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Seasonal and spatial variation in the stable isotopic composition (δ18O and δD) of precipitation in south Florida

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Working Title: **Seasonal and Spatial variation in the stable isotopic composition ($\delta^{18}O$ and δD) of precipitation in south Florida**

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Abstract

Precipitation data collected from 5 sites in south Florida indicate a strong seasonal and spatial variation in $\delta^{18}O$ and δD, despite the relatively limited geographic coverage and low-lying elevation of each of the collection sites. Based upon the weighted-mean stable isotope values, the sites were classified as coastal Atlantic, inland, and lower Florida Keys. The coastal Atlantic sites had weighted-mean values of $\delta^{18}O$ and δD of -2.86 ‰ and -12.8 ‰, respectively, and exhibited a seasonal variation with lower δD and $\delta^{18}O$ values in the summer wet-season precipitation ($\delta^{18}O$ = -3.38 ‰, δD = -16.5 ‰) as compared to the winter-time precipitation ($\delta^{18}O$ = -1.66 ‰, δD = -3.2 ‰). The inland site was characterized as having the highest d-excess value (+13.3 ‰), signifying a contribution of evaporated Everglades surface water to the local atmospheric moisture. In spite of its lower latitude, the lower Keys site located at Long Key had the lowest weighted mean stable isotope values ($\delta^{18}O$ = -3.64 ‰, δD = -20.2 ‰) as well as the lowest d-excess value of (+8.8 ‰). The lower δD and $\delta^{18}O$ values observed at the Long Key site reflect the combined effects of oceanic vapor source, fractionation due to local precipitation, and slower equilibration of the larger raindrops nucleated by a maritime aerosol. Very low δD and $\delta^{18}O$ values ($\delta^{18}O < -6$ ‰, $\delta D < -40$ ‰) were observed just prior to the passage of hurricanes from the Gulf of Mexico as well as during cold fronts from the north-west. These results suggest that an oceanic vapor source region to the west, may be responsible for the extremely low δD and $\delta^{18}O$ values observed during some tropical storms and cold fronts.

1.1 Introduction

Natural variations of $\delta^{18}O$ and δD in precipitation have been used in a variety of hydrologic, ecological, and climate studies. As an integral part of the hydrologic cycle, $\delta^{18}O$ and δD in precipitation was used as a tracer of groundwater recharge (Gat, 1971; Lee et al., 1999; Price and Swart, 2006; Scholl et al., 1998), as well as a source of river water (Dutton et al., 2005; Welker, 2000) and lake water (Gonfiantini, 1986; Hostetler and Benson, 1994). In ecological studies, δD values of precipitation have been used to determine the migration patterns of birds (Hobson et al., 2001; Hobson and Wassenaar, 1996) and other animals (Rubenstein and Hobson, 2004), as well as plant physiological functions (Ehleringer et al., 1991; Flanagan et al., 1992). In climate studies, historical variations in $\delta^{18}O$ and δD of precipitation have been inferred as preserved in tree cellulose (Anderson et al., 1998), ice cores (Dansgaard et al., 1993), and carbonates (Hays and Grossman, 1991). The δD and $\delta^{18}O$ of precipitation can be used as an indicator of climatic conditions as higher precipitation amounts tend to produce lower δD and $\delta^{18}O$ values (Dansgaard, 1964). In addition, the δD and $\delta^{18}O$ of precipitation from hurricanes and tropical storms tend to be very low (Lawrence and Gedzelman, 1996), as they act as efficient fractionation chambers (Gedzelman et al., 2003; Trenberth, 2005). Meteorological opinion is divided on the effects on Atlantic Tropical Cyclone (TC) numbers and intensity of global warming (Emanuel 2005, Webster et al. 2005, Pileke et al. 2005, Pielke 2007) or natural cycles (Goldenberg et al. 2001, Mann and Emanuel 2006).The 107 year (1900-2006) quantitative record is too short relative to documented natural climatic variations and suffers from observational lacunae before 1960 when meteorological satellites came into use (Landsea et al. 2006, Landsea 2007). Consequently, geological proxy records will prove essential as baselines for assessing both anthropogenic changes in hurricane activity and natural variability in the unforced climate

(Liu 2004). There is an observed increase in surface sea temperature (Emanuel 2005, Webster et al. 2005), which in turn is expected to lead to increased evaporation and atmospheric moisture. This could lead to higher precipitation amounts and potentially to a change in the stable isotopic signature of precipitation and subsequently surface waters and groundwaters of these regions.

The δD and $\delta^{18}O$ of precipitation is currently measured at over 300 stations across the globe as part of the Global Network for Isotopes in Precipitation (GNIP), which is co-operated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) (http://isohis.iaea.org). Despite the large number of stations in the GNIP, there are only four active coastal sites (Cuba; Bermuda; Hatteras, North Carolina, and the Dominican Republic) in the tropical Atlantic where hurricanes are frequent. Although a site in Miami, Florida is currently part of the GNIP for tritium, it is not included for the stable isotopes of oxygen and hydrogen. Amount-weighted annual precipitation maps produced from the GNIP data set have the isotopic composition of precipitation in south Florida between -2 ‰ and -6 ‰ for $\delta^{18}O$, and -6 ‰ to -38 ‰ for δD. Precipitation collected from the region and published to date corresponded with the GNIP values (Price and Swart, 2006; Swart et al., 1989; Wilcox, 2004). Each of those studies reported variability in the isotopic composition of precipitation in south Florida, but there was no attempt to correlate precipitation $\delta^{18}O$ and δD values on a seasonal or event driven basis. The objectives of this study were 1) to establish a long-term data set of the oxygen and hydrogen isotopic composition of precipitation in south Florida in order to assist in hydrologic and ecohydrologic studies being conducted in the region; 2) to document the seasonal (short-term) and spatial variability in the stable isotopic composition of precipitation in a semi-tropical, coastal region where temperature changes are minimal; and 3) to show the influence of hurricanes on the isotopic composition of subtropical rainfall.

1.2 South Florida Weather

The Miami metropolitan area has a tropical, maritime climate (Trewartha 1954) characterized by a June-October rainy season (Fig. 1). In summer and early fall, prevailing winds blow from the southeast. The winds circle around the western end of the Bermuda High and import Maritime-Tropical Air from the tropical North Atlantic. During this period, south Florida weather is dominated by the diurnally forced sea-breeze, occasional easterly waves that originate from Africa, and tropical cyclones that may drop tens of centimeters of precipitation in a single event as they make landfall.

The months of November through May are characterized by a quasi-periodic alternation of Maritime-Tropical Air with modified Continental-Polar Air from a high latitude North-American source. The four- to eight- day middle-latitude cyclone cycle sets the tempo of the weather. Most of the time, even in winter, Maritime Tropical air covers South Florida. As cold fronts approach, the south-easterlies strengthen. Brief, but sometimes intense, precipitation occurs as the front passes and the wind veers from the northwest or north and temperatures fall. Many winters see episodes with single-digit (Celsius) temperatures, but frost is rare. In the days after frontal passage the wind veers from the northeast, east, and finally from the southeast again.

Most of the moisture that falls as precipitation in southeast Florida originally evaporated from the trade-wind belt of the topical North Atlantic. Air entering the Trades of the African coast has a low inversion capped by a strong surface mixed layer with much drier air above. As it follows a westward trajectory, evaporation from the sea moistens the air below the inversion while convectively generated turbulence raises the inversion by downward entrainment and moistening of dry air from above (Riehl and Malkus 1957). Showers confined to the most air below the inversion further fractionate the stable isotopes toward low ratio values. During the

South Florida rainy season, upstream diurnal convection over the Bahamas and Greater Antilles as well as nighttime convection offshore over the Gulf Stream enhance this effect.

Rarely during the cool season, when a deep, long-wave trough digs southward near longitude 80^{o} W, the resulting low-latitude westerlies bring moisture from the Gulf of Mexico, Caribbean, or even the tropical Western Pacific. While local evapotranspiration rates are high over the Florida peninsula in summer, air-mass residence times over the land are so short that little moisture is recycled locally. Price and Swart (2006) have determined through a stable isotope evaporation model, that evaporated seawater is the dominant contributor of atmospheric moisture that moves over south Florida, and that evaporation of Everglades surface water contritubes between 7 and 12% of the local atmospheric vapor.

2.0 Methods

Precipitation samples were collected at five sites in south Florida (Fig. 2). Two sites were located along the eastern coastline of south Florida; one on the roof of the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS) and the other at the headquarters of Biscayne National Park (BNP). Two sites are located along the Florida Keys, one at Key Largo and the other in Long Key. The precipitation collectors at BNP, Key Largo, and Long Key were on docks positioned either over the water or adjacent to the coastline. The elevation of these collectors were less than 2 m above mean sea level. The Redlands site is located approximately 16 km at an elevation of about 3 m above sea level. The RSMAS precipitation collector was located about 100 m inland at an approximate elevation of 13 m.

At all but the Redlands site, precipitation was collected in a wet/dry collector made by Aerochemitrics. This collector has two buckets, one to collect dry deposition and the other to collected wet deposition (precipitation). Contents of the dry deposition bucket were not used in this study. The collector was equipped with a sensor that when wet activated a mechanical arm that moved a cover from the wet collection bucket to the dry collection bucket, thereby exposing the wet collection bucket to receive precipitation. The sensor was heated and allowed for rapid evaporation of atmospheric moisture that had collected on it at the end of a precipitation event, and once dry, the mechanical arm moved back to cover the wet collection bucket. The cover consisted of a foam pad encased in plastic wrap and formed a tight seal over the wet collection bucket to prevent evaporation of the sample. On a weekly basis, water from the collector was transferred to a 40 mL glass bottle and sealed with a rubber stopper and crimp cap. At the Redlands site, precipitation was collected in a standard forestry 6-inch rain gauge on a daily basis and then transferred to a dark, capped bottled that was kept indoors. On an approximately monthly basis, water from this bottle was transferred to a smaller 120-mL plastic bottle with a screw cap.

Precipitation amount was recorded at the RSMAS site by measuring volumetrically the amount of water collected. At the Redlands site, precipitation amount was recorded from the 6-inch forestry rain gauge. At the Key Largo site and Long Key sites, precipitation amount was recorded by measuring with a ruler inside of the collection bucket, which had straight sides. Precipitation amounts were missing from the BNP site, therefore, precipitation data recorded at the Homestead Airforce Base (NOAA web site reference), approximately 1 mile inland of BNP was used instead (Fig. 2). The precipitation amount was combined with the δD and δ^{18}O values to determined amount-weighted mean values for each site.

This paper presents precipitation data collected at five sites in south Florida (Fig. 2) from 1997 through 2006. The collection times at each of the sites varied (Table. 1). The longest record is from the RSMAS site with about five years of approximately weekly data spanning two time periods from Dec. 1999 until Aug. 2001, and then between Aug. 2003 and Dec. 2006. Four years of monthly precipitation samples were collected at the Redland site between Aug. 1997 and Aug. 2001. Three years of weekly precipitation data was collected at BNP between Sept. 2003 and Sept. 2006. Precipitation was collected for one year at the Key Largo and Long Key sites; however, breakage of many of the sample bottles from Key Largo resulted in only 18 weekly samples available for isotope analysis. Concerns over loosing the collectors at the Key Largo, RSMAS and BNP sites in hurricane force winds, often prompted the removal of these collectors several days prior to the approach of hurricanes. As a result, precipitation was not collected during landfall of some hurricanes including hurricane Mitchell between November 3 – 19, 2001 and hurricanes Katrina and Wilma in August and October of 2005, respectively.

The number of samples collected at each of the sites was not evenly distributed throughout the year. A lack of precipitation during the dry-season months of February through April resulted in very few precipitation samples collected during these months. There were often 2 to 3 times as many precipitation samples available at each site during the rainy season months of June through November, than for the dry season months. For example, of the 64 samples analyzed from BNP, only 11, representing 17% of the samples, were collected between January and May, with no precipitation samples collected in April. At the Redland site, 2 or fewer samples were available for the months of December, March and April. Seasonal amount weighted-mean values of δ^{18}O, δD and d-excess were determined at four sites: Redlands, RSMAS, BNP, and Long Key as at least 1 year of data was obtained from these sites. The data from each site was grouped into wet-season (June through October) and dry season (November through May). In order to determine the seasonal trends in the δD and δ^{18}O values, the RSMAS data set (the site with the longest record) were averaged into weekly values using retangular interpolation methods and subjected to frequency analysis using Statistica.

A total of 286 samples of precipitation were analyzed in duplicate for $\delta^{18}O$ and δD at RSMAS by mass spectrometry using modified methods of (Epstein and Mayda, 1953) and (Coplen et al., 1991), respectively. The δD and $\delta^{18}O$ values are reported using the conventional notation relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. The mass spectrometer used was a Europa Geo 20-20 equipped with an autosampler-equilibration unit (Europa WES). Samples were analyzed in duplicate. The precision of these methods was ±0.08 ‰ for $\delta^{18}O$ and ±1.5 ‰ for δD. Deterium excess (d-excess or '*d*') of each of the water samples was estimated as $d = \delta D - 8\delta^{18}O$ (Dansgaard, 1964).

Climatologically data for south Florida was obtained from the National Climatic Data Center (http://www.ncdc.noaa.gov). Long-term data (1971 – 2006) was obtained from Miami International Airport. Precipitation and air temperature data were obtained from this site and compared to isotopic data collected in this investigation.

3.0 Results

3.1 Stable isotopic variation by location

The $\delta^{18}O$ values of all the precipitation data ranged from -10.31 ‰ to +1.53 ‰, with 92 % of the values occurring between -4.5 ‰ and +1.5 ‰ (Tables 2-6). Precipitation δD values ranged from -77.8 ‰ to +21.0 ‰, with 92% of the values occurring between -30 ‰ and +20 ‰. The $\delta^{18}O$ and δD values plot close to the Global Meteoric Water Line (GMWL) as defined by (Craig, 1961) as having a slope of 8 and an intercept of 10 (Fig. 3). A least square regression of the data resulted in the equation:

$$\delta D=(7.4 \pm 0.2)\ \delta^{18}O+(8.62 \pm 0.49)\ r^2=0.86\ n=280; \qquad (1)$$

while an orthogonal regression of the data resulted in the equation:

$$\delta D=(8.6 \pm 0.4)\ \delta^{18}O+(11.0 \pm 0.9)\ r^2=0.86\ n=280. \qquad (2)$$

The weighted-mean values of all the data were $\delta^{18}O = -2.98 \pm 0.12$ ‰ and $\delta D = -12.9 \pm 0.9$ ‰ (Fig. 3).

Weighted-mean values of $\delta^{18}O$ and δD varied by site (Fig. 4). Precipitation collected at the Long Key site had the lowest precipitation amount weighted-mean $\delta^{18}O$ and δD of -3.64 ‰ and -20.2 ‰, respectively, and were significantly different than values obtained for the other four sites. The weighted-mean stable isotope values for precipitation collected at RSMAS, BNP, and Key Largo were similar and overlapped within their respective standard error. The weighted-mean stable isotope value for the Redland site fell to the left of the GMWL (Fig. 4).

3.2 Stable isotope variation with time

Observation of the $\delta^{18}O$ values for each site with time, indicate events with large negative shifts (Fig. 5). These events are identified by the names of tropical storms where appropriate or by their dates of collection when there was no tropical cyclone. Some of these events, such as Hurricane Irene (Oct. 1999) (Fig. 5) and the No-name storm (Oct. 2000) coincide with high amounts of precipitation in which over 254 mm of precipitation fell within a 24-hour period.

However, the lowest stable isotope values were recorded from precipitation collected one and two weeks prior to Hurricane Wilma making landfall on October 2005.

The results of the spectral analysis of the RSMAS data resulted in strong positive peaks at 52 weeks, 31 to 33 weeks, and 12-14 weeks (Fig. 6) The 52 week period reflects an annual variation in the $\delta^{18}O$ values, while the 31-33 week peak reflects differences between the isotopic values of the precipitation in the wet and dry seasons. When the precipitation data were grouped into wet and dry seasons, significantly lower values in $\delta^{18}O$ and δD were obtained at RSMAS and BNP during the wet season as compared to the dry season (Table 7). The seasonal averaged $\delta^{18}O$ and δD values for the Redland and Long Key sites were within the standard error for the wet and dry seasons. Amount-weighted, annual values of $\delta^{18}O$ and δD were determined for those sites with a complete year of data (Table 8). At the Redlands site, for the years 1998 through 2000, the most negative $\delta^{18}O$ and δD values were observed in 1999, while the least negative values were observed in 1998. Precipitation collected at the RSMAS and BNP had the least negative isotopic values in 2004, and the most negative values in 2005.

South Florida precipitation as measured at the Miami International Airport (MIA; NCDC web site) indicates that during the 10 years of this study, annual precipitation varied from 138 cm yr^{-1} in 2004 to 183 cm yr^{-1} in 2003 (Fig. 7). The 10-year average of 167 cm yr^{-1}, was higher than the 30-year average (1976-2005) value of 155 cm yr^{-1}. In general, above average precipitation occurred throughout the 10-year period except for 2004 (Fig. 7).

4.0 Discussion

4.1 Spatial Variability

Dansgaard (1964) was the first to recognize that the δD and δ^{18}O composition of precipitation was negatively correlated with temperature, latitude, altitude, distance from the coast, and the amount of precipitation. Of those correlations, temperature and the continual loss of moisture from an air mass as it moves away from its evaporative vapor source are considered to be overriding factors (Yurtsever 1975; Gat 1996). However, mixing of different air masses from local vapor sources (Gat and Matsui, 1991) as well as storm trajectory (Friedman et al., 1992; Lawrence et al., 1982) also influence the isotopic signature of local precipitation.

Despite the relatively limited geographic coverage and low-lying elevation of each of the collection sites, the precipitation data from the five sites monitored in south Florida can be grouped into the 3 geographic classifications based upon their isotopic signatures: 1) coastal Atlantic; 2) inland; and 3) lower Keys. These classifications are similar to the coastal, continental, and marine sites, respectively, first defined by Rozanski et al. (1993) during the review of the GNIP network. The coastal Atlantic sites in south Florida include RSMAS, BNP, and Key Largo. These sites are characterized as having the highest mean δ^{18}O and δD values (Table 1) that fall on or near the GMWL (Fig. 4) and are located within 100 m of the coastline. The Redlands site is classified as an inland site. Although most common for inland sites to have lower δD and δ^{18}O values than coastal sites due to "rain-out" of a moisture air mass as it moves inland, this effect can be lessened with an intense recycling of water from within a basin by evapotranspiration as observed in the Amazon Basin (Martinelli et al., 1996). The plotting of the weighted-mean δD and δ^{18}O values of the Redland data to the left of the GMWL (Fig. 4) along with a high d-excess value (>13 ‰), particularly in the wet season (Table 7) points to a contribution of evaporated surface water from the Everglades to the local atmospheric moisture, which can be as high as 12% (Price and Swart, 2006).

The δD and $\delta^{18}O$ composition of precipitation from Long Key is significantly more negative compared to the other south Florida sites (Fig. 4). It also has the lowest d-excess value of all the sites, particularly in the wet season (Table 7). This period of data collection at the Long Key site, however, only partly overlaps the Key Largo station, and not at all with the other sites. Low d-excess values (<10 ‰) tend to be found over oceanic vapor source regions with high annual relative humidity (>85%) (Bowen and Revenaugh, 2003; Merlivat and Jouzel, 1979). Annual relative humidity (R.H.) over the waters of the west Florida Shelf average near 75% (Virmani and Weisberg, 2005), with lower R.H. values in the summertime due to higher air temperatures. This average annual R.H is also similar to that measured at Miami airport of 74% (www.ncdc.noaa.gov), therefore, higher R.H. values do not seem to be responsible for the lower d-excess and lower isotopic values measured at Long Key. Higher precipitation amounts have been correlated with lower isotope values (Dansgaard, 1964), however, precipitation amounts in south Florida lesson towards the south. For instance, during the year that precipitation was collected at Long Key (2002) precipitation amounts varied from north to south from 1,600 mm at Miami International Airport to 1,510 mm in Key Largo and 993 mm at Long Key (www.ncdc.noaa.gov/7.17.07). This is consistent with a sea-breeze effect causing more rain over the mainland of Florida as compared to adjacent islands (Pielke, 1974).

The air passing over Long Key derives predominantly from the tropical North Atlantic. It contains a maritime aerosol with ~10^2 condensation nuclei cm^{-3} exhibiting a wide range of activities. Convective clouds forming in this air produce precipitation easily through the collision coalescence at temperatures warmer than -10°C. The resulting large raindrops fall to the surface quickly without opportunity to equilibrate with lower-tropospheric vapor. By contrast, continental aerosols contain ~10^3 condensation nuclei cm^{-3} and produce precipitation primarily through the Bergeron-Findeisen process. Although hydrometeors form at colder temperatures, convective instability is generally too weak to produce hail. In these clouds, snow produced at temperatures colder than -20°C, falls though the 0°C isotherm (at ~6 km) and melts to form relatively small raindrops (Fletcher 1969). Because of their large area to volume ratios and slow terminal velocities, they have a chance to equilibrate with lower-tropospheric isotope ratios. Also precipitation over the ocean tends to occur in the late evening to early morning hours when temperatures are cooler as compared to most land areas in the afternoon when precipitation peaks (Yang and Smith, 2006). Both larger raindrops as well as the potential for more night-time precipitation (Yang and Smith, 2006) may explain the lower isotopic signature of precipitation at the Long Key site. Remember, that the observations at the Long Key site are based on only one year of precipitation data, and additional monitoring may be necessary to confirm the results presented here.

4.2 Seasonal Variability

A seasonal variation in the δD and $\delta^{18}O$ signature of the precipitation in south Florida is observed with lower values obtained during the wet season (Table 7). Lower air temperatures are most commonly associated with lower δD and $\delta^{18}O$ values and are most responsible for seasonal patterns observed in the isotopic values of precipitation in mid-latitude temperate climates (Rozanski et al., 1993; Vreča et al., 2006). However, this is generally not the case in tropical coastal settings where there is a minimal annual variation in air temperature (Rozanski et al., 1993), nor is this the case in South Florida. Lower δD and $\delta^{18}O$ values tend to be found in precipitation during the wet season (Table 7), from June through October, when the air temperature is highest (Fig. 1), fractionation by regional upstream precipitation is most common, and disequilibrium of larger hydrometeors as they fall through the lower troposphere is greatest. In addition, lower isotope values in precitation as a result of increased storm activity over the ocean has been observed in the Tropics (Lawrence et al., 2004). The drop in δD and δ^{18}O values in the beginning (May-June) and end (October-November) of the rainy season (Fig. 5) is interesting and suggestive of different atmospheric sources during these months as compared to the other rainy season months of July through September. Evaporation in south Florida is highest in March through August, with the highest values typically observed in May (Abtew, 2001; Price et al., 2007). Surface water levels in the Everglades, however, often decline throughout the winter dry season with the lowest levels in April or May (Harvey et al., 2004; Price et al., 2003). Although evaporation rates are highest in May, there is often little to no surface water available to contribute to the local atmospheric moisture. The first rains of the wet-season that occur in May or sometimes June, therefore, must originate from an oceanic source. Surface water levels increase from June through October allowing for its evaporation and contribution to the local atmospheric moisture. Tropical cyclones are most common in September and October, and the large negative isotopic values observed in precipitation from these months are a result of these large oceanic forming cyclones passing over south Florida.

October cyclones often originate from the Gulf of Mexico, as opposed to the eastern Atlantic and track eastward toward Florida. The Gulf of Mexico storms, such as hurricane Irene (1999), the No-name storm (2000) and hurricane Wilma (2005) produced very low isotope values of δ^{18}O <-6‰ and δD <-40‰ (Fig. 5). The lowest stable isotope values were obtained from precipitation collected at both the RSMAS and BNP sites, 1 to 2 weeks prior to the passage of Hurricane Wilma. Hurricane Wilma was a category 5 storm that sat over the Yucatan peninsula for 3 to 5 days prior to moving east and making landfall in south Florida as a category 2 storm on October 24, 2005. Although precipitation was not collected during the landfall of this storm (as all of the precipitation collectors were moved inside at least 1 week prior as part of hurricane preparations in the region), the extremely low stable isotopic values collected 2 weeks prior to the storm are indicative of the storm's influence on the region despite its location over the Yucatan Peninsula, approximately 1000 km to the southwest (Fig. 2). Similar observations of low isotope values in precipitation in Houston, Texas were reported from a squall line associated with Hurricane Opal (Sept. 1995) despite the hurricane not passing over Houston (Lawrence et al., 1998). In addition, low isotope values ($\delta^{18}O$=-16 ‰) were reported in precipitation of the lower Florida Keys during Tropical Storm Gilbert (Sept. 2001) although the storm did not cross the Keys (Lawrence et al., 2004). These events combined with that of the large negative producing events observed in this study, suggests that storms that cross over south Florida from the west tend to bring lower isotope values. Other precipitation events monitored in this study that produced isotopically low values happened in December (1999; 2000) at the Redlands station. The cold-fronts originate from middle latitude North America, and it is common for interior portions of the Florida peninsula to experience colder temperatures than the coastal locations during their winter-time passage.

During the 10-year period of study, there were one strong (1997-1998), and two moderate (2002-2003 and 2006) El Niño-Southern Oscillation (ENSO) events (Childers et al., 2006). ENSO events are known to suppress tropical cyclone activity in the western Atlantic and so was the case in those years. A summary of hurricane activity during the decade long study revealed that the average number of tropical cyclones in the Atlantic Ocean was 12. The highest number was recorded in 2005, when 3 cyclones crossed over Florida including Katrina and Wilma. The lowest number of tropical cyclones was recorded during the ENSO years of 1997 and 2006. Although ENSO events tend to reduce tropical cyclone activity they tend not to reduce the amount of annual precipitation in south Florida (Childers et al., 2006). What results is a shift in the precipitation pattern toward more precipitation during the beginning of the dry season (December through February) and even less precipitation than normal at the end of the dry season (March through May). The limited data collected in this investigation precludes a comprehensive analysis of isotopic values in south Florida precipitation with ENSO events. However, low isotope values observed prior to passage of hurricanes, along with the lowest annual average isotopic values observed at RSMAS and BNP during 2005 (Table 8), the year with the most hurricanes, suggests a relationship of lower isotopic values with increased hurricane frequency.

Due to the data being composited on weekly and monthly time intervals, it is difficult to reconstruct the isotopic signature of particular cyclones. Often there is extreme variability in the isotopic composition of precipitation throughout a single rain event (Gambell and Frieman, 1965; Miyake et la., 1968; Rindsberger et al., 1983) and even spatially within a tropical cyclone Gedzelman et al., 2003). However, hydrological and paleo-climatological data such as obtained from the isotopic composition of groundwater from wells, often represent smoothed or average precipitation values, therefore weekly or monthly data collection is justified. Price and Swart (2006) illustrate from the monthly collection of surface water and groundwater from the Everglades, there is a seasonal signal in isotopes with lower isotope values observed in the wet-season as compared to the dry-season, corroborating the precipitation isotope patterns found in this study. Inspection of the stable isotopic signature of tree rings, freshwater ostracods or benthic foraminifera in the Everglades may provide a paleoclimate signal for seasonal variation in the isotopic composition of precipitation in south Florida. The Everglades and south Florida has been recognized as a litmus for climate change in a recent NAS report. Sealevel rise, seawater intrusion, and flooding along with the potential loss of freshwater Everglades habitat and its ecosystem species are all concerns. Continued observation of the isotopic composition of precipitation can be used to as an indicator of climate change and its effect on the hydrology of south Florida and the Everglades.

5.0 Conclusion

The results of this study indicate a spatial and seasonal variation in the δD and $\delta^{18}O$ of precipitation in south Florida. Spatially, the weighted-mean δD and $\delta^{18}O$ values of precipitation tends to be more positive along the coastal Atlantic regions. Inland sites tend to have more positive d-excess values due to recycling of Everglade surface water. Precipitation from the lower Keys seems to be influenced from a more maritime source, where low cloud condensation nucleus content controls droplet size.

The δD and $\delta^{18}O$ signature of precipitation in south Florida varies seasonally with lower δD and $\delta^{18}O$ values observed at the start and end of the summer wet season, and slightly higher isotopic values observed in June through August. The lower δD and $\delta^{18}O$ values suggest a more oceanic vapor source, fractionation by upstream rainout, and the effect of greater disequilibrium between larger hydrometeors as they fall through lower tropospheric isotope ratios whereas the higher values indicate influence of evaporated Everglades surface water. Low δD and $\delta^{18}O$ values also are observed in tropical cyclones and cold fronts that come from the west and northwest.

6.0 Acknowledgements

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Table 1. Summary of precipitation collection dates, latitude, longitude, number of samples (n), weighted mean $\delta^{18}O$, δD, and d-excess for each of the five sites in south Florida.

Site	Latitude	Longitude	Collection Dates	n	Weighted mean $\delta^{18}O$ (‰)	S.E. $\delta^{18}O$ (‰)	Weighted mean δD (‰)	S.E. δD (‰)	Weighted mean d-excess (‰)
Redland	25° 31′ 08.43″ N	80° 29′ 28.95″W	8/97-8/01	43	-3.22	0.26	-12.2	2.1	13.4
RSMAS	25° 43′ 57.00″ N	80° 09′ 47.65″W	12/99-8/01, 8/03/12/06	120	-2.80	0.18	-12.3	1.3	10.1
BNP	25° 27′ 50.82″ N	80° 20′ 04.75″W	9/03-1/06	59	-2.82	0.23	-12.9	2.0	9.6
Key Largo	25° 05′ 12.03″ N	80° 27′ 11.14″W	7/01-7/02	14	-2.84	0.37	-12.8	3.3	9.9
Long Key	25° 50′ 14.53″ N	80° 48′ 02.89″W	1/02-12/02	36	-3.64	0.34	-20.2	2.9	8.8

Table 2. Precipitation amount, $\delta^{18}O$, and δD for samples collected at Biscayne National Park (BNP).

Date (m/d/yr)	amount[1] (mm)	$\delta^{18}O$ ‰	δD ‰
9/4/2003	0.25	-0.72	-0.1
9/26/2003	219.20	-2.63	-8.7
10/21/2003	101.60	-3.55	-17.9
10/28/2003	107.19	-1.74	2.9
10/29/2003	2.29	-1.30	-2.6
10/31/2003	7.37	-1.88	-2.8
11/3/2003	8.64	-1.40	2.0
11/5/2003	59.44	-2.67	-6.7
11/7/2003	154.94	-3.29	-12.9
11/12/2003	3.30	-1.54	-1.2
11/20/2003	3.05	-0.85	2.4
11/24/2003	(a)	-0.05	6.4
12/3/2003	(a)	-0.82	8.2
12/11/2003	23.88	-1.45	4.1
1/15/2004	22.35	-1.22	6.9
1/27/2004	20.07	0.40	3.5
2/6/2004	52.58	-1.34	-0.9
2/26/2004	1.27	-2.44	-5.2
3/17/2004	41.15	-0.46	5.4
3/26/2004	1.78	-0.94	11.0
5/27/2004	224.54	-0.49	5.7
8/30/2004	330.20	-0.06	8.4
9/21/2004	99.57	-0.60	0.4
10/12/2004	177.29	-0.66	1.7
10/19/2004	188.98	-4.62	-27.0
10/21/2004	55.88	-2.72	-16.9
10/25/2004	13.46	-1.62	-0.1
11/1/2004	0.76	-0.64	3.0
11/8/2004	1.02	-1.21	3.2
11/10/2004	5.08	-1.34	2.5
11/15/2004	(a)	-0.87	0.0
11/26/2004	7.87	-0.85	0.1
12/9/2004	68.07	0.90	11.3
12/21/2004	0.51	-0.61	14.3
12/23/2004	2.54	-1.16	5.3
12/27/2004	(a)	-2.40	-11.9
1/4/2005	0.51	0.11	10.7
1/20/2005	0.76	-1.33	11.5
6/14/2005	5.59	-4.21	-27.8
6/20/2005	404.37	-5.83	-39.4
6/21/2005	94.23	-8.72	-58.4
6/28/2005	112.01	-2.71	-19.8
6/30/2005	1.27	-2.57	-12.9
7/5/2005	7.62	-0.57	-0.6
7/12/2005	91.95	-4.33	-30.7
7/19/2005	12.70	-1.37	-3.0
7/21/2005	6.60	-1.35	-0.9
7/28/2005	10.67	-0.68	-1.7
8/2/2005	10.16	-1.16	-5.4
8/9/2005	82.30	-4.06	-22.3
8/23/2005	21.34	-1.62	-4.9
9/16/2005	553.97	-3.47	-14.6
10/4/2005	42.42	-3.74	-19.7
10/6/2005	1.78	-3.40	-16.7
10/11/2005	43.94	-9.15	-62.0
10/18/2005	10.92	(a)	-4.4
11/8/2005	8.38	-1.32	-3.3
11/10/2005	0.25	-1.41	0.7
11/15/2005	18.80	-1.08	8.3
11/29/2005	12.45	-0.38	7.9
12/1/2005	10.92	-1.06	-22.3
12/8/2005	1.02	0.20	9.2
1/17/2006	41.91	-0.14	-0.7
1/19/2006	0.76	0.25	9.1

[1] Rainfall data obtained from Homestead Airforce Base (http://www4.ncdc.noaa.gov)

(a) data not available

1

Table 3. Precipitation amount**,** $\delta^{18}O$, and δD for samples collected at Key Largo.

Date (m/d/yr)	amount (mm)	$\delta^{18}O$ ‰	δD ‰
7/20/2001	32.26	-2.08	-6.5
8/17/2001	11.18	-1.32	2.7
8/24/2001	6.10	-0.07	7.3
8/31/2001	8.64	-1.54	6.7
9/4/2001	5.33	-0.42	6.1
11/2/2001	20.83	-3.01	-8.3
11/30/2001	20.60	-0.99	9.4
2/15/2002	113.50	-2.40	-2.0
3/4/2002	36.76	-4.00	-26.6
4/12/2002	76.95	-1.01	-0.8
6/6/2002	88.64	-4.18	-26.4
7/1/2002	173.00	-4.36	-28.2
7/8/2002	122.50	-2.63	-12.9
7/17/2002	109.00	-2.02	-4.5

Table 4. Precipitation amount, δ^{18}O, and δD for samples collected at Long Key.

Date (m/d/yr)	amount (mm)	δ^{18}O ‰	δD ‰
7/23/2001	36.50	-2.67	-6.8
7/30/2001	20.33	-2.36	-6.2
8/6/2001	115.00	-2.98	-15.6
8/27/2001	2.94	-1.42	5.9
9/3/2001	0.24	1.32	14.0
12/11/2001	34.00	-3.60	-18.3
12/17/2001	0.24	-0.67	3.7
12/26/2001	2.45	-1.65	4.5
1/7/2002	55.37	-5.66	-32.4
1/28/2002	1.72	-0.12	10.4
2/11/2002	48.02	-1.11	7.7
2/18/2002	8.33	-3.10	-13.0
2/25/2002	30.38	-2.28	-4.3
3/11/2002	11.27	-2.18	-4.0
3/25/2002	1.96	-2.05	-6.6
5/13/2002	2.94	0.66	11.2
5/20/2002	28.18	-5.10	-36.2
5/28/2002	28.67	-6.15	-48.7
6/3/2002	1.72	-4.39	-29.3
6/10/2002	1.47	-2.23	-8.0
6/17/2002	123.48	-7.95	-59.9
6/24/2002	80.85	-2.15	-8.0
7/1/2002	23.52	-0.22	3.6
7/8/2002	20.83	-2.57	-8.1
7/17/2002	26.95	-3.28	-17.7
7/23/2002	0.25	0.61	13.3
8/26/2002	26.71	-1.97	-0.9
9/3/2002	18.87	-0.22	2.7
9/16/2002	17.60	-2.37	-7.5
9/23/2002	19.60	-5.24	-32.9
9/30/2002	4.65	-4.67	-28.1
10/15/2002	1.72	-0.77	7.5
10/21/2002	56.84	-3.10	-21.7
11/18/2002	13.00	-1.74	-7.5
11/25/2002	4.41	-1.51	6.2
12/2/2002	0.10	-0.27	14.2

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Table 5. Precipitation amount**,** δ^{18}O, and δD for samples collected at Redland.

Date (m/d/yr)	amount (mm)	δ^{18}O ‰	δD ‰
8/31/1997	282.10	-1.40	0.3
9/21/1997	224.90	-4.91	-19.1
10/10/1997	59.10	-4.01	-20.8
12/1/1997	81.40	-1.82	-0.7
12/7/1997	75.00	-6.38	-34.0
1/11/1998	91.46	-1.94	-0.9
2/3/1998	119.00	-3.36	-11.2
3/1/1998	136.20	-1.59	2.0
5/11/1998	108.66	-2.94	-8.1
6/1/1998	72.00	-3.44	-21.7
7/19/1998	112.89	-2.88	-10.7
9/24/1998	483.80	-3.81	-18.5
11/17/1998	197.70	-2.96	-11.4
12/31/1998	48.60	-1.88	-1.9
2/12/1999	99.60	-2.42	-5.2
3/22/1999	4.40	-1.37	-6.1
5/21/1999	91.40	-3.10	-12.5
7/3/1999	197.50	-3.39	-15.4
8/1/1999	299.00	-2.18	-5.6
9/1/1999	125.60	-3.43	-15.2
10/1/1999	116.40	-2.98	-3.7
10/31/1999	197.00	-7.57	-50.6
12/1/1999	21.70	-2.68	-18.2
3/1/2000	39.40	-1.19	9.1
5/1/2000	54.72	-1.27	5.0
5/24/2000	6.50	-7.62	-51.5
6/1/2000	79.00	-0.72	2.4
6/6/2000	30.00	-1.87	-2.6
6/13/2000	101.50	-3.79	-17.8
6/30/2000	218.10	-2.77	-7.8
8/2/2000	183.00	-2.53	-6.0
8/31/2000	178.20	-4.22	-19.9
10/1/2000	75.00	-1.94	-2.5
10/10/2000	155.00	-4.02	-15.8
12/31/2000	66.80	-7.43	-42.9
5/27/2001	18.30	-3.94	-16.1

Table 6. Precipitation amount, δ^{18}O, and δD for samples collected at the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS).

Date (m/d/yr)	amount (mm)	δ^{18}O ‰	δD ‰	Date (m/d/yr)	amount (mm)	δ^{18}O ‰	δD ‰	Date (m/d/yr)	amount (mm)	δ^{18}O ‰	δD ‰
12/9/1999	35.00	-0.69	8.9	12/10/2003	23.41	-1.48	5.8	10/10/2005	4.55	-3.10	-20.1
12/22/1999	60.00	-0.14	11.7	12/12/2003	11.02	-1.46	2.5	10/17/2005	43.76	-10.31	-77.9
1/21/2000	1.00	0.62	19.0	12/15/2003	18.10	-2.71	-8.7	11/18/2005	18.45	-0.95	-1.5
1/28/2000	9.00	-2.72	-7.6	12/17/2003	4.20	-0.29	9.5	11/22/2005	13.14	-0.28	4.3
2/11/2000	40.00	-0.83	17.2	12/22/2003	9.25	-1.16	14.5	12/29/2005	5.09	-1.67	-5.6
2/25/2000	55.00	-1.09	4.2	12/24/2003	7.03	1.01	7.1	2/6/2006	47.30	-1.99	-6.5
3/3/2000	1.00	1.47	20.6	1/19/2004	38.19	-3.81	-12.3	2/25/2006	34.73	-1.20	3.5
3/22/2000	120.00	-0.74	1.7	1/28/2004	5.21	0.40	6.3	2/27/2006	7.65	-0.08	2.5
6/6/2000	30.00	-1.77	-2.6	2/2/2004	74.74	-1.76	-16.4	3/24/2006	72.08	-1.30	-2.5
6/13/2000	75.00	-3.81	-17.4	2/17/2004	6.24	-2.19	-2.4	4/10/2006	26.95	-2.01	-6.3
7/3/2000	118.00	-2.19	-8.4	2/26/2004	62.70	1.11	10.1	4/12/2006	12.61	0.75	8.6
7/17/2000	114.00	-0.63	6.7	3/22/2004	(a)	-0.58	6.8	5/16/2006	23.58	-2.67	-4.6
8/3/2000	140.00	-1.08	3.3	3/25/2004	(a)	-0.80	-8.5	5/18/2006	55.44	-5.56	-28.6
8/18/2000	30.00	-0.53	5.4	3/25/2004	8.36	-0.19	7.1	5/26/2006	28.89	-5.23	-29.4
8/29/2000	100.00	-2.16	-7.8	4/3/2004	6.24	0.28	8.6	6/1/2006	69.60	-3.33	-10.5
9/8/2000	85.00	-2.59	-7.6	4/12/2004	15.00	-2.24	-4.8	6/5/2006	60.58	-1.86	-6.4
9/22/2000	77.00	-1.36	-0.4	4/24/2004	(a)	-1.67	2.4	7/10/2006	58.81	-2.72	-17.6
10/3/2000	225.00	-9.00	-55.9	5/4/2004	67.30	-3.71	-17.8	7/18/2006	26.41	-0.01	2.8
10/9/2000	163.00	-6.11	-33.9	6/10/2004	6.94	-1.93	-6.6	7/20/2006	23.41	-2.07	-3.5
12/11/2000	145.00	-1.44	1.0	6/27/2004	7.12	-0.68	-5.9	7/21/2006	12.96	-2.23	-1.9
1/2/2001	1.00	0.40	14.4	6/29/2004	4.47	0.12	8.7	7/28/2006	7.48	-0.12	3.6
3/20/2001	28.00	0.25	8.2	7/4/2004	8.71	0.90	21.1	7/31/2006	11.90	0.79	4.5
6/29/2001	9.80	-0.45	4.8	7/14/2004	7.65	-1.15	-1.5	8/7/2006	16.33	-0.66	-2.5
7/6/2001	4.40	-0.25	15.1	7/23/2004	21.64	-4.39	-24.8	8/15/2006	86.68	-3.09	-14.4
7/10/2001	1.20	-0.20	6.3	7/26/2004	6.59	-3.10	-12.0	8/16/2006	10.75	-2.06	-10.1
7/17/2001	51.40	-2.86	-13.0	7/28/2004	44.65	-4.46	-20.4	8/21/2006	20.93	-2.13	-1.7
7/24/2001	38.60	-1.28	-3.2	8/20/2004	(a)	-2.29	-3.2	9/12/2006	15.26	-5.57	-28.2
8/2/2001	13.00	-3.82	-21.7	10/8/2004	17.56	-0.13	1.0	9/29/2006	7.92	0.94	3.8
8/3/2001	(a)	0.24	8.9	12/5/2004	(a)	-0.57	12.2	10/10/2006	10.57	-1.44	-6.6
8/6/2001	32.00	-0.95	-0.3	2/3/2005	23.41	-2.06	6.5	10/13/2006	49.07	-3.88	-16.5
8/1/2003	(a)	-0.55	-14.3	2/28/2005	9.07	0.06	8.4	10/24/2006	6.77	-0.82	1.8
8/15/2003	(a)	-1.24	-4.4	3/4/2005	29.78	-3.25	0.2	10/31/2006	16.33	-0.75	2.0
9/24/2003	91.55	-3.69	-38.5	3/10/2005	42.17	-4.08	-12.5	11/2/2006	16.77	-4.36	-19.1
9/26/2003	21.07	-2.42	-8.9	3/18/2005	44.65	-3.65	-16.0	11/16/2006	17.21	-2.69	-7.3
9/29/2003	20.31	-3.12	-31.3	3/24/2005	26.95	-0.57	-1.4	11/28/2006	(a)	0.61	0.9
9/30/2003	30.49	-3.04	-33.9	4/8/2005	49.78	-2.15	-11.3	12/14/2006	5.97	-0.22	3.7
10/1/2003	13.67	-0.45	2.6	4/18/2005	5.79	-0.93	5.1	12/15/2006	9.42	-1.06	-8.5

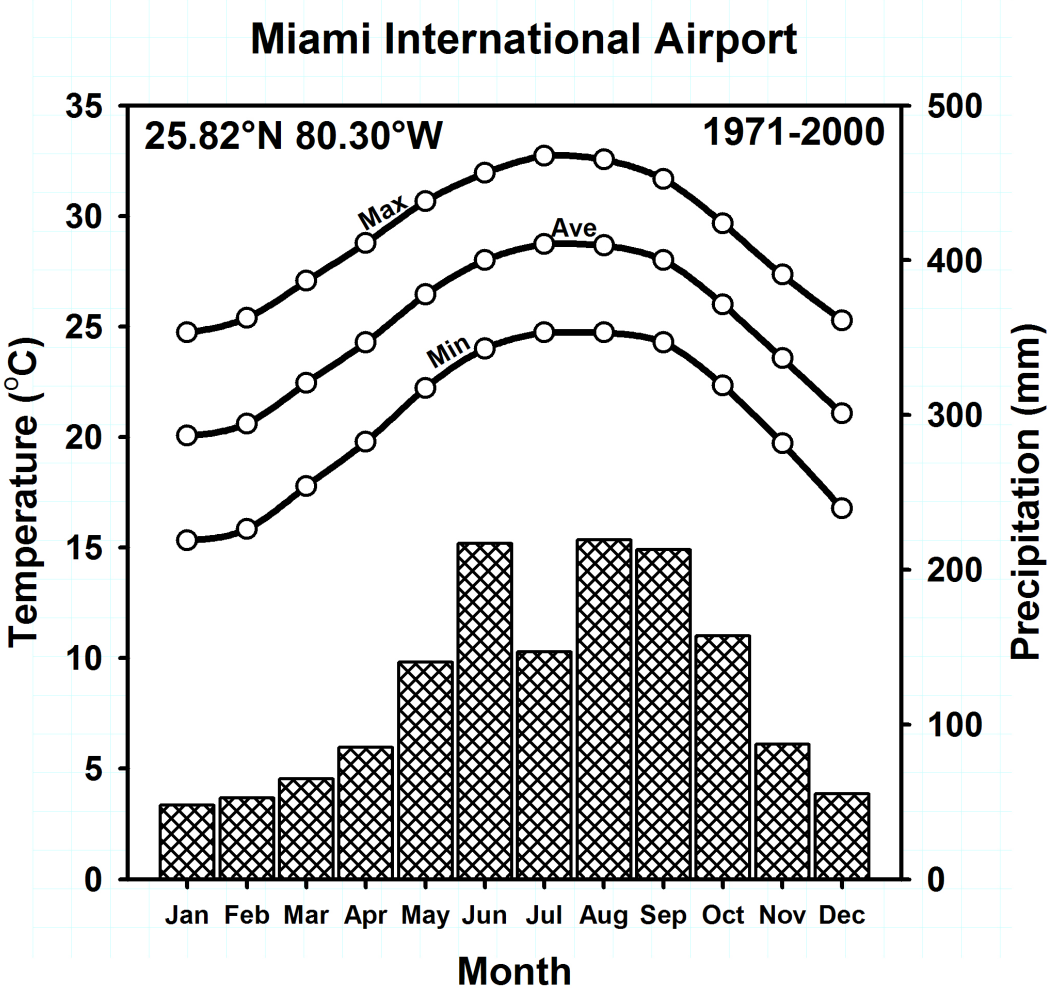
10/21/2003	8.36	-2.18	-9.4	5/4/2005	31.02	-2.27	-7.4	12/18/2006	16.33	-2.31	-5.9
10/29/2003	32.26	-3.27	-15.8	5/6/2005	27.12	-2.32	-19.7	12/19/2006	4.91	1.53	7.2
10/31/2003	8.18	-1.45	-1.6	8/5/2005	6.41	-0.07	7.3				
11/2/2003	10.84	-2.17	-9.2	8/11/2005	3.40	0.86	12.2				
11/6/2003	132.26	-6.03	-39.4	8/19/2005	16.33	-1.24	5.8				
11/7/2003	21.19	-4.77	-34.7	8/22/2005	3.53	0.81	8.9				
11/9/2003	11.02	-1.64	-11.8	8/23/2005	17.39	-3.42	-14.0				
11/10/2003	5.88	-0.89	0.1	9/6/2005	40.40	-4.50	-27.7				

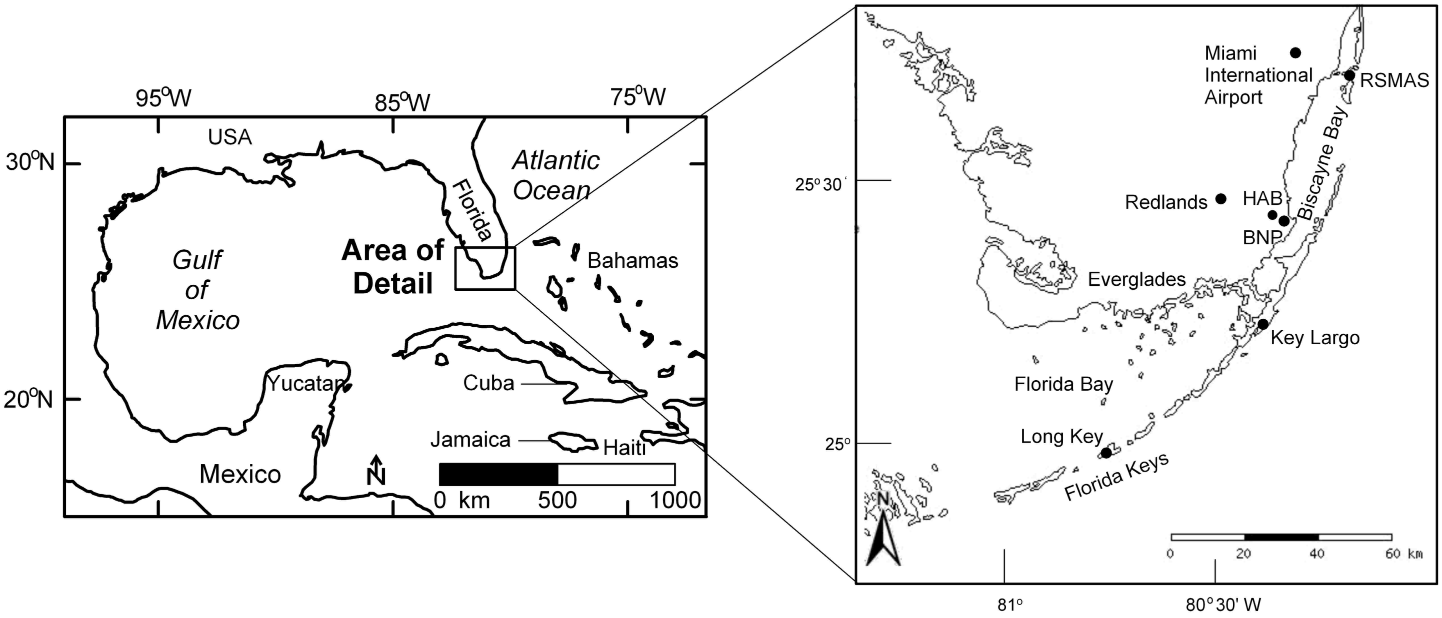
Table 7. Seasonal weighted-mean values of δ^{18}O, δD, and d-excess along with the number of precipitation samples (n) and the standard error (s.e.) for four sites with at least 1 year of data.

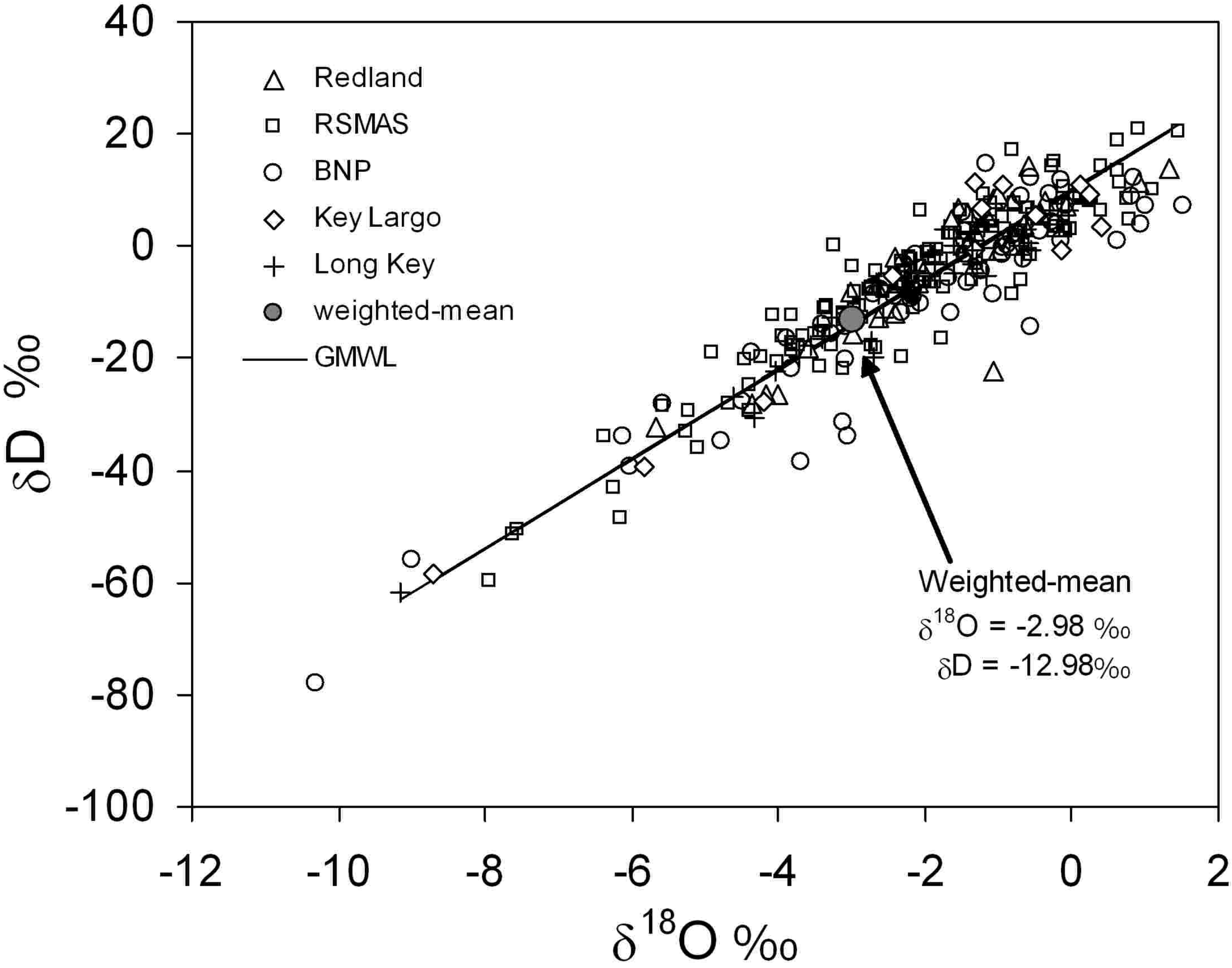
Site	Redland		RSMAS		BNP		Long Key	
Season	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
n	24	19	62	58	29	30	20	16
δ^{18}O (‰)	-3.36	-2.86	-3.30	-2.13	-3.26	-1.19	-3.68	-3.56
s.e.	0.30	0.45	0.27	0.22	0.40	0.15	0.46	0.48
δD (‰)	-13.44	-9.40	-16.54	-6.65	-16.60	0.25	-21.51	-17.57
s.e.	2.60	3.62	2.14	1.64	2.98	1.34	3.90	4.48
d-excess	13.43	13.51	9.90	10.40	9.50	9.80	7.91	10.89
s.e.	0.66	1.14	0.76	0.86	0.73	1.12	0.90	1.22

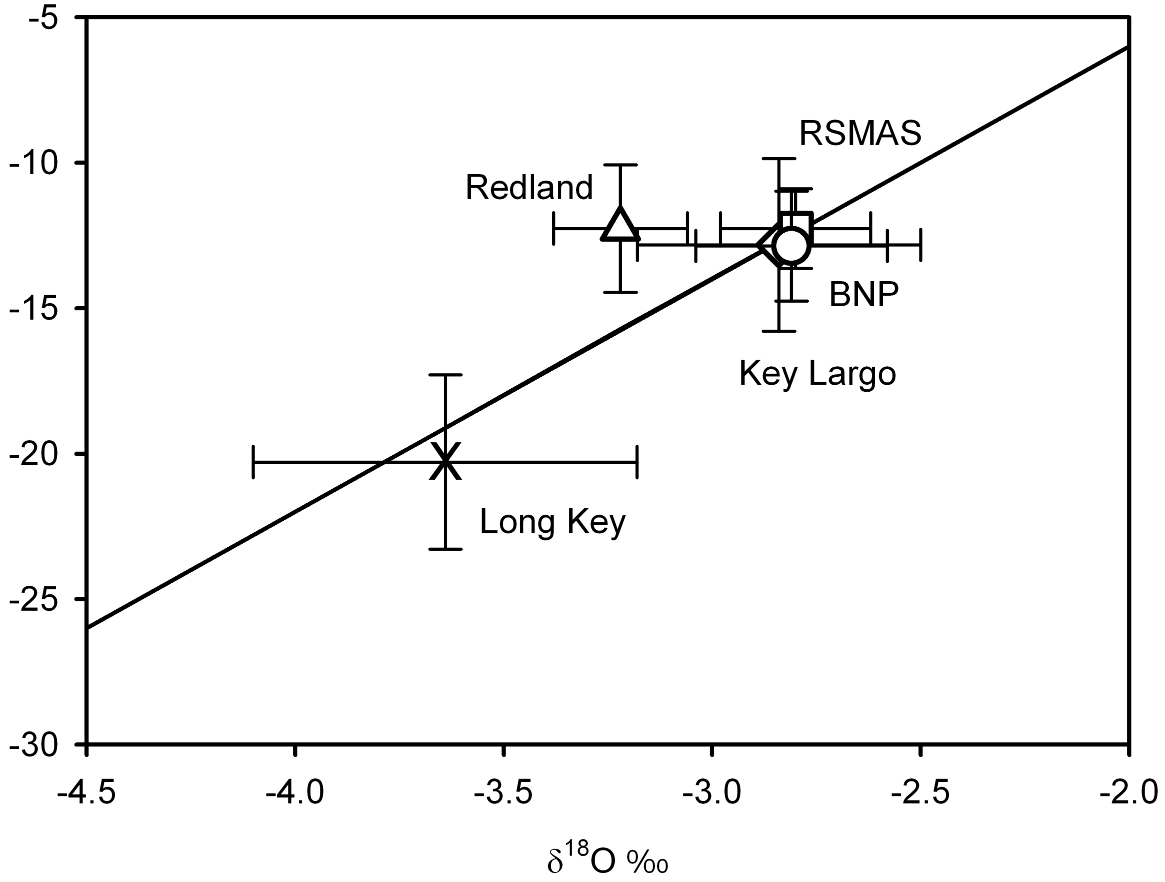
Table 8. Annual amount-weighted values of $\delta^{18}O$, δD for sites with over 1 year of data.

Site	Year	$\delta^{18}O$ (‰)	δD (‰)
Redland	1998	-3.07	-10.02
	1999	-3.62	-16.58
	2000	-3.16	-11.14
RSMAS	2000	-3.15	-12.63
	2004	-2.02	-8.74
	2005	-3.23	-15.12
	2006	-2.44	-9.29
BNP	2004	-1.08	-0.32
	2005	-4.38	-25.79

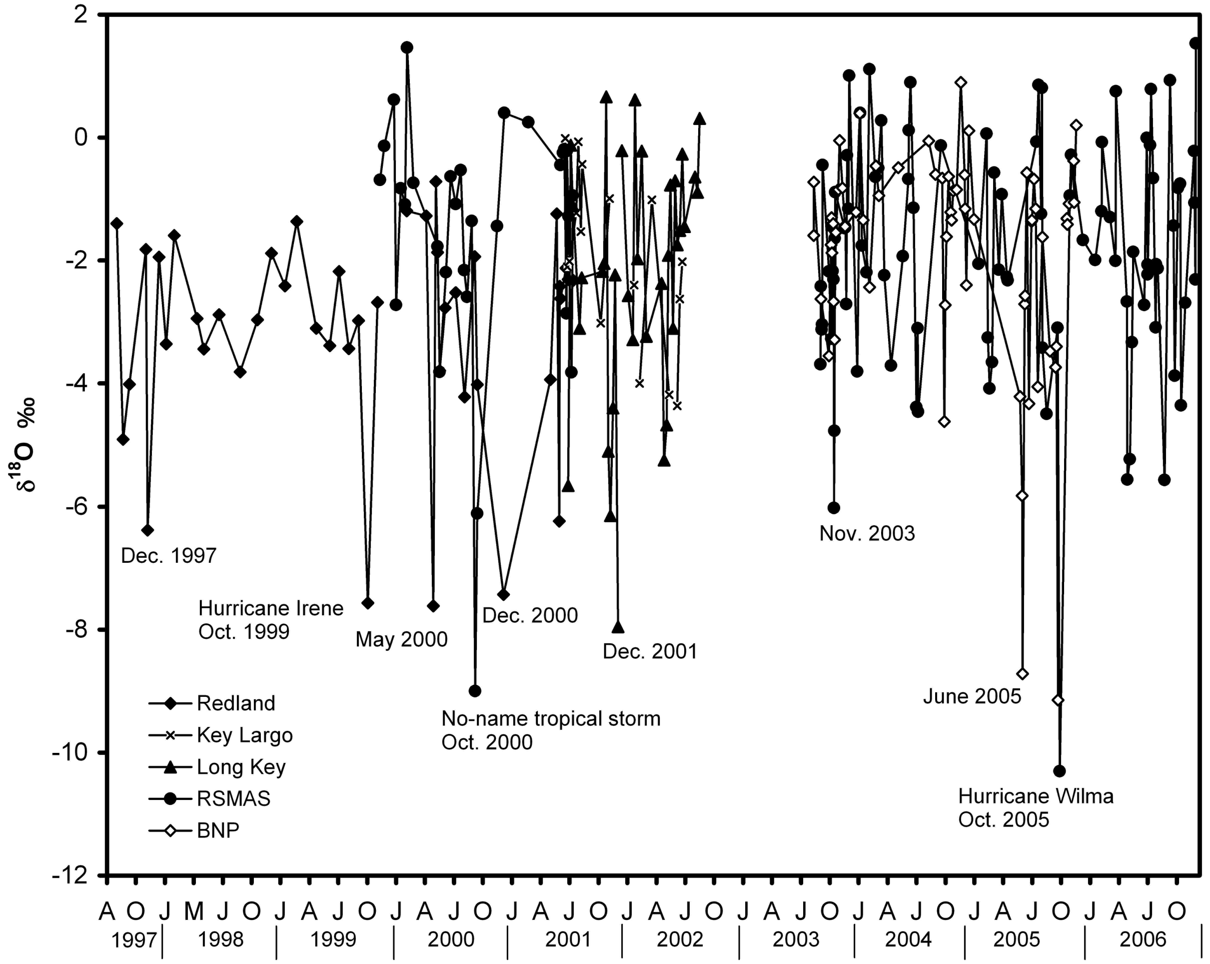

Miami International Airport
25.82°N 80.30°W
1971-2000
Max
Ave
Min
Temperature (°C)
0
5
10
15
20
25
30
35
Precipitation (mm)
0
100
200
300
400
500
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Month

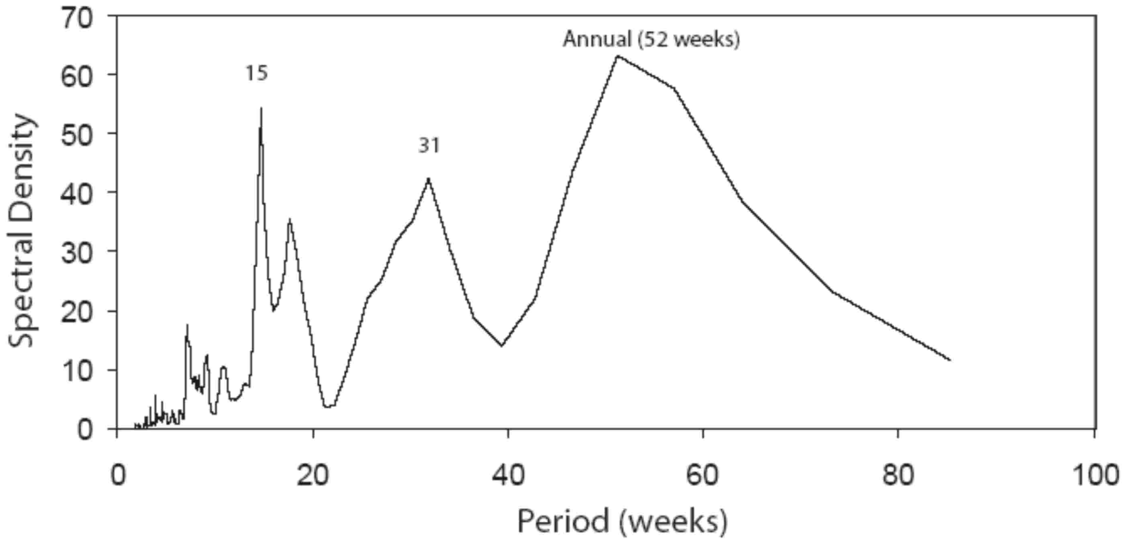

95°W
85°W
75°W
30°N
20°N
USA
Atlantic Ocean
Florida
Gulf of Mexico
Area of Detail
Bahamas
Yucatan
Cuba
Jamaica
Haiti
Mexico
N
0 km
500
1000
Miami International Airport
RSMAS
Biscayne Bay
25° 30´
Redlands
HAB
BNP
Everglades
Key Largo
Florida Bay
25°
Long Key
Florida Keys
N
0
20
40
60 km
81°
80° 30' W

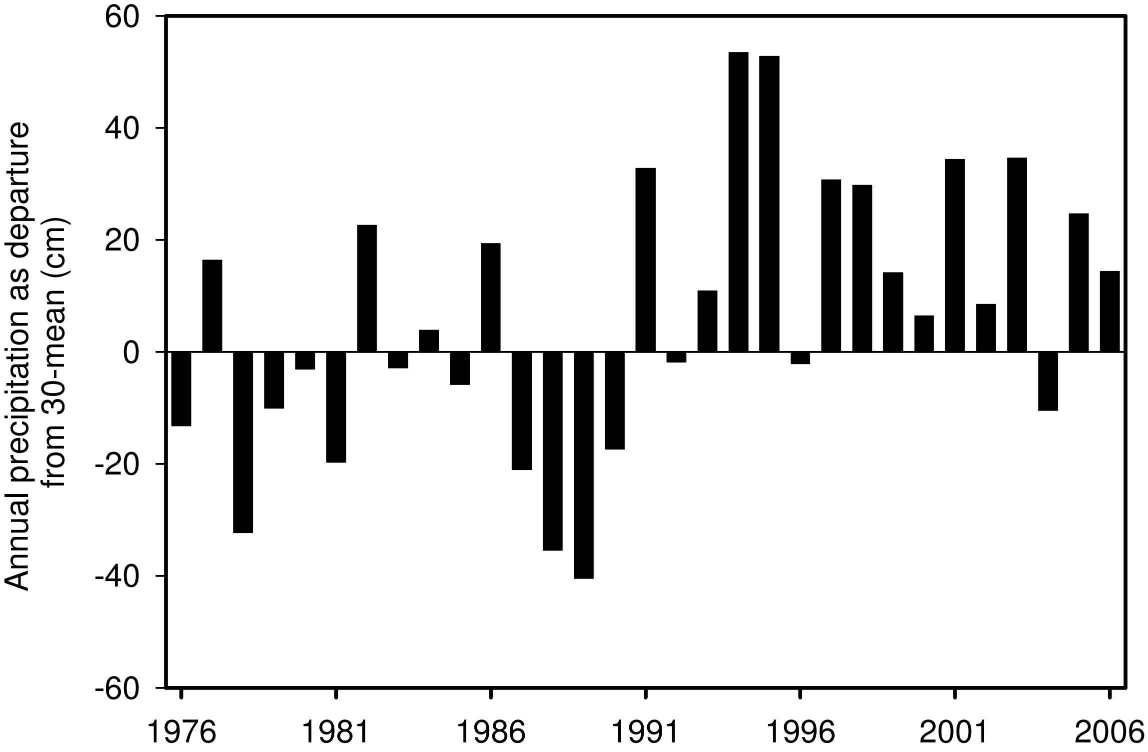

40
20
0
-20
-40
-60
-80
-100
δD ‰
-12
-10
-8
-6
-4
-2
0
2
δ18O ‰
Redland
RSMAS
BNP
Key Largo
Long Key
weighted-mean
GMWL
Weighted-mean
δ18O = -2.98 ‰
δD = -12.98‰



-5
-10
-15
-20
-25
-30
δD ‰
RSMAS
Redland
BNP
Key Largo
Long Key
-4.5
-4.0
-3.5
-3.0
-2.5
-2.0
δ18O ‰


2
0
-2
-4
-6
-8
-10
-12
$\delta^{18}O$ ‰
Dec. 1997
Hurricane Irene
Oct. 1999
May 2000
Dec. 2000
No-name tropical storm
Oct. 2000
Dec. 2001
Nov. 2003
June 2005
Hurricane Wilma
Oct. 2005
Redland
Key Largo
Long Key
RSMAS
BNP
A O J M J O J A J O J A J O J A J O J A J O J A J O J A J O J A J O J A J O
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006


Annual (52 weeks)
15
31
Spectral Density
70
60
50
40
30
20
10
0
0
20
40
60
80
100
Period (weeks)


Annual precipitation as departure from 30-mean (cm)
60
40
20
0
-20
-40
-60
1976
1981
1986
1991
1996
2001
2006