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### Cover Page Footnote

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# Using Geochemical Tracers to Determine Seasonal Inputs of Freshwater to a Coastal Estuary: Biscayne Bay, FL

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Biscayne Bay is a coastal estuary that historically relied on rainfall and groundwater inputs from the karst Biscayne aquifer. The construction of major canals along the coastline has released point-source freshwater inputs into the bay, detrimentally affecting the Bay's ecosystem balance. This project investigates the proportional inputs of freshwater between the wet and dry seasons in Deering Estate, adjacent to Biscayne Bay. The objective of this project was accomplished by analyzing the water chemistry of the bay using naturally occurring geochemical tracers. Water sampling occurred from May to August (wet season 2022) and January to March (dry season 2023); at an inland freshwater spring and on Biscayne Bay. Water samples were analyzed for $\delta^{18}O$ and $\delta^{2}H$ values, and $Sr^{2+}/Ca^{2+}$ ratios as geochemical tracers. The highest and lowest salinity values observed in the wet and dry seasons, at both the freshwater spring and Biscayne Bay sites, were before and after a major rain event, respectively. The chemical analysis supports that rain is the dominant source of freshwater input into the bay at our sampling location, and the freshwater spring is dominated by groundwater and canal water during the wet season. During the dry season, groundwater and canal water are the dominant source for the sampling location in Biscayne Bay and the dominant source of freshwater input for the freshwater spring. However, all three endmembers contribute seasonally. Understanding freshwater inputs to this crucial estuary will provide important information for current restoration efforts of Biscayne Bay, specifically around the Deering Estate area.

**Keywords**: *water chemistry, seasonal inputs, coastal estuary, geochemical tracers*

## Introduction

Biscayne Bay is a federally protected, subtropical estuary located in southeastern Florida. Due to its ecological, environmental, and economic services, Biscayne Bay is one of Florida's most important resources, supporting a variety of flora and fauna (Lee & Bwenge, 2006). Underlying and adjacent to Biscayne Bay is the Biscayne Aquifer, a karst (Meeder and Harlem, 2019), shallow, and permeable aquifer that millions of people rely on for domestic, industry, and agricultural use (Alarcon et al., 2022). The Biscayne Aquifer is known to discharge freshwater into Biscayne Bay (Abd-Elaty et al., 2022; Stalker et al., 2009). Historically, precipitation and surface water that would drain from the Everglades, and groundwater were the main sources of freshwater input into Biscayne Bay (Langevin, 2001; Langevin 2003). However, due to the increase in the human population in South Florida over the last two centuries, canals and levees were built to redirect water from flowing south into the Everglades to discharge directly to the coast (Caccia & Boyer, 2007; Langevin, 2001; Langevin, 2003). What was once the transverse glades (low-lying areas that ran parallel to the Florida coastline), were dredged to build canals that would drain the wetlands and control flooding. In doing so, the groundwater table was lowered, increasing the risk of saltwater intrusion and dehydrating many existing wetlands (Langevin, 2001; Langevin 2003). The water management operations in South Florida resulted in increasing the direct inputs of freshwater via canals into Biscayne Bay while decreasing the quantity of groundwater discharge (Caccia & Boyer, 2007; Stalker et al., 2009). The quality, timing, and quantity of freshwater in the bay are crucial to the health and biodiversity of this ecosystem (Caccia & Boyer, 2007; Stalker et al., 2009).

Deering Estate, adjacent to Biscayne Bay, is a Miami-Dade County Park and the area of study for this paper. Deering Estate is part of the Biscayne Bay Coastal Wetlands project (BBCW) (U.S. Army Corps of Engineers, 2007) which is a project under the Comprehensive Everglades Restoration Plan (CERP). The aim of the BBCW project is to divert some of the canal water going directly into the bay, because water quality is dependent on this type of watershed (Caccia & Boyer, 2005) and instead redirect that canal water into freshwater and saltwater wetlands. Rehydrating the coastal wetlands, like the Deering Glade and Cutler Slough, promotes groundwater flow to the bay, and minimizes point source freshwater discharge from the canals and into the bay (U.S. Army Corps of Engineers, 2007; Lin et al., 2004). Geochemical tracers have been used to differentiate freshwater endmembers like precipitation from groundwater, or surface water (Swart and Price, 2002; Stalker et al., 2009, Stalker et al., 2014). Geochemical tracers such as the stable isotopes of oxygen and hydrogen ($\delta^{18}O$ and $\delta^{2}H$), and strontium and calcium ($Sr^{2+}/Ca^{2+}$) ratios are tools that help to differentiate and understand the quality and quantity of freshwater sources (Meyers et al., 1993, Stalker et al., 2014; Stalker et al., 2009; Yang et al., 2019). The geochemical tracers that were used in Stalker et al.'s research, to determine inputs of freshwater along Biscayne Bay, were also used in this investigation to determine the sources of freshwater inputs to Biscayne Bay, but within the Deering Estate area (Stalker et al., 2009). This research will provide new data on the Deering Estate's current seasonal freshwater inputs.

**Figure 1**

*Water sampling sites*


*Note*: This map demonstrates the two water sampling sites in Deering Estate, adjacent to Biscayne Bay, using two red dots to indicate the sites and study area of this project.

## Methods

### *Sample Collection and Analysis*

Water sampling occurred at two sites at the Deering Estate: one site was a freshwater inland spring inside a mangrove preserve, and the second site was on the western shore of Biscayne Bay (**Figure 1**). Surface water sampling occurred for two and a half months, in the 2022 wet season (May to August) and in the 2023 dry season (January to March). Water samples were collected two to three times a week. Prior to collecting water samples, the date and time were recorded. Other field parameters such as the salinity, temperature, and specific conductivity of the sites were collected using a PRO 2030 YSI. The surface water samples were collected with a syringe, rinsed three times with water from the site, and then filtered through a 0.45 µm filter to remove any sediment and particles present in the water. Water samples were kept in 125 mL polyethylene bottles (two bottles per site) and rinsed three times with surface water from the site before collection. The samples were then stored in a cooler with ice until transported to a refrigerator for a holding period of 30 days at Florida International University's (FIU) Hydrogeology Lab.

Both wet and dry season water samples were analyzed for the stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) with the Los Gatos DLT-100 Liquid-Water Isotope Analyzer instrument (Los Gatos Research; 67 East Evelyn Avenue, Suite 3, Mountain View, CA 94041) in the Hydrogeology Laboratory at the Modesto A. Maidique (MMC) Campus of FIU. Additionally, water samples were analyzed in FIU's CREST CAChE

Lab located on the Biscayne Bay Campus (BBC) for strontium, and the Hydrogeology Lab at MMC for calcium (for wet season water samples) using a Dionex Aquion Ion Chromatography System for cations. Dry season samples were analyzed for calcium using an ICP-OES Varian Vista Pro; at the University of Miami's Stable Isotope Laboratory. Water samples analyzed for cations were acidified to a pH of 2 to prevent adsorption of the cations to the sides of the bottles and to ensure the accuracy of results. The cation samples were then diluted to 1/100 of the samples that were acidified. Two binary mixing models were used to identify the sources of freshwater discharge into Biscayne Bay and Deering Spring.

**Linear Regression Isotope Method.** The $\delta^{18}O$ and $\delta^{2}H$ values were both compared to the salinity of the water samples that were recorded on the day of collection of the water samples. There were three endmembers of freshwater inputs to the bay: groundwater, canal water, and rainwater. The salinity of the three freshwater endmembers was given a value of 0. The isotropic values of these three endmembers were collected from Stone and Price (2021) and compared to the Biscayne Bay and the freshwater inland spring samples in an effort to determine the influence of the endmembers on the change in salinity at the two study sites. The wet and dry season data were divided and plotted separately to determine the $\delta^{18}O$ and $\delta^{2}H$ values at a zero-salinity intercept. This method allows the use of the isotopic signature of water to differentiate freshwater sources like precipitation and groundwater from each other. In this paper, using $\delta^{18}O$ and $\delta^{2}H$ values of the water samples allowed us to differentiate the three freshwater endmembers from each other.

**Cation Mixing Model.** Underlying Biscayne Bay is the Biscayne Aquifer, a limestone aquifer composed of minerals like calcite and other trace minerals like aragonite. Strontium ($Sr^{2+}$) ions can be found in soil and rocks and commonly replace calcium ($Ca^{2+}$) ions in calcium carbonate minerals during the recrystallization process. Therefore, $Sr^{2+}/Ca^{2+}$ ratios can be used to determine freshwater inputs as there is a relationship between the host rock of Biscayne Bay and local groundwater (Swart et al. 2001; Meyers et al. 1993). Using only isotropic signatures of the water samples does not allow to fully distinguish precipitation and groundwater signatures, thus, the need to use $Sr^{2+}/Ca^{2+}$ mixing ratios with salinity (Stalker et al., 2009). The data points of the water samples were plotted with the three endmembers mixing with seawater to identify how the three freshwater endmembers are interacting with one another at the two sites of study in this paper.

## Results and Discussion

### *Stable Isotopes of Oxygen and Hydrogen*

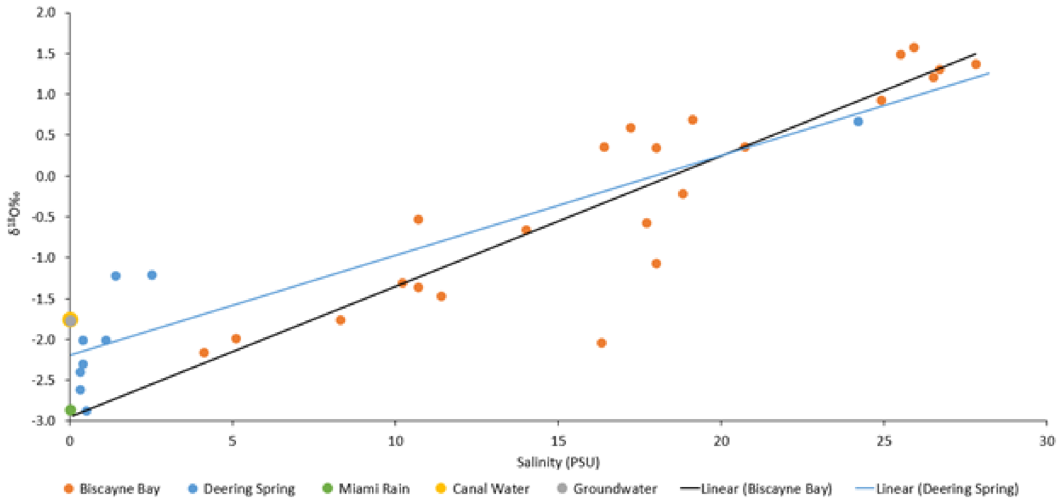
The best-fit, linear regression line, representing the change in $\delta^{18}O$ with salinity (**Figure 2**) for the Biscayne Bay water samples collected in the wet season, intercepted with the Miami rain freshwater endmember. For the Deering Spring water samples, most had lower salinity than that of Biscayne Bay with values $\delta^{18}O$ varying between the three freshwater endmembers (e.g. rainwater, groundwater, and canal water). The intercept of the best-fit linear regression line of $\delta^{18}O$ with salinity of the Deering Spring water samples on the best-fit, linear regression fell close to the canal water and groundwater end-member. The results of $\delta^{2}H$ with salinity (**Figure 3**) for both the Biscayne Bay and Deering Spring water samples supported the $\delta^{18}O$ with salinity results (**Figure 2**). The isotope results suggest that Miami rain is the dominant freshwater input for Biscayne Bay during the wet season while the salinity of Deering Spring is influenced by groundwater and canal water. During the wet season, it is common for large amounts of rainfall to occur throughout May through August at the time that the water samples were collected. Approximately 75% of the total rainfall throughout the year occurs during the wet season (Alarcon et al., 2022). The greater influence of canal water and groundwater on the variation in salinity of Deering Spring may be due to its more inland location.

A comparison of $\delta^{18}O$ and $\delta^{2}H$ of both Biscayne Bay and Deering Spring water samples collected in the wet season (**Figure 4**) tend to fall either on or below the solid black line which represents the global meteoric water line (GMWL). Samples plotting below the GMWL fall along a linear regression line that is representative of both an evaporation line and a seawater-freshwater mixing line. The evaporation line in **Figures 4** and **7** allows us to distinguish between the isotropic signatures of the different freshwater endmembers (Bowen et al., 2018). The evaporation line intersects the GMWL in the vicinity of Miami rainfall indicating that rain is the original source of freshwater for those water samples.

The dry season results are slightly different than what was observed in the wet season. For instance, the best-fit, linear regression line between $\delta^{18}O$ and salinity for the Biscayne Bay water samples intercepted the $\delta^{18}O$ axis near the canal water and groundwater endmember (**Figure 5**), and Miami rain as a contributing source. For Deering Spring, major inputs of freshwater came from Miami rain with the other freshwater endmembers contributing as freshwater inputs. Results from the $\delta^{2}H$ (**Figure 6**) showed similar results from **Figure 5**: the linear regression of the Biscayne Bay samples demonstrated that Biscayne Bay received a majority of freshwater input from canal water and groundwater in the dry season. Deering Spring received major inputs from Miami rain and contributions of freshwater inputs from groundwater and canal water. During the dry season, there is much less precipitation during this time of the year, as most of the rainfall occurs during the wet season, therefore there is minimal input from precipitation into the bay. As for Deering Spring, it is located in an ecotone of dense tropical hardwood hammock and mangrove forest, permitting minimal evaporation. The results of this investigation support the idea that progress towards the rehydration of the coastal wetlands in the Deering Estate area can bring groundwater flow back to Biscayne Bay. **Figure 7** compares the isotropic signatures of the water samples' $\delta^{18}O$ and $\delta^{2}H$ to the GMWL. Below the GMWL is the evaporation line and seawater-freshwater mixing line for the Biscayne Bay water samples. The isotopic signatures of each of the three freshwater endmembers are also plotted for comparison. Note that the line through the Biscayne Bay water samples intersects the GMWL on the Miami rain endmember further confirming that Miami rain is the source of freshwater to Biscayne Bay in the dry season. Note that the best-fit, linear regression is based on a limited amount of data, therefore, data points that do not fall directly on the linear regression lines suggest that the freshwater endmembers are mixing with one another.

**Figure 2**

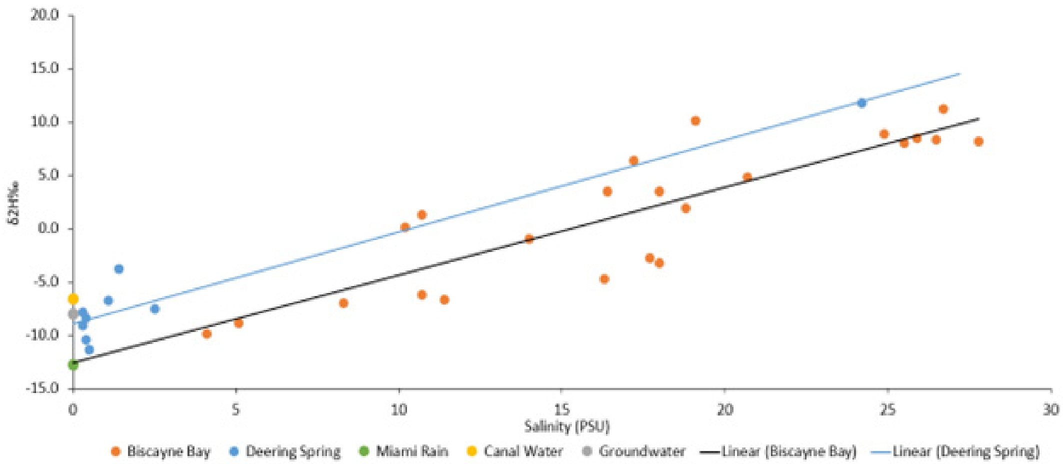
*Wet season isotope of oxygen data*




*Note*: The wet season results of δ$^{18}$O values of Biscayne Bay and Deering Spring water samples, plotted against three freshwater endmembers (groundwater, Miami rain, and canal water). The black line represents a linear regression of the bay samples, and the blue line represents a linear regression of the Deering Spring samples.

**Figure 3**

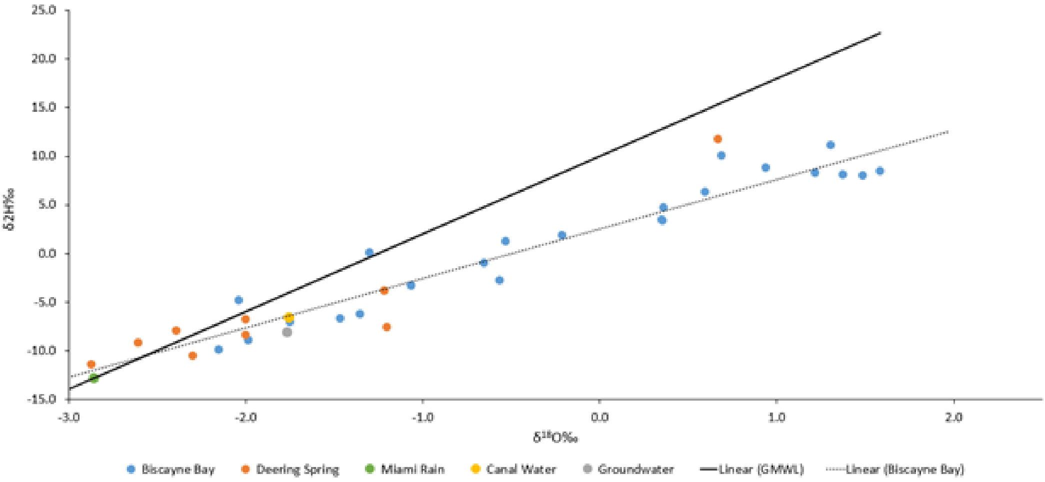
*Wet season isotope of hydrogen data*




*Note*: The wet season results of δ$^{2}$H values of Biscayne Bay and Deering Spring water samples, plotted against three freshwater endmembers (groundwater, Miami rain, and canal water). The black line represents a linear regression of the bay samples, and the blue line represents a linear regression of the Deering Spring samples.

**Figure 4.**

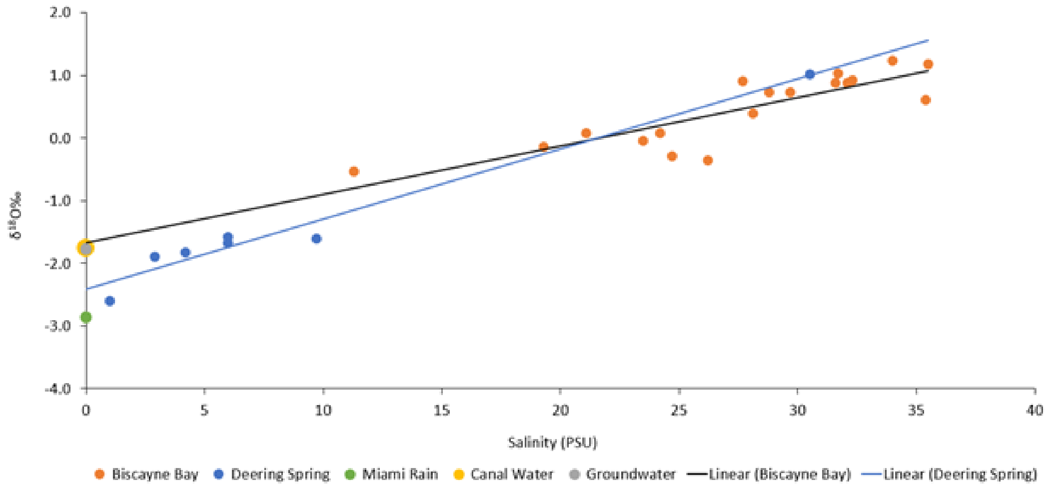
*Global Meteoric Water Line Graph for wet season results*




*Note*: Mixing with seawater and evaporative processes (below the GMWL), the data points near the solid line are influenced by rain. Groundwater and canal water reside on the evaporation line. The dashed line represents linear regression of Biscayne Bay samples.

**Figure 5**

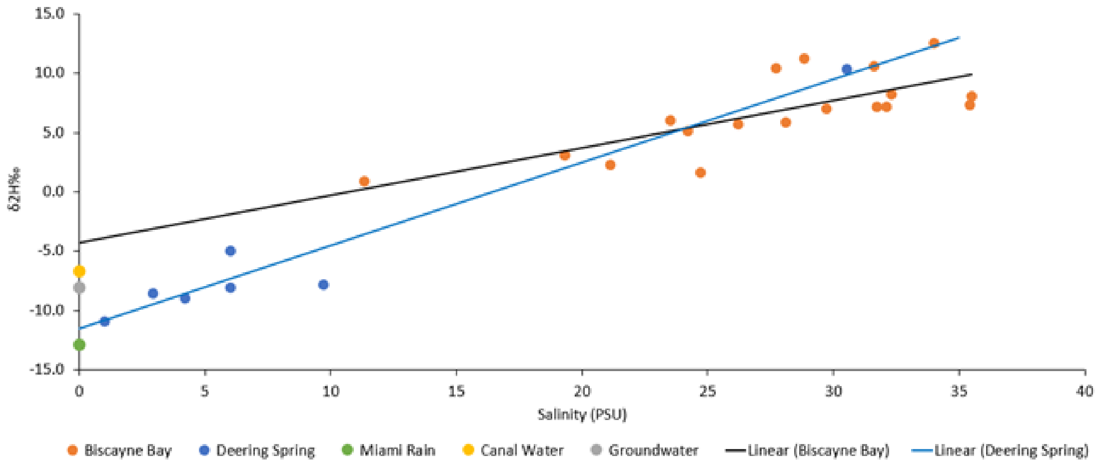
*Dry season isotope of oxygen data*




*Note*: Dry season $\delta^{18}O$ values plotted against the salinity of Biscayne Bay and Deering Spring water samples. The graph shows a linear regression line through the Biscayne Bay samples and another linear regression line through the Deering Spring samples. The water samples are compared against the three freshwater endmembers.

**Figure 6**

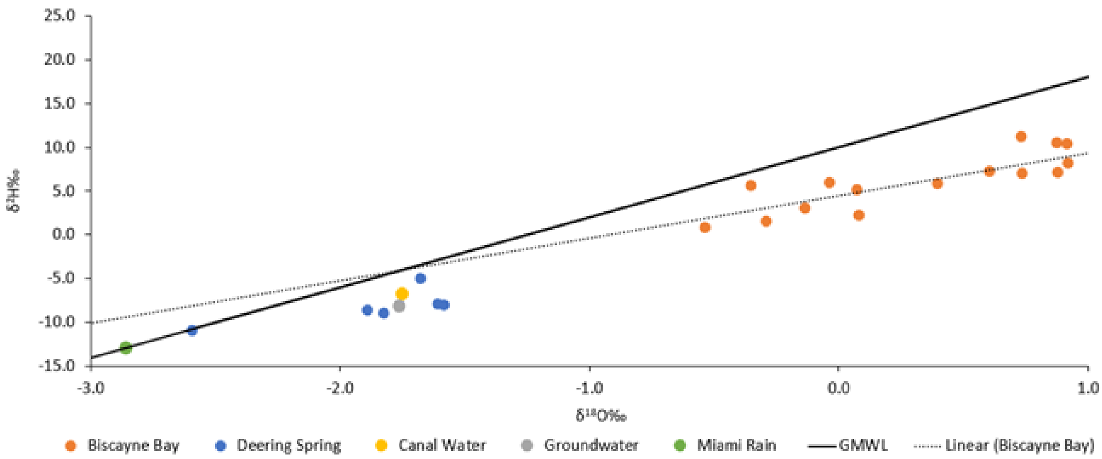
*Dry season isotope of hydrogen data*




*Note*: Dry season $\delta^2H$ values plotted against salinity of Biscayne Bay and Deering water samples. Linear regression is shown through the Biscayne Bay samples with a black line, and a blue line to show the Deering Spring linear regression. The water samples are compared to three freshwater endmembers found to be freshwater inputs in the bay.

**Figure 7**

*Global Meteoric Water Line Graph for dry season results*



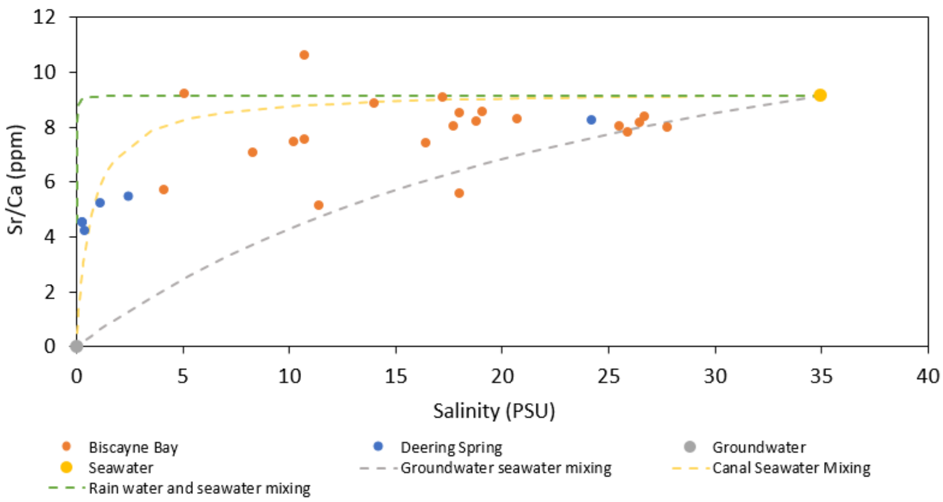

*Note*: Mixing with seawater and evaporative processes (below the GMWL), the data points near the solid line are influenced by rain. Groundwater and canal water reside on the evaporation line. The dashed line represents linear regression of Biscayne Bay samples.

**Cation Mixing Model.** The variation of strontium/calcium ratios with salinity of the water samples was compared with mixing models (dashed line curves) of how the three freshwater endmembers would be expected to mix with seawater (**Figures 8** and **9**). Some data points do not directly lie on the curves but lie between two curves within the graph. Those results can be interpreted as more than one freshwater endmember interacting with one another and discharging into the water sample collection sites. The wet season results (**Figure 8**) exhibit that freshwater inputs to the Biscayne Bat site can come from all freshwater sources: rainfall, canal water, and groundwater. The Deering Spring site received major inputs from canal water with portions of freshwater inputs from rainwater and groundwater. The dry season results (**Figure 9**) showed that canal water and groundwater were a major freshwater input for Biscayne Bay, as well as rainwater being a minor contributor. Deering Spring water samples indicate that groundwater is a major contributor to freshwater input as well as canal water influencing freshwater inputs.

The results of the variations of Ca/Sr with salinity can be interpreted as all three freshwater sources, groundwater, canal water, and rainwater are all important contributors of freshwater to Deering Spring and Biscayne Bay. However, rainwater is the ultimate source of freshwater contributing to both groundwater and canal water in the region. The results presented in this investigation may differ from those obtained in an earlier investigation conducted by Stalker et al. (2009) as a larger data set was included in that investigation. Stalker et al. (2009) collected water samples from twenty-five stations in Biscayne Bay, twelve groundwater wells, and ten canals over a period of two years. Also, the Stalker et al. (2009) project covered a larger area of Biscayne Bay compared to only two site samples over one year in the present investigation. Nonetheless, the data presented in this investigation are a good indication of how the BBCW restoration plan is restoring groundwater flow into Biscayne Bay through the wetlands at Deering Estate.

**Figure 8**

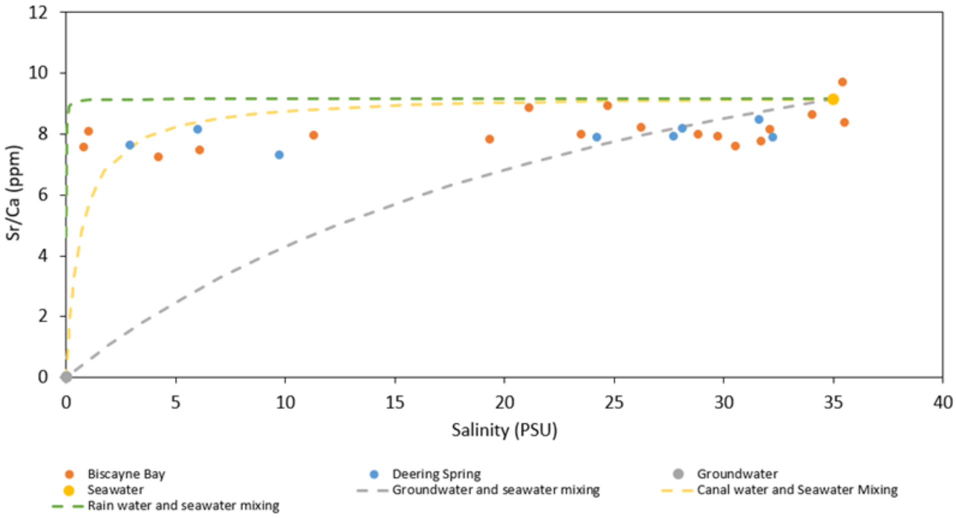
*Wet season strontium to calcium mixing ratio model*




*Note:* The wet season results of the strontium/calcium ratio mixing model between the three freshwater endmembers mixing with seawater plotted against the salinity of the water samples. The three dashed lines represent canal water, groundwater, and precipitation as the freshwater endmembers mix with seawater.

**Figure 9**

*Dry season strontium to calcium mixing ratio model*




*Note*: The dry season results of the strontium/calcium ratio mixing model between the three freshwater endmembers mixing with seawater plotted against the salinity of the water samples. The three dashed lines represent canal water, groundwater, and precipitation as the freshwater endmembers mix with seawater.

**Salinity.** During the wet season, the salinity ranges of the Deering Spring water samples site ranged from 0.3 to 24.2 PSU, which was lower than the salinity range of the Biscayne Bay water samples site which was 4.1 to 27.8 PSU. Most high and low salinities recorded were before and after a rainstorm, respectively. During the dry season, the salinities of the Deering Spring water samples site ranged from 0.8 to 30.5 PSU, while the Biscayne Bay site had a salinity range of 11.3 to 35.5 PSU.

## Conclusion

The results of this investigation demonstrate that rainwater is the original source of freshwater for Biscayne Bay and Deering Spring. A combination of stable isotopes, strontium/calcium ratios, and salinity were used to indicate that canal water and groundwater are also contributing sources of freshwater inputs for Deering Spring and Biscayne Bay. The goal of South Florida Water District Management and the Army Corps of Engineers of the BBCW project is to restore groundwater flow back to Biscayne Bay through the Deering Estate wetlands. The results of this investigation suggest that this is indeed happening. Especially during the dry season when precipitation occurrence is lower than in the wet season. Canal water that is being pumped into Deering Estate's wetlands is contributing to shallow groundwater but can still be identified as isotopically different. Further research should include nutrient input from the wetlands into Biscayne Bay within the Deering Estate area to understand how this may be affecting the water quality and properties of soil of the Deering Estate wetlands and Biscayne Bay.

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