification of the natural watershed, it has been thought that freshwater inputs to the bay were delivered as surface water which principally discharged through manmade canals on an as need basis (Kohout 1960). Control gates were installed in the later part of the century to prevent and reverse saltwater intrusion. The South Florida Water Management District (SFWMD; http://www.sfwmd.gov) measures discharge at a majority of these canals at the control structures on a daily basis.

As a result of the initial construction of the canal system, fresh groundwater levels were lowered, and the consequent input to the bay significantly decreased (Kohout 1960). Currently, there is an absence of physical measurement of the amount of groundwater discharged. A recent modeling effort suggested that groundwater discharge into Biscayne Bay is only 6% of surface water discharge and most of the groundwater discharge occurs in the northern portion of the bay (Langevin 2001).

Precipitation in south Florida totals approximately 130 cm annually with input being divided into two seasons: a wet season occurring from June through November when the majority of total annual rainfall occurs (Duever et al. 1994). The wet season precipitation is primarily from daily convective thunderstorm activity with acute rainfall additions from tropical storm systems. The dry season occurs

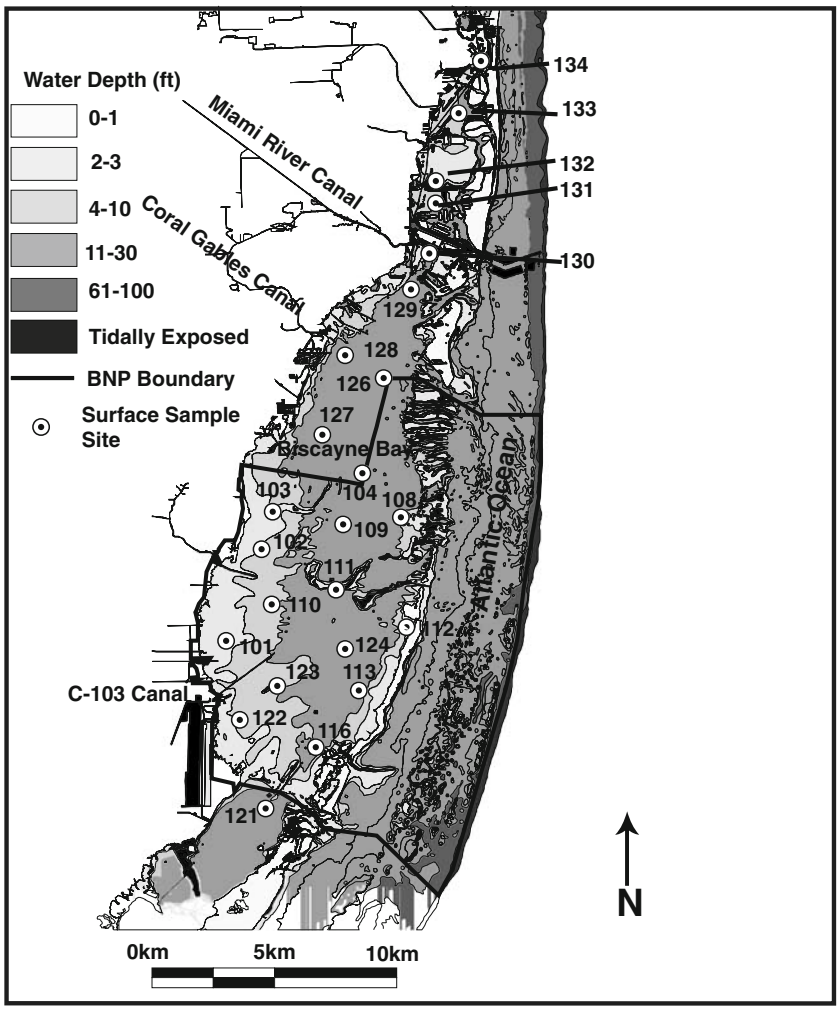

Fig. 1 Overview of the location of Biscayne Bay in South Florida and the surface sampling sites for isotopes and trace metals in Biscayne Bay. Each site was sampled by boat monthly by the Southeastern Environmental Research Center and analyzed for salinity, stable isotopes of oxygen and hydrogen, and major cations

from December until May and precipitation is generally related to cold fronts moving south across the Florida peninsula.

Biscayne Bay and its coastal wetlands are included in the Comprehensive Everglades Restoration Plan (http://www.evergladesplan.org) with water flow in the region to be changed from the point-source discharges via canals to more non-point source discharges through the wetlands and groundwater flow. Unfortunately, the mechanisms for the delivery of fresh and saline water to Biscayne Bay are not well constrained. The influence and magnitude of SGD is especially poorly constrained and may play a critical role in the movement of nutrients and contaminates to coastal ecosystems and estuaries (Price et al. 2006; Swarzenski et al. 2004). The purpose of this study is to utilize stable isotopes of oxygen and hydrogen coupled with Sr^{2+}/Ca^{2+} ratios as naturally occurring conservative tracers to estimate the proportional contributions of freshwater sources into Biscayne Bay, including fresh SGD, both spatially and temporally.

Methods

Sample Collection and Analysis

Surface water samples were collected from 25 stations in Biscayne Bay (Fig. 1) in conjunction with Florida International University's (FIU) Southeast Environmental Research Center water quality monitoring program (http://www.serc.fiu.edu/wqmnetwork). Samples were collected on a monthly basis from 2004 to 2006 in order to detect seasonal and annual variations. Precipitation samples were collected at two stations: one at the north end of Biscayne Bay at the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS) and the other near the southern end of Biscayne Bay on Elliot Key (Fig. 2). The precipitation samples were collected using a wet–dry precipitation-collecting device that was designed to prevent exposure of the rain to post-collection evaporation effects. The precipitation samples were collected on a weekly basis and then combined to form a monthly water sample. Water samples

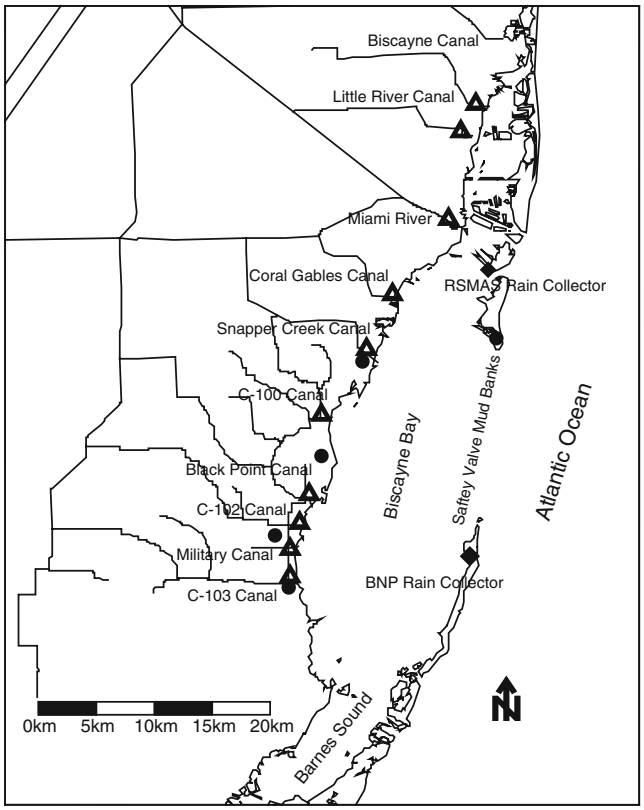

Fig. 2 Freshwater end-member sampling sites. Sites were sampled once a month from July 2004 to July 2006. Sites consisted of the ten major canals contributing to the bay (*triangles*), five groundwater well clusters (*circles*), and two precipitation collectors (*diamonds*). These samples were all end-members that make up freshwater inputs to Biscayne Bay. Samples were analyzed for stable isotopes of oxygen and major cations and anions

from ten canals were collected on the upstream (freshwater) side of the structure so as to identify the chemical composition of the canals prior to its discharge into Biscayne Bay (Fig. 2). In addition, 12 groundwater wells were sampled on a monthly basis (Fig. 2). All of these wells were pre-existing and installed by the United States Geological Survey, the SFWMD, and the Montgomery Botanical Research Center. The wells selected were completed to depths of 6 m or less so as to sample shallow groundwater prior to its discharge to the bottom of Biscayne Bay. Two wells were completed to deeper depths of 9 and 10 m. Furthermore, all of the wells were finished with a limited screen interval of 1.5 m or less so as to collect groundwater samples from a discreet interval in the aquifer. Prior to sampling, the groundwater wells were purged of at least three standing well volumes.

All water samples were analyzed for the stable isotopes of oxygen and hydrogen at the RSMAS Stable Isotope Laboratory on a Europa Geo 20–20 mass spectrometer with an auto sampler-equilibration unit (Europa WES). Water samples were analyzed for oxygen by equilibration with a reference CO_2 gas similar to the procedure described by Epstein and Mayeda (1953). Samples with excessive amounts of H_2S are first treated with elemental copper to remove the H_2S from biological activity, which could lead to fouling of the platinum catalyst. Hydrogen was analyzed by gas equilibration with a reference hydrogen gas in the presence of a platinum catalyst as described by Coplen et al. (1991). Standards are analyzed before and after each sample run to correct for instrument drift. Error resulting from these analyses is ±0.08‰ for oxygen analysis and ±1.5‰ for hydrogen analysis. All isotope samples are in reference to Vienna Standard Mean Ocean Water. Trace metal analysis was conducted on a Varian ICP-OES at RSMAS. ICP analytic standards were created from the International Association of Physical Sciences of the Oceans seawater standard, and analyzed every ten samples to correct for instrument drift. Additionally, samples were analyzed in duplicate and averaged for quality control and to minimize analytical error. Surface water and groundwater samples were diluted 1/100 prior to analysis. Rainfall samples were analyzed undiluted. Samples were treated with 0.1 molar nitric acid to dissociate ions from the walls of the sample vessels prior to analysis and 10% of the samples were duplicated for quality control analysis.

Linear Regression Isotope Method

Two separate binary mixing models were used to quantify the dominant sources of freshwater discharge into Biscayne Bay. One model utilized the stable isotopes of oxygen and hydrogen compared to salinity (Swart and Price 2002), and the other the molar ratio of Sr^{2+} to Ca^{2+} compared to salinity. Although there were three end-members contributing to freshwater inputs to Biscayne Bay (precipitation, groundwater, and canal water), the groundwater and precipitation had a similar isotopic composition; thus, these two were combined into one end-member (precipitation/groundwater) for the isotope modeling. The other end-member was the canal water. The precipitation and groundwater inputs were then separated using the Sr^{2+}/Ca^2 mixing equations.

In the first model, the sum of the freshwater components of canal discharge (x) and precipitation/groundwater flow (y) were related according to the equation:

$$1 = x + y \tag{1}$$

The intercept method developed by Swart and Price (2002) utilizing the change in stable isotopic composition of oxygen with changing salinity was applied to Biscayne Bay surface data. In this method, the $\delta^{18}O$ values for surface waters in the Bay were plotted against the salinity of the sample and a best-fit linear regression is determined. The data were divided into wet and dry seasons and then

plotted to determine the $\delta^{18}O$ value at the zero salinity intercept, and the ±95% confidence interval intercepts for each individual site (Fig. 1). The ratio of freshwater end-members for the change in salinity at each surface water location throughout the 2 years of this project was determined by modifying Eq. 1 to utilize isotope values to the following equation:

$$\delta^{18}O_{\text{interpret}} = (v)\delta^{18}O_{\text{cw}} + (1-v)\delta^{18}O_{\text{p/gw}} \quad (2)$$

In Eq. 2, the subscripts cw and p/gw refer to canal water and the combined precipitation and groundwater end-members, respectively. The term $\delta^{18}O_{\text{intercept}}$ refers to the $\delta^{18}O$ composition of the surface water sample at zero salinity as determined by a best-fit linear regression. This intercept is included in Eq. 2 which is then solved for (v). The variable (v) represents the ratio of canal water in the sample and ($1-v$) represents the precipitation/groundwater ratio. The percentage for each of the surface sites was then entered to an interpolation program and contoured to create maps of freshwater influence across Biscayne Bay. Areas receiving high amounts of canal water plot dark, while areas with a higher percentage of groundwater and precipitation input are represented by white. A mix of the two sources will be shades of gray.

Cation Mixing Model

Groundwater discharging to Biscayne Bay occurs in the Biscayne Aquifer, a limestone aquifer composed primarily of the minerals calcite with minor amounts of aragonite (Evans and Ginsburg 1987; Ginsburg 1953). Strontium ions commonly replace calcium ions in the crystalline structure of calcium carbonate minerals and during recrystallization process. Sr^{2+} can both be discriminated against or preferentially incorporated by the precipitating mineral. Regardless of the process, there is a relationship between the Sr^{2+}/Ca^{2+} ratio in the host rock and the local groundwater (Swart et al. 2001; Dwyer and Cronin 2001; Meyers et al. 1993). Seawater has a relatively high concentration of Sr^{2+} and Ca^{2+} (98.3 μM and 10.81 mM, respectively) and a distinctive Sr^{2+}/Ca^{2+} ratio. Precipitation has very low concentrations of strontium and calcium, but a ratio which is in the same range as that in seawater (as most of the Ca^{2+} and Sr^{2+} concentrations in rainwater ultimately are derived from seawater aerosols).

A numerical geochemical mixing model was developed using salinity and the Sr^{2+}/Ca^{2+} ratio for each of the freshwater sources mixing with marine water. Both freshwater end-members when mixed with seawater create a distinct mixing curve on a plot of salinity and Sr^{2+}/Ca^{2+} ratios. These curves are calculated by combining three binary mixing equations, for Sr^{2+}, Ca^{2+}, and salinity. In this model, canal water is a mixture of precipitation and groundwater and would fall on a line between precipitation and groundwater. Curve calculation for the freshwater end-member (precipitation or groundwater) mixing with seawater is calculated as follows:

$$\text{Sr}_{\text{sample}} = \text{Sr}_{\text{sea}}(y) + \left(\text{Sr}_{\text{gw}}(x) + \text{Sr}_{\text{precip}}(1-x)\right)(1-y) \quad (3)$$

$$\text{Ca}_{\text{sample}} = \text{Ca}_{\text{sea}}(y) + \left(\text{Ca}_{\text{gw}}(x) + \text{Ca}_{\text{precip}}(1-x)\right)(1-y) \quad (4)$$

$$y = \left(\text{Salinity}_{\text{sample}} - \text{Salinity}_{\text{fw}}\right) \times \left(\text{Salinity}_{\text{sea}} - \text{Salinity}_{\text{fw}}\right)^{-1} \quad (5)$$

$$x = \frac{\left[\frac{\left[\left(\text{Sr}^{2+}_{\text{sample}} \times \text{Ca}^{2+}_{\text{sea}} \times y\right) - \left(\text{Ca}^{2+}_{\text{sample}} \times \text{Sr}^{2+}_{\text{sea}} \times y\right)\right]}{(1-y)}\right] - \left[\left(\text{Ca}^{2+}_{\text{sample}} \times \text{Sr}^{2+}_{\text{precip}}\right) + \left(\text{Sr}^{2+}_{\text{sample}} \times \text{Sr}^{2+}_{\text{precip}}\right)\right]}{\left(\text{Ca}^{2+}_{\text{sample}} \times \text{Sr}^{2+}_{\text{gw}}\right) - \left(\text{Ca}^{2+}_{\text{sample}} \times \text{Sr}^{2+}_{\text{precip}}\right) - \left(\text{Sr}^{2+}_{\text{sample}} \times \text{Ca}^{2+}_{\text{gw}}\right) + \left(\text{Sr}^{2+}_{\text{sample}} \times \text{Ca}^{2+}_{\text{precip}}\right)} \quad (6)$$

In Eqs. 3, 4, and 6, the terms (Sr^{2+}) and (Ca^{2+}) refer to concentrations of strontium and calcium in millimoles. The subscripts "gw", "precip", "fresh", "sample", and "sea" refer to groundwater, precipitation, the freshwater end-member, samples of bay surface water, and seawater. The seawater end-member concentrations were taken from samples of Atlantic Ocean water. The variable (x) refers to the proportion of a groundwater present in each bay water surface water sample. The variable (y) refers to the proportion of seawater present in each surface sample from the bay. In Eq. 6, $\text{Salinity}_{\text{sample}}$ refers to the salinity of Biscayne Bay surface water at each sample site, while $\text{Salinity}_{\text{fw}}$ refers to the salinity of freshwater (0) and $\text{Salinity}_{\text{sea}}$ the salinity of seawater (36). Samples with salinities greater than 36 were not used.

Equations 3, 4, and 5 are combined and solved for (x) which represents the proportion of groundwater in given surface bay water sample (Eq. 6). Equation 6 was calculated for all samples at each surface water site in the bay from July 2004 to July 2006 (Fig. 1) to obtain a

groundwater to precipitation ratio. As (y) approaches 1, the sample is very close to the Sr^{2+} and Ca^{2+} values found in seawater and the solution for x becomes undefined; essentially, there is no freshwater input to differentiate, the sample is representative of seawater. As (y) approaches 0, the first term on the top of the equation drops out and it becomes a simple mixing of the Sr^{2+} and Ca^{2+} values of groundwater and of precipitation. As (x) goes to 0, the Sr^{2+} and Ca^{2+} values resemble precipitation mixing with seawater. As (x) goes to 1, the Sr^{2+} and Ca^{2+} values resemble groundwater mixing with seawater. An average for each site in both the wet and dry seasons was determined as was a standard deviation and a standard error. These ratios were then combined with the results from the isotope model to present a ratio of all three end-members at each surface site.

Bay-Wide Water Balance Model

The overall influence of each freshwater end-member was compared to all sources of water in the bay, both saline and fresh. This helped discern the relative importance of the freshwater sources as total volume contributions to the bay water. This overall input ratio was determined by first calculating the balance of freshwater and saltwater in the bay using Eq. 6. Once the ratio of freshwater in the bay was calculated, this fraction is then subdivided using the freshwater end-member ratios from the isotope and trace metal models.

Results

Isotope Model

Oxygen isotope values ($\delta^{18}O$) varied from −4.1‰ to +3.0‰, while hydrogen isotope (δD) values ranged from −24.5‰ to +26.7‰. Groundwater samples tended to have the most negative or depleted isotopic values. Average fresh groundwater values for $\delta^{18}O$ and δD were −3.52‰ and −18.20‰ in the wet season and −2.18‰ and −9.8‰ in the dry season, respectively. Average weighted mean precipitation values for $\delta^{18}O$ and δD were −3.28‰ and −16.57‰ in the wet season and −1.83‰ and −4.49‰ in the dry season, respectively (Table 1).

Canal samples had enriched oxygen and hydrogen isotope values compared to groundwater and precipitation. The average canal water values were $\delta^{18}O = -0.55$‰ and $\delta D = -2.78$‰. This distinguished canal water from precipitation and groundwater (Fig. 3). A similar Sr^{2+}/Ca^{2+} geochemical mixing model has shown that up to 40% of the water in the canal system is derived from groundwater (Stalker 2008). However, the difference in the isotope signatures for the canal water and the groundwater/precipitation was sufficient to separate the influence of these freshwater sources into the bay. The Sr^{2+}/Ca^{2+} mixing model was used to separate the precipitation input from the groundwater.

Oxygen and hydrogen isotope values for groundwater and precipitation fell within the error of one another in both the wet and dry seasons (Fig. 3). Therefore, the two sources of freshwater could not be differentiated using these chemical parameters. The surface bay regression result for each site was then applied to the binary mixing equation, using different end-member $\delta^{18}O$ values for the wet and dry seasons. This calculation produces a mixing ratio between fresh canal water and precipitation/groundwater (Table 2). Mixing models using oxygen isotopes converged for over 100% of the surface sites, proving them to be robust. A similar model using deuterium, however, converged for only 80% of the surface sites. The lower convergence rate in the deuterium model may partly be attributed to the relatively high sensitivity of hydrogen isotopes to changes

Table 1 Fresh/seawater end-member geochemical values

End-member	$\delta^{18}O$	SD	δD	SD	n	Sr^{2+} (μM)[a]	Ca^{2+} (mM)[a]	Sr^{2+}/Ca^{2+} (μM/mM)[a]	n
Precipitation									
Wet	−3.28	0.96	−16.57	7.14	100	$0.0064 \pm 1.0 \times 10^{-4}$	$0.0167 \pm 2.4 \times 10^{-4}$	0.89±0.017	48
Dry	−1.83	1.22	−4.49	8.42					
Groundwater									
Wet	−3.52	0.50	−18.20	3.16	98	$0.344 \pm 2.0 \times 10^{-2}$	4.90±0.02	0.07±0.001	98
Dry	−2.18	0.48	−9.8	2.20					
Canal water									
Wet	−0.47	1.34	−5.31	6.10	222	n/a	n/a	n/a	222
Dry	−0.40	0.96	−4.88	7.51					
Atlantic seawater	n/a	n/a	n/a	n/a	n/a	98.92±1.04	10.81±0.15	9.38±0.10	25

n/a values were not used in this portion of the study

[a] An annual average was used for both seasons

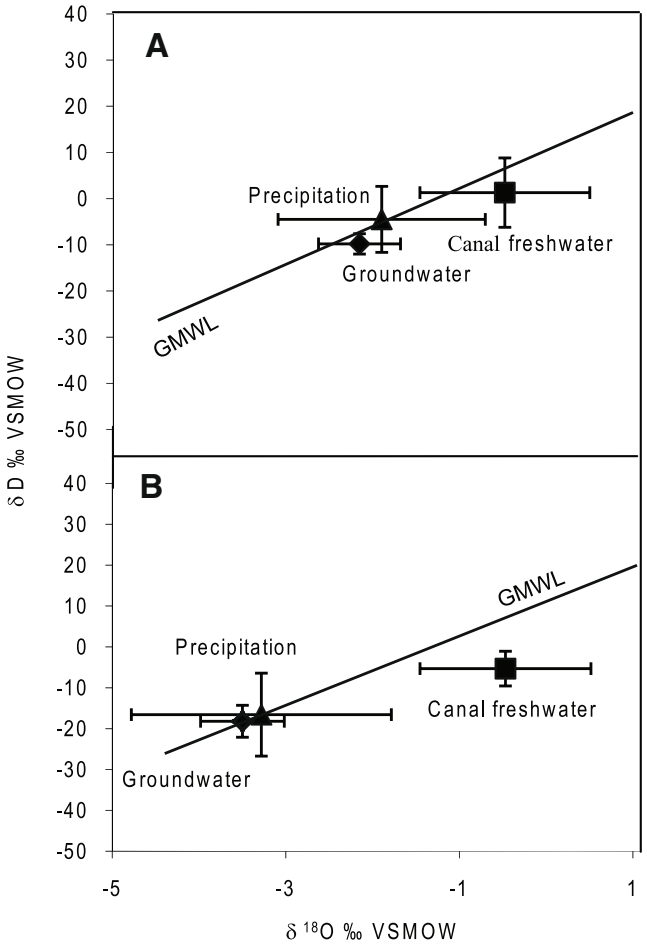

Fig. 3 Average isotope values of the freshwater end-members sampled in this study in the wet and dry seasons. All points are an average of 2 years of data for all sites that fall in the same category of end-member type. *Error bars* were calculated using the standard deviation of each data type. The Global Meteoric Water Line (*GMWL*) is plotted for reference. **a** Isotope values in the dry season (December–May), **b** isotope values in the wet season (June–November)

in temperature, humidity in the fractionation process, or analytical difficulties. Since the oxygen model proved more robust, conclusions were drawn only from the oxygen modeling results.

Errors associated with the estimate of the intercept from the regression modeling are large for sites with small salinity ranges typical of the near ocean sites (±43%) and decreased as the salinity range increased, typical of sites near the western shoreline (±10%; Fig. 4). Confidence intervals for the linear regressions at all sites produced an extrapolated intercept within the limits indicated by the freshwater end-member data. By using the 95% confidence interval intercepts as the higher and lower bounds for the regression analysis resulted in an average of ±20% error bay-wide in both the wet and dry seasons.

Salinity

The salinities of the end-members were 0 for the freshwater end-members, and 36 for the local seawater end-member. The Biscayne Bay surface site salinities ranged from 10.41 to 44.13 with an average of 33.70±0.61 (Table 3). The average salinity in the Bay was 32.46±1.00 in the wet season and 35.34±0.62 in the dry season. The lowest monthly and average salinities occurred at sites near the western shoreline, while higher monthly and average salinities occurred near the eastern edge of the bay near the Atlantic Ocean. The hyper-saline values from 39 to 44.13 occurred at a number of the surface sites (101, 102, 103, 110,113, 122, 124, 123, 126, 127, 128, and 129) in July 2004.

Cation Model

Strontium values for the 98 groundwater samples ranged from 0.12 to 0.58 μM, with an average of 0.34±0.02 μM. The Ca^{2+} concentrations for the groundwater samples ranged from 2.5 to 8.4 mM with an average of 4.9± 0.06 mM. The Sr^{2+}/Ca^{2+} ratios in millimolar per molar ranged from 0.02 to 0.28 with an average of 0.07 (Table 1). Concentrations for both Ca^{2+} and Sr^{2+} varied 15% on a seasonal basis; however, the Sr^{2+}/Ca^{2+} ratios varied only 2% from season to season. Thus, an annual average Sr^{2+}/Ca^{2+} ratio was chosen for use in the model end-member. The groundwater cation concentrations did not display any geographical trends, north or south in the study area or east to west from near the bay to inland areas.

Precipitation Sr^{2+} values for 40 samples ranged from 0.000148 to 0.043 μM with an average of 0.0079± 0.0001 μM. Calcium values for precipitation ranged from 0.004 to 0.095 mM with an average of 0.021±0.002 mM. The Sr^{2+}/Ca^{2+} in micromolar per millimolar values ranged from 0.34 to 2.38 with an average of 0.84±0.07 mM/M. The concentrations of both Sr^{2+} and Ca^{2+} were lower in the wet season on average (Sr^{2+}=0.0046±0.0007 μM, Ca^{2+}= 0.0128±0.0012 mM) compared to the dry season (Sr^{2+}= 0.0098±0.0009 μM, Ca^{2+}=0.0281±0.0029 mM). However, the ratio of Sr^{2+} to Ca^{2+} in millimolar per molar was not significantly different from the wet (0.87± 0.04) to dry seasons (0.80±0.07). This is an indication of dilution of concentrations, but conservation of the ratio of the ions in precipitation in the area from the wet to dry season.

The local seawater Sr^{2+} and Ca^{2+} concentrations were taken from 25 seawater samples collected offshore in the Atlantic Ocean and near the ocean outlets in Biscayne Bay. The Sr^{2+} concentration ranged from 86 to 125 μM with an average of 98.9±1.7 μM. Ca^{2+} concentrations ranged from a high of 11.5 mM to a low of 8.8 mM with an average of 10.81±0.15 mM. The ratio Sr^{2+}/Ca^{2+} in millimolar per molar for the seawater samples ranged from 8.2 to 10.4 with an

Table 2 Oxygen isotope modeling values and binary mixing model results for the wet season, dry season, and annual average for all surface sites in Biscayne Bay

Site no.	Site name	Latitude (deg)	Longitude (deg)	Percent canal	Percent precipitation	$\delta^{18}O$ intercept	SE	Percent error
101	Convoy Point	25.47833	−80.32083	54	46	−1.44	0.31	9
102	Black Point	25.54583	−80.29467	69	31	−1.03	0.31	9
103	Near Black Ledge	25.57333	−80.28667	61	39	−1.20	0.27	8
104	BNP Marker C	25.60167	−80.22083	0	100	−3.23	0.06	2
108	Marker G-1B	25.56917	−80.19250	0	100	−3.77	0.69	20
109	Midbay North	25.56417	−80.23500	15	85	−3.41	0.55	16
110	Fender Point	25.50500	−80.28750	67	33	−1.14	0.32	9
111	Featherbed Bank	25.51583	−80.24000	0	100	−3.21	0.66	19
112	Sands Cut	25.48833	−80.18833	0	100	−4.24	0.11	13
113	Elliott Key	25.44167	−80.22333	16	84	−2.54	0.49	14
116	Rubicon Keys	25.40000	−80.25500	10	90	−2.71	0.57	17
121	Card Sound North	25.35500	−80.29167	47	53	−1.95	0.45	13
122	West Arsenicker	25.42017	−80.31083	41	59	−1.82	0.28	8
123	Pelican Bank	25.44500	−80.28333	32	68	−2.35	0.37	11
124	Midbay South	25.47250	−80.23333	59	41	−1.37	0.63	18
126	BNP Marker B	25.67167	−80.20500	37	63	−2.18	0.51	15
127	Shoal Point	25.63000	−80.25000	49	51	−1.99	0.42	12
128	Matheson Beach	25.68833	−80.23333	53	47	−1.41	0.48	14
129	Marker G-71	25.73667	−80.18500	53	47	−1.25	0.45	13
130	South Dodge Island	25.76333	−80.17167	53	47	−1.45	0.55	16
131	North Venetian Basin	25.80000	−80.16667	48	52	−1.89	0.47	14
132	North I-195 Basin	25.81667	−80.16667	34	66	−2.07	0.53	15
133	North Normandy Isle	25.86667	−80.15000	65	35	−1.23	0.34	10
134	Oleta River Park	25.90500	−80.13333	88	12	−0.44	0.27	8

average of 9.89±0.10. These values represent local evaporated seawater (Sal=36 to 37) which are higher than typical Atlantic Ocean water (Sal=34.5, Sr^{2+}=91 μM, Ca^{2+}= 10.25 mM). However, this local seawater source is considered to be the primary source of saline water to Biscayne Bay.

Surface water samples from Biscayne Bay contained concentrations of Sr^{2+} ranging from 4 to 130 μM with an average of 90±3 μM. The concentrations of calcium in the Bay ranged from 1.32 to 13.8 mM with an average of 10.01± 0.25 mM. The ratios of Sr^{2+}/Ca^{2+} ranged from 3.10 to 11.86 with an average of 8.96±0.126. The concentrations of Sr^{2+} and Ca^{2+} and the Sr^{2+}/Ca^{2+} ratios increase with increasing distance from the western shoreline.

Seasonal concentrations of Sr^{2+} and Ca^{2+} displayed modest changes in concentrations from the wet season to the dry season in precipitation and in groundwater. The ratio of Sr^{2+}/Ca^{2+} did not display a significantly different value from the wet to the dry season in all three of the end-members (precipitation, groundwater, and seawater). Therefore, an annual average was used for all three end-members in the Sr^{2+}/Ca^{2+} mixing model. However, the surface water Sr^{2+}/Ca^{2+} model results were divided into a wet and dry season in order to make the results compatible with the isotope model.

The cation mixing model results can be presented in terms of either percentage of groundwater (x) or as the percentage of precipitation ($1-x$). Results here were presented in terms of groundwater discharge. The model converged for 95% of data points, the remaining 5% fell out of the boundaries of the model. This may be due to precipitation or dissolution processes affecting the concentrations of Ca^{2+} or Sr^{2+}, or the presence of saline SGD influence which was not described in this model. The ratio percentage of fresh groundwater discharge influence on the salinity variation (x) at all the sites Biscayne Bay varied from 0% to 88% (Table 3). In general, sites nearest the western shoreline (Fig. 1, sites 101,102, 103, 110, and 122) and sites along the northern shoreline of Biscayne Bay (Fig. 1, sites 127–134) displayed the highest percentages of groundwater influence. Sites further east nearer to the saline source (Fig. 1, sites 104, 108, 109, 111, 112, 113, 116, 121, 123, 124, and 126) had little or no groundwater influence during the study period. Error in this model was determined using standard errors from the averaging of the end-member

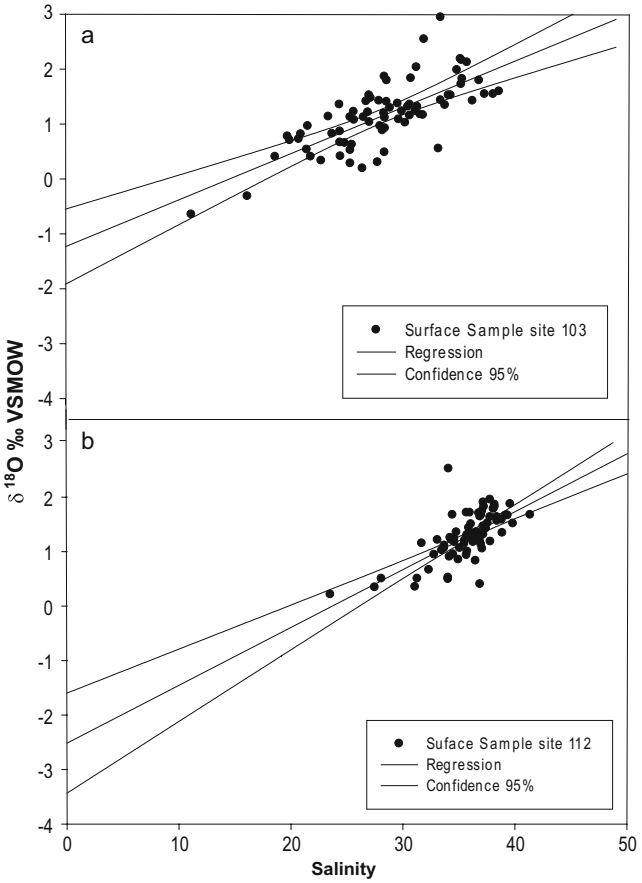

Fig. 4 Examples of isotope regression analysis of oxygen isotope ratio and salinity for **a**) near-shore and **b**) far-shore surface sites. The zero salinity intercept represents the isotope ratio of the mixing ratio of freshwaters contributing to salinity variation at the given site. The *center dark line* is the regression extrapolated back to zero salinity and is bracketed by the 95% confidence interval. Data at each surface site was separated into the wet and dry seasons for each year of the study for regression analysis

sample concentrations and added an error estimate of ±5% to the final model estimates. The average groundwater discharge value for the entire 2-year study was 8±5%, and this can be further broken down into a value of 5±5% in the dry season and 10±5% in the wet season.

The Sr^{2+}/Ca^{2+} groundwater and precipitation ratios obtained in the trace metal model (Table 3) were then combined with the precipitation groundwater end-member ratio result obtained from the isotope model (Table 2). This separated the signals due to groundwater, precipitation, and canal discharge from one another giving a three-constituent end-member mixing model for the three major inputs of freshwater into Biscayne Bay with the combined error from the two models (20+5%=25%). When the two models were combined, the freshwater input to the bay consisted of canal input of 38±25%, precipitation of 52±25%, and a groundwater input of 10±25% in the wet seasons. In the dry seasons, the freshwater input to the bay was comprised of a canal input of 37±25%, precipitation of 58±25%, and a groundwater input of 5±25%.

Bay-Wide Water Balance

Freshwater accounted for 15% of all (saline and fresh) water in the bay during the dry season and 20% in the wet season. When this percentage was subdivided by the ratios determined by the isotope/trace metal freshwater end-member results, the ratio of canal water/precipitation/groundwater was determined to be 5.5%:8.5%:1% during the dry season and 7.5%:9.5%:2% in the wet season.

Discussion

Spatial Inputs of Freshwater

The combined mixing model results indicate that the freshwater inputs to Biscayne Bay are dominated by the discharging canal systems (surface water) near the western shoreline (Fig. 5), while areas further east and closer to the ocean inputs indicate a dominance of precipitation (Fig. 6). This spatial relationship of precipitation influence farther away from the mainland is similar to the results from studies on freshwater influence in Florida Bay (Swart and Price 2002; Top et al. 2001). This relationship is not unusual as the discharging canals are all located on the western side of the bay. However, in Biscayne Bay, there is the added influence of groundwater discharge (Fig. 7), and some areas near discharging canals that should have increased canal influence had higher precipitation/groundwater signatures in the isotope model. This is indicative of the presence of a groundwater source and is apparent in the model results. The influence of groundwater is apparent at sites 101, 102, 103, 122, and 129–133 (Figs. 1 and 7), which are located near large discharging canals, and sites 101, 102, and 103 are located in regions of known springs (Langevin 2001). The extent of groundwater influence includes the entire near shore area of Biscayne Bay, including the narrow portion in between the barrier island system and the shoreline in the north during both the wet and dry seasons (Fig. 7). The largest percentages of groundwater influence are at sites 101, 102, and 103 (Fig. 1, Table 2). There is a significant canal input signal in the isotope models in the far south of Biscayne Bay near site 121 (Fig. 5). This signal may be related to the presence of a large nuclear power plant near the shoreline (just inland from sites 121, Fig. 1) area discharging water from cooling canals into Biscayne Bay. This signal could also be accounted for by the prescience of large canals that connect with the southern portion of the bay outside of the study

Table 3 Sr^{2+}/Ca^{2+} modeling results for the wet season and dry season in surface sites in Biscayne Bay

Site no.	Sr^{2+} wet season (mM)	Ca^{2+} wet season (mM)	Salinity wet season	Average groundwater discharge wet season (z)	Sr^{2+} dry season (mM)	Ca^{2+} dry season (mM)	Salinity dry season	Average groundwater discharge dry season (z)
101	0.081	9.04	27.96	0.33	0.082	9.28	32.41	0.22
102	0.073	7.97	23.39	0.35	0.084	9.56	31.86	0.37
103	0.076	8.48	27.74	0.26	0.089	10.04	33.08	0.34
104	0.094	9.61	35.41	0.00	0.094	9.52	36.93	0.00
108	0.096	9.69	35.78	0.00	0.096	10.71	36.87	0.00
109	0.101	10.90	35.81	0.00	0.096	10.78	37.15	0.00
110	0.093	10.03	31.99	0.28	0.096	10.83	35.80	0.00
111	0.098	9.91	35.88	0.01	0.097	10.81	37.34	0.00
112	0.100	8.44	36.12	0.00	0.097	10.87	37.17	0.00
113	0.099	10.07	35.92	0.00	0.099	11.10	37.55	0.00
116	0.098	9.89	35.34	0.00	0.100	11.16	37.29	0.00
121	0.095	8.78	34.00	0.21	0.094	10.53	36.24	0.00
122	0.089	9.16	31.68	0.24	0.097	10.83	33.91	0.24
123	0.093	8.71	33.02	0.00	0.100	11.23	36.08	0.00
124	0.098	9.12	35.83	0.00	0.101	11.22	37.22	0.00
126	0.078	8.82	32.54	0.22	0.094	10.42	35.35	0.00
127	0.080	7.80	31.47	0.10	0.097	10.86	35.80	0.00
128	0.076	7.57	30.09	0.18	0.095	10.61	34.87	0.14
129	0.080	8.51	30.87	0.16	0.096	10.62	34.98	0.22
130	0.077	7.87	30.10	0.20	0.094	10.42	34.79	0.22
131	0.080	8.20	30.25	0.20	0.094	10.36	33.63	0.26
132	0.084	7.84	29.54	0.20	0.092	10.19	33.30	0.21
133	0.074	6.16	28.06	0.15	0.090	9.93	33.68	0.00
134	0.068	6.49	28.88	0.17	0.094	10.36	34.96	0.00
Average	0.089	8.72	27.96	0.15	0.098	10.53	32.41	0.08

area. Additionally, this is the edge of the dataset and may in part be explained by kriging interpolation effects.

Proportional Variation of Freshwater Inputs

Surface Water and Precipitation

In both the wet and dry seasons, precipitation is the dominant freshwater input (52% and 55%) to the bay. During the wet season, high precipitation amounts contribute freshwater throughout the entire bay. Although there is a significant amount of discharge from the canals during the wet season, it is limited to point-source discharges to the western portion of the Bay. During the dry season, there is a lower amount of precipitation, but the canal structures generally remain closed to keep groundwater and canal water levels high for water supply as well as to curb seawater intrusion. The total volumes of fresh water input from each of the three end-members (canal water, groundwater, and precipitation) are higher in the wet season and lower in the dry season; however, the relative proportions of each end-member appear to be similar in both seasons.

Groundwater accounts for 10% of all freshwater inputs during the wet season and 5% during the dry season. This change in the amount of groundwater input is smaller than the total error (25%); however, the chemical signatures of groundwater input are detectable and remain a consistent contributor to the freshwater budget for both the wet and dry seasons. In addition, the influence of groundwater appears to extend further into the bay during the wet season (Fig. 7a) and becomes a much higher percentage of total freshwater inputs in the west–central and southwestern portions of the Bay. This may indicate that SGD can be a locally important source of freshwater and nutrient inputs in both the wet and dry seasons, especially in the western portion of the bay. While yearly groundwater input percentages for the entire bay are lower compared to the other sources of freshwater, monthly groundwater input percentages can account for upwards of 60% of freshwater input at sites near the western shoreline. This local input of

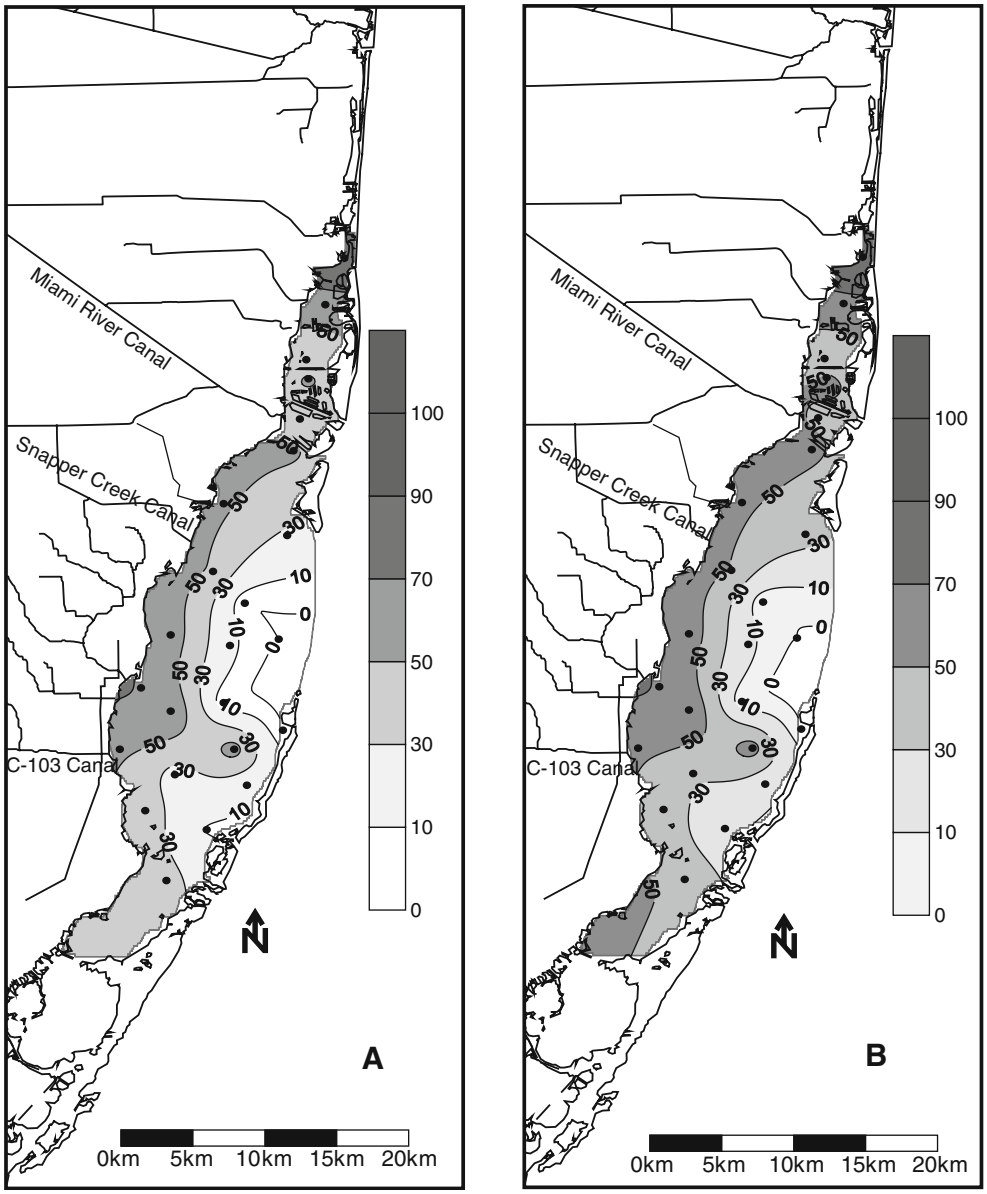

Fig. 5 The percentage of canal water influence contributing to surface water salinity variation in Biscayne Bay surface water in the **A**) wet seasons (June–November) and **B**) dry seasons (December–May) from 2004 to 2006. *Areas of darker* shading indicate a strong canal water signature. *Areas in white* indicate a strong groundwater/precipitation signature

groundwater may in part explain the relatively high concentrations of nitrogen and phosphorous in the surface waters found near the western shoreline of Biscayne Bay (Caccia and Boyer 2007).

In order to compare the results of this study to other local and global studies, fresh SGD to Biscayne Bay as calculated in this study can be expressed in three ways: first as 1–2% of total water inputs, second as 5–10% of all freshwater inputs, and third as 10–25% of canal water (surface water) inputs. The proportion of fresh SGD (1–2%) in the freshwater budget found in this study was similar to the 0.85% of total water input suggested by long-term unpublished seepage studies conducted in Biscayne Bay (Steve Krupa, SFWMD pers. comm. 2007). The estimate of 10–20% of canal water input is equal to or higher than the estimate of 10% of the canal input suggested by groundwater modeling (Langevin 2001). The fresh SGD estimated by the geochemical models in this study fell within the ranges of 0.1–10% of total water flux or 0.5–41% of surface water flux found in global SGD studies (Taniguchi et al. 2002).

The error related to the ratio estimates in this study limits the confidence in statements to relative changes from season to season and the relative influence of each of the inputs. Improvements in error could be obtained by sampling closer to the shoreline, which would result in a greater range of salinity variation. This would increase the reliability of the regression analysis and reduce the confidence interval related to the zero salinity intercept at the near shore sites where the majority of SGD is expected

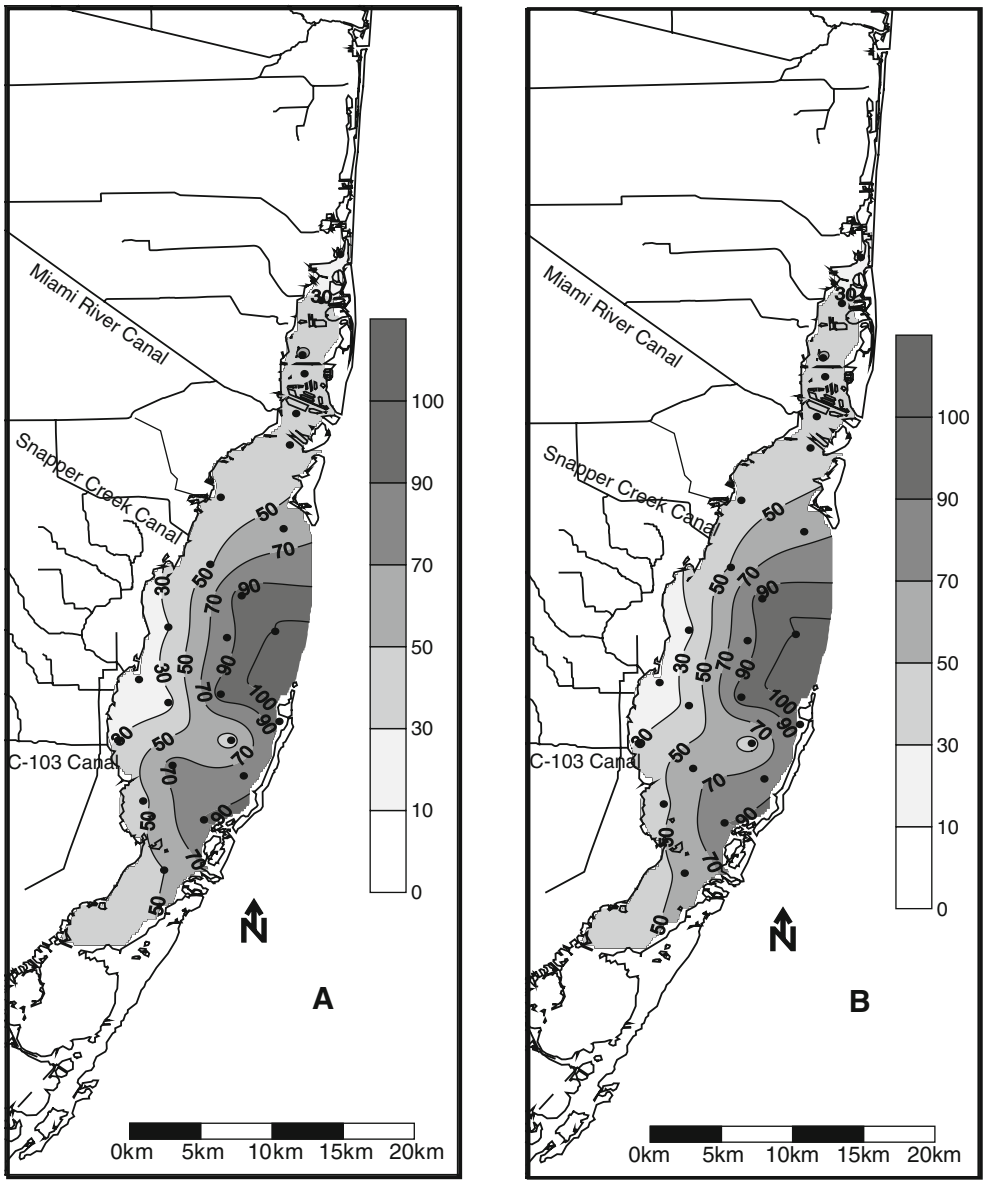

Fig. 6 The percentage of precipitation influence contributing to salinity variation in Biscayne Bay surface water in the **A**) wet seasons (June–November) and **B**) dry seasons (December–May) from 2004 to 2006. *Areas of darker shade* indicate a strong precipitation water signature. *Areas in white* indicate a stronger groundwater or canal water signature

to occur. The spatial relationship with error also suggest that the western side of the bay behaves as an estuarine system with relatively large salinity changes related to terrestrial freshwater sources, while the eastern side of the bay may behave more like a marine-dominated system.

The error derived from this geochemical modeling is equivalent or less to the two other methods (seepage meters and groundwater models) that have been used to measure SGD into Biscayne Bay. Seepage meter measurements have uncertainty related to design and physical limitations and have errors of greater than 50% (Harvey et al. 2002) and have the added limitation of being a point measurement in a heterogeneous environment. The karst bedrock of Biscayne Bay is heterogeneous with areas of numerous cavities and channels with relatively high outputs of groundwater and areas of less permeable solid limestone with smaller groundwater output (Cunningham et al. 2006). Groundwater models have unknown error related to SGD input and are limited by spatial information and generalizing critical terms such as hydraulic conductivity. In addition, groundwater models rely on Darcy's law and the assumption of laminar flow, which may be an incorrect assumption in a karst environment (White 2002). This geochemical method provides a reasonable estimate of freshwater inputs and avoids the problems related to point measurements and groundwater flow assumptions. In addition, the geochemical modeling techniques presented here integrate all the sources of freshwater in a particular area in one model and have a greater spatial coverage than seepage meter measurements.

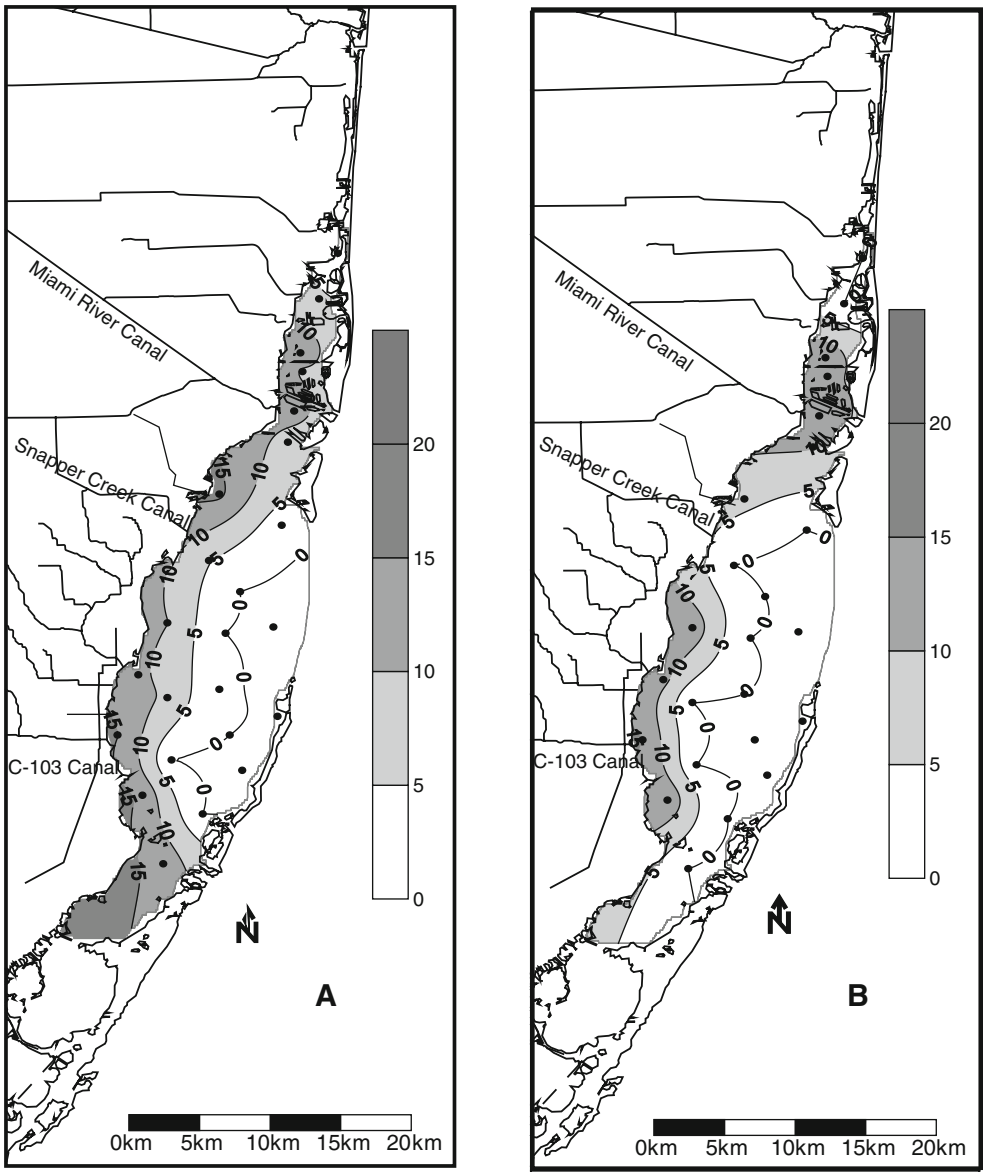

Fig. 7 The percentage of groundwater influence contributing to salinity variation in Biscayne Bay surface water in the **A**) wet seasons (June–November) and **B**) dry seasons (December–May) from 2004-2006, determined by subdividing the isotope model ratio value for the precipitation/groundwater end-member with the Sr^{2+}/Ca^{2+} model results for groundwater input. *Darker shades* represent higher groundwater percentages. *White* indicates higher percentages of precipitation and canal water influence

Conclusions

This geochemical modeling method provides a reasonably accurate ratio comparison of freshwater inputs to Biscayne Bay. The combined stable isotope and cation-mixing models indicate a ratio of canal input/precipitation/groundwater of 38%:52%:10% in the wet season and 40%:55%:5% in the dry season with an error of 25% indicating rainfall is the dominant source of freshwater to Biscayne Bay. For a bay-wide water budget that includes saltwater and freshwater mixing, fresh groundwater accounts for less than 2% of the total input. These estimates are comparable to earlier estimates using different methods in Biscayne Bay and are comparable to similar studies in other estuaries around the world. While the importance of SGD in Biscayne Bay may be minor compared with all inputs of water to the bay, the importance of the nutrients and other chemical constituents input though SGD may be significant, and SGD inputs may provide a critical input in nutrient balances and ecological models especially in local areas near the western shoreline. Spatially, canal discharge dominates the western shoreline while precipitation dominates the eastern portion of the bays. Groundwater inputs seem to be restricted to the near shore sites and not in the mid-bay or eastern fringe sites.

The isotope method presented in this study could be applicable to any estuarine system and provides another method for quantifying SGD in coastal aquifer systems. Different trace metals can be substituted for strontium and calcium for aquifers with varying lithologies. Isotopes and

trace metals provide a naturally occurring alternative to introduced tracers such as dyes or tagged molecules and can be applied to studies on many scales and could be combined with other existing tracers to gain greater resolution and smaller errors. Logistically, the sample collection scheme is relatively simple compared to physical studies such as seepage meters, and the sample analysis is well established. Finally, if these geochemical tracer studies are conducted for long periods of time, changes in relative influence and spatial influence of the freshwater sources in relationship to changes in water usage and management or natural variation in the climate or physical system could be discerned.

Acknowledgments We would like to thank the Florida Seagrant Project No. R/C-E-51, The National Park Service, and especially Richard Curry of Biscayne National Park for logistical support. The Florida International University Graduate School Dissertation Year Fellowship is also thanked for funding. Dr. Price's contribution was partially funded by the National Science Foundation under Grant no. DBI-0620409 and Grant no. DEB-9910514. Dr. Swart's contribution was partially funded by the Stable Isotope Laboratory at the University of Miami. This is Southeastern Environmental Research Center research contribution 422.

References

Bokuniewicz, H. 1980. Groundwater seepage into Great South Bay, New York. *Estuarine Coastal and Shelf Science* 10:437–444.

Burnett, W.C., H. Bokuniewsicz, M. Huettel, W.S. Moore, and M. Taniguchi. 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry* 66:3–33. doi:10.1023/B:BIOG.0000006066.21240.53.

Burnett, W.C., and H. Dulaiova. 2003. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *Journal of Environmental Radioactivity* 69(1–2):21–35.

Cable, J.E., W.C. Burnett, J.P. Chanton, and G.L. Weatherley. 1996. Estimating groundwater discharge into the Northeastern Gulf of Mexico using radon-222. *Earth and Planetary Science Letters* 144:591–604. doi:10.1016/S0012-821X(96)00173-2.

Caccia, V.G., and J.N. Boyer. 2007. A nutrient loading budget for Biscayne Bay, Florida. *Marine Pollution Bulletin* 54:994–1008. doi:10.1016/j.marpolbul.2007.02.009.

Caccia, V.G., and J.N. Boyer. 2005. Spatial pattering of water quality in Biscayne Bay, Florida as a function of land use and water management. *Marine Pollution Bulletin* 50:1416–1429. doi:10.1016/j.marpolbul.2005.08.002.

Coplen, T.B., J.D. Wildman, and J. Chen. 1991. Improvements in the gaseous hydrogen–water equilibration technique for hydrogen isotope ratio analysis. *Analytical Chemistry* 63:910–912. doi:10.1021/ac00009a014.

Corbett, R.D., J. Chanton, W. Burnett, K. Dillon, and C. Rutkowski. 1999. Patterns of groundwater discharge into Florida Bay. *American Society of Limnology and Oceanography* 44:1045–1055.

Cunningham, K.J., R.A. Renken, M.A. Wacker, M.R. Zygnerski, E. Robinson, A.M. Shapiro, and G.L. Wingard. 2006. Application of carbonate cyclostratigraphy and borehole geophysics to delineate porosity and preferential flow in the karst Limestone of the Biscayne aquifer, SE Florida. In *Perspectives on karst geomorphology, hydrology, and geochemistry—A tribute volume to Derek C. Ford and William B. White*, eds. R.S. Harmon, and C. Wicks. Geological Society of America Special Paper 404: 191–208, doi:10.1130/2006.2404(16).

Duever, M.J., J.F. Meeder, L.C. Meeder, and J.M. Mc-Collum. 1994. The climate of South Florida and its role in shaping the Everglades ecosystem. In *Everglades: The Ecosystem and its Restoration*, eds. SM Davis, and JC Ogden, 225–248. Delray Beach, Florida, USA: St. Lucie.

Dwyer, G.S., and T.M. Cronin. 2001. Ostracode shell chemistry as a paleosalinity proxy in Florida Bay. *Bulletin of American Paleontology* 361:249–276.

Epstein, S., and T.K. Mayeda. 1953. Variation of O^{18} content of waters from natural sources. *Geochemica et Cosmochemica Acta* 4:213–254.

Evans, C.C., and R.N. Ginsburg. 1987. Fabric selective diagensis in the late pleistocene Miami Limestone. *Journal of sedimentary Petrology* 51(2):311–318.

Ginsburg, R.N. 1953. Beachrock in South Florida. *Journal of Sedimentary Petrology* 23:85–92.

Gonzalez, F.U.T., J.A. Herrera-Silverira, and M.L. Aguirre-Macedo. 2007. Water quality variability and eutrophic trends in karstic tropical coastal lagoons of the Yucatan peninsula. *Estuarine, Coastal and Shelf Science* 76(2):418–430.

Harvey, J.W., S.L. Krupa, and J.M. Krest. 2002. Ground water recharge and discharge in the central Everglades. *Groundwater* 42(7):1090–1102. doi:10.1111/j.1745-6584.2004.tb02646.x.

Hussain, N., T.M. Church, and G. Kim. 1999. Use of Rn-222 and Ra-226 to trace groundwater discharge into the Chesapeake Bay. *Marine Chemistry* 65(1–2):127–134.

Kohout, F.A. 1960. Cyclic flow of salt water in the Biscayne Aquifer of Southeastern Florida. *Journal of Geophysical Research* 65 (7):2133–2141. doi:10.1029/JZ065i007p02133.

Kroger, K.D., P.W. Swarzenski, C. Reich, and W.J. Greenwood. 2007. Submarine groundwater discharge to Tampa Bay, nutrient fluxes and biogeochemistry of the coastal aquifer. *Marine Chemistry* 104:85–97. doi:10.1016/j.marchem.2006.10.012.

Langevin, C.D. 2001. Simulation of ground-water discharge to Biscayne Bay, Southeastern Florida, USGS WRI: 00-4251.

Li, L., D.A. Barry, F. Stagnitti, and J.-Y. Parlange. 1999. Submarine groundwater discharge and associated chemical input to a coastal sea. *Water Resources Research* 35:3253–3260. doi:10.1029/1999WR900189.

Meyers, J.G., P.K. Swart, and J.L. Meyers. 1993. Geochemical evidence for groundwater behavior in an unconfined aquifer, South Florida. *Journal of Hydrology* 148:249–272. doi:10.1016/0022-1694(93)90263-9.

Moore, W.S. 1999. The subterranean estuary: a reaction zone of ground water and sea water. *Marine Chemistry* 65:111–125. doi:10.1016/S0304-4203(99)00014-6.

Moore, W.S., and T.M. Church. 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature* 380:612–614121–122.

Parker, G.G., G.E. Gerguson, and S.K. Love. 1955. Water resources of Southeastern Florida with special reference to geology and groundwater of the Miami areas: USGS Water Supply Paper 1255.

Price, R.M., P.K. Swart, and J.W. Fourqurean. 2006. Coastal groundwater discharge—an additional source of phosphorus for the oligotrophic wetlands of the Everglades. *Hydrobiologia* 569:23–36. doi:10.1007/s10750-006-0120-5.

Rutkowski, C.M., W.C. Burnett, R.L. Iverson, and J.P. Chanton. 1999. The effect to groundwater seepage on nutrient delivery and seagrass distribution in the Gulf of Mexico. *Estuaries* 22:1033–1040. doi:10.2307/1353081.

Shinn, E.A., C.D. Reich, and T.D. Hickey. 2002. Seepage meters and Bernoulli's revenge. *Estuaries* 25:126–132. doi:10.1007/BF02696056.

Slomp, C., and P. Van Cappellen. 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology* 295(1–4): 64–86.

Smith, L., and W. Zawadski. 2003. A hydrogeologic model of submarine groundwater discharge: Florida intercomparison experiment. *Biogeochemistry* 66:95–110. doi:10.1023/B:BIOG.0000006108.80520.c9.

Stalker, J.C. 2008. Hydrological dynamics between a coastal aquifer and an adjacent estuarine system, Biscayne Bay, South Florida. Dissertation, Florida International University.

Stone, J.R., T.M. Cronin, G.L. Brewster-Wingard, S.E.Ishman, B.R. Wardlaw, and C.W. Holmes. 2000. A Paleoecological Reconstruction of the history of Featherbed Bank, Biscayne National Park, Biscayne Bay, Florida. USGS OFR: 00-191.

Swart, P.K., and R.M. Price. 2002. Origin of salinity variations in Florida Bay. *Limnology and Oceanography* 47:1234–1241.

Swart, P.K., R.M. Price, and L. Greer. 2001. The relationship between stable isotopic variations (O, H, and C) and salinity in waters and corals from environments in South Florida: implications for reading the paleoenvironmental record. *Bulletin of American Paleontology* 361:17–30.

Swarzenski, P., B. Burnett, C. Reich, H. Dulaiova, R. Peterson, and P. Meunier. 2004. Novel geophysical and geochemical techniques used to study submarine groundwater discharge in Biscayne Bay, Florida. USGS OFR: 2004-3177.

Swarsenski, P.W., C. Reich, K. Kroeger, and M. Baskaran. 2007. Ra and Rn isotopes and natural tracers of submarine groundwater discharge in Tampa Bay, FL. *Marine Chemistry* 104:68–94.

Taniguchi, M., W.C. Burnett, J.E. Cable, and J.V. Turner. 2002. Investigation of groundwater Discharge. *Hydrologic Processes* 16(11):2115–2129. doi:10.1002/hyp.1145.

Top, Z., L.E. Brand, R.D. Corbett, W. Burnett, and J.P. Chanton. 2001. Helium and radon as tracers of groundwater input into Florida Bay. *Journal of Coastal Research* 17:859–868.

Uchiyama, Y., K. Nadaoka, P. Rolke, K. Adachi, and H. Yagi. 2000. Submarine groundwater discharge into the sea and associated nutrient transport in a sandy beach. *Water Resources Research* 36 (6):1467–1479. doi:10.1029/2000WR900029.

Wanless, H.R., R.W. Parkinson, and L.P. Tedesco. 1994. Sea level control on stability of Everglades wetlands. In *Everglades, the ecosystem and its restoration*, eds. SM Davis and JC Ogden 199–224. Boca Raton, FL: St. Lucie.

White, W.B. 2002. Karst hydrology, recent developments and open questions. *Engineering Geology* 65(2–3):85–105.

Younger, P.L. 1996. Submarine groundwater discharge. *Nature* 382:121–122. doi:10.1038/382121a0.