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Stable Isotopic and Geochemical Variability within Shallow Groundwater beneath a Hardwood Hammock and Surface Water in an Adjoining Slough (Everglades National Park, FL)

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Abstract

Data from a ten-month monitoring study during 2007 in south Florida provide insight into the variation of $\delta^{18}O$, δD, and $\delta^{13}C$ of DOC in surface water and shallow groundwater of the Everglades ecosystem. Bi-monthly samples were taken from surface water and time-averaged precipitation at Taylor Slough, and shallow groundwater from a well and a small cave within Palma Vista Hammock, an exposure of the Upper Pleistocene Miami Limestone.

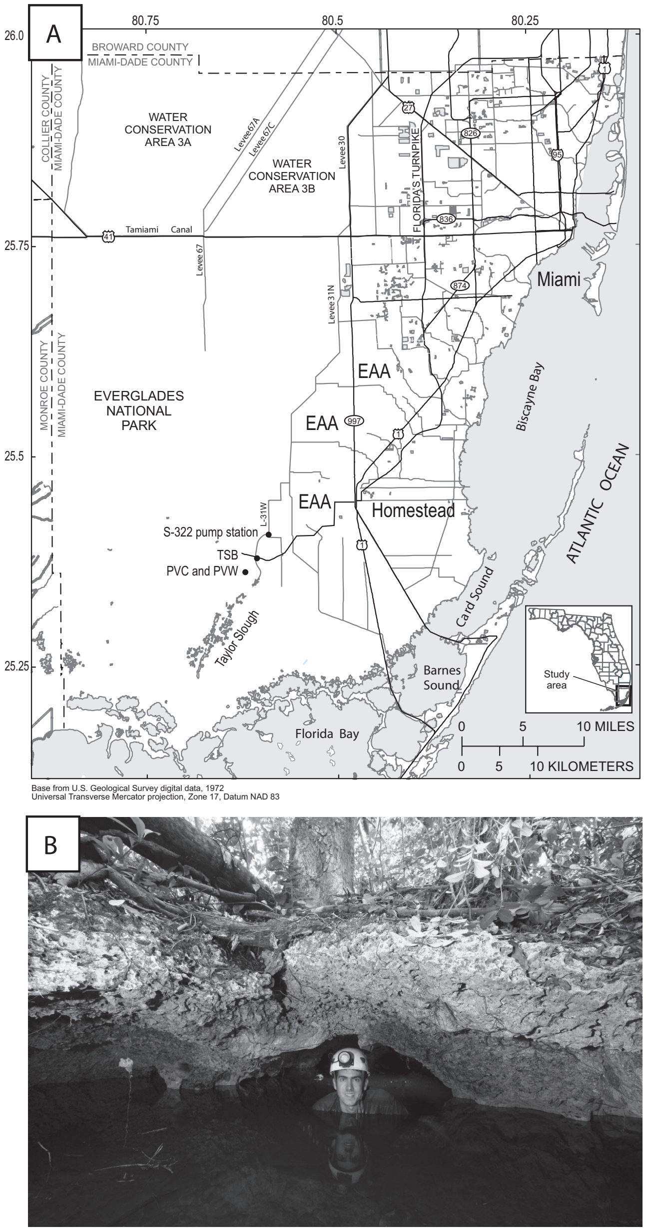
$\delta^{18}O$ and δD values in shallow groundwater from the well and cave remain near the mean of -2.4 ‰ and -12 ‰, respectively (VSMOW scale). ^{18}O and D are enriched in surface water compared to shallow groundwater. $\delta^{18}O$ and δD values in surface water fluctuate in sync with, but to a lesser amplitude than, those measured in rainfall. The local meteoric water line (LMWL) for precipitation is in close agreement to the global meteoric water line (GMWL); however, the local evaporation line (LEL) for surface water and shallow groundwater is $\delta D = 5.6\ \delta^{18}O + 1.5$ ($R^2=0.97$), a sign that these waters have experienced evaporation. The intercept of the LMWL and LEL indicates that the primary recharge to the Everglades occurs primarily from tropical or frontal sources. Local convection merely recycles available water.

Time-series of deuterium excess (D_{ex}), clearly reveals two moisture sources for precipitation; an evaporation-dominated source with $D_{ex}>10$ and a source significantly influenced by transpiration with $D_{ex}<10$. Samples with higher D_{ex} cluster in the fall and winter, and appear to be associated with maritime moisture carried along the Trade Winds. Samples with lower D_{ex} cluster in the late spring and summer, and could reflect continental moisture carried by the Westerlies or local convection.

Values of $\delta^{13}C_{DOC}$ between -22.6 and -28.0‰ suggest C-3 vegetation as the primary source of DOC at all sample sites. C:N ratios of DOC averaging 20:1 at the cave indicate that organic matter originates from woody material, while an average of 15:1 at the well along with $\delta^{13}C_{DOC}$ similar to the cave indicate further decomposition of the organic matter entering the cave. C:N ratios of DOC the slough averaged 15:1, and with $\delta^{13}C_{DOC}$ values, suggest sources of organic matter not present at the cave and well.

INTRODUCTION

Everglades National Park encompasses 1.5 million acres of grassland glades, tropical hardwood hammocks, pine rocklands, cypress strands, and mangrove marshes. Subtle differences in elevation, salinity, and seasonal rainfall control the spatial distribution of these ecosystems. Of particular interest to this study are freshwater sloughs, often miles wide, which convey freshwater from Lake Okeechobee in the north to Florida Bay in the south, and the tropical hardwood hammocks associated with Upper Pleistocene limestones in the east-central portion of Everglades National Park. In particular, this study encompasses the central portions of Taylor Slough and adjacent Palma Vista Hammock (Figure 1a).



Base from U.S. Geological Survey digital data, 1972
Universal Transverse Mercator projection, Zone 17, Datum NAD 83

Figure 1. A) Study area in Everglades National Park in southeast Florida with the Taylor Slough labeled. Taylor Slough has its origin at the S-322 pumping station on the L-31W canal. Sampling stations are identified: Taylor Slough (TS) and Palma Vista Cave and Well (PVC and PVW). B) Brian Killingbeck in the entrance to Palma Vista Cave within a hardwood hammock that adjoins Taylor Slough (photo by Alan Cressler).

Palma Vista Hammock, other nearby tropical hardwood hammocks, and nearby pine rocklands comprise the southwestern limits of the Atlantic Coastal Ridge, a relatively high, but low-relief topographic feature in southeast Florida. Much of the coastal ridge has been urbanized in the past century; the relatively higher elevations now host the Greater-Miami metropolitan area and the large agricultural district surrounding the city of Homestead.

The bedrock of the study area is the Upper Pleistocene Miami Limestone that was deposited during marine isotope substage (MIS) 5e. Lithologically this unit is a pelloidal-algal grainstone that is porous, permeable ($10^{-12.4}$ m^2 as measured using pressure decay on core plug, and $10^{-13.5}$ m^2 measured using a gas minipermeameter), and locally riddled with touching-vug macropores created by the syndepositional bioturbation by endobenthic organisms (Cunningham et al., 2009). XRD analyses of four samples of the Miami Limestone in Palma Vista Hammock reveal a composition dominated by calcite with lesser amounts of aragonite (av. 12% by weight) and trace amounts of quartz (av. < 1% by weight).

The bedrock throughout the Everglades ecosystem is greatly modified by dissolution. In the pine rocklands and tropical hardwood hammocks, for example, solution pits and other epikarst features convey recharge to the water table. Shallow collapse features in these limestones provide access to small, horizontal caves situated at the average perennial water table (Florea and Yuellig, 2007, Figure 1b). Access to water and development of soils in these collapse features make them analogous to the "banana holes" of small carbonate islands (Mylroie et al., 1995).

In the adjacent slough, the seasonal water table resides above the mean land surface. Sawgrass prairies dominate, growing from a layer of peat that mantles a complex corrosion surface.

This surface has considerable relief, perhaps as much as a meter. A light-red-stained caliche is pervasive on this surface, indicating exposure and soil development since the last sea level fall at the end of MIS 5e. The peat, with an average permeability of $10^{-12.5}$ m^2, ranges in thickness from 0.2 to 2 m (Harvey et al., 2004).

Character of rainfall, δD, and δ^{18}O

Rainfall in the Everglades ecosystem is strongly seasonal; some maps of the Köppen classification depict south Florida as Aw (tropical, dry winter) climate (Aguado and Burt, 2004), where the seasonality results from the summer poleward shift of the Intertropical Convergence Zone (ITCZ). Others further subdivide the southeast coast of Florida as Am (tropical, monsoonal), where easterly waves entrained within the Trade Winds convey seasonal moisture evaporated from the Gulf Stream (Kottek et al, 2006).

The rainfall regimen in south Florida is dominated by frequent, and often intense, convection storms during the summer months and less frequent tropical cyclones during the late summer and early fall. Typical annual hyetographs in south Florida also reveal a mid-summer (July to early August) period of reduced rainfall. Termed the mid-summer drought (MSD), this pervasive phenomena of the Caribbean region is thought, at least in the central Caribbean, to be the product of an increase in surface pressure caused by changing wind fields (Curtis and Gamble, 2008).

Source waters for precipitation in the Everglades, therefore, come from four main sources: continental moisture brought primarily during the winter and spring months as occasional frontal systems entrained in the prevailing Westerlies; convective moisture, locally derived, during the warm summer months; convective moisture, brought onshore from nearby tropical waters during the summer; and tropical waves and cyclones, conveyed from a distance primarily by the Trade Winds during the late summer and fall. Each of these four moisture sources is likely to have a characteristic signature of δD and δ^{18}O with fractionation of these isotopes caused primarily by variation in factors related to the degree of Rayleigh distillation during cloud rainout, source and event latitude, altitude of condensation, and the amount and duration of precipitation events. In fact, these factors control the global variation of δD versus δ^{18}O, which gives the global meteoric water line (GMWL) equation: $\delta D = 8(\delta^{18}O) + 10$ (Craig, 1961).

A second group of processes, which are significant in Florida, are caused by variation in the ratio of hydrogen to oxygen isotope fractionation factors during evaporation, and these processes potentially produce deviations from the GMWL. Waters that have undergone significant evaporation during or after rainfall will be enriched in the heavier isotopes, and the ratio of enrichment of D to ^{18}O is proportional to relative humidity. In the Everglades where the relative humidity averages 75%, the theoretical slope of the Local Meteoric Water Line (LMWL) should be between 5 and 6 (Gonfiantini, 1986), and this is validated by long-term monitoring of surface waters from Florida which show a LMWL with a slope of 5.43 (Kendall & Coplen, 2001).

The effect of evaporation upon the stable isotopes is often quantified using the equation $D_{ex} = \delta D - (8x\delta^{18}O)$, which calculates the excess of D to ^{18}O from that predicted by the GMWL. Assuming no additional input of moisture, precipitation following the GMWL during rainout will preserve a D_{ex} value of 10. Precipitation derived from evaporation will have greater Dex than that derived from transpiration-based moisture sources because there is no fractionation of soil water during transpiration (Gonfiantinai, 2001). We propose that the variation of D_{ex} in Taylor Slough and the eastern Everglades may vary according to the wind patterns. Whereas the Westerlies from the late winter until the MSD could bring terrestrial-derived, and thus transpiration-influenced, moisture from the west and northwest, the Trade Winds after the MSD through the early winter might bring maritime-derived, and thus exclusively evaporation-based, moisture from the Bahamas and the Straits of Florida (Figure 1a).

Character of vegetation and $\delta^{13}C$

The main vegetation found in the grassland portions of the Everglades includes sawgrass, cattail, water hyacinth, and periphyton, all of which utilize the C-3 photosynthetic pathway (e.g. Wang et al., 2002). C-3 plants are adapted to moist, temperate environments with relatively high atmospheric CO_2 concentrations, and fix carbon using the enzyme RuBisCO. Because the large kinetic fractionation factor associated with RuBisCO fixation is fully expressed, C-3 plants have average $\delta^{13}C$ values of -27‰. However, RuBisCO also photorespires causing a net loss of carbon, and the rate of photorespiration increases at higher leaf temperatures. This fact makes C-3 plants less water-use-efficient than C-4 plants, and less capable of fractionating against $^{13}CO_2$ during hot and water-stressed conditions (Farquhar et al., 1989).

Conversely, C-4 plants such as sugarcane, corn, millet and tropical grasses, are better adapted to warmer growing seasons and drier climates and have an average $\delta^{13}C$ value of -12‰. Though C-4 plants also fractionate against $^{13}CO_2$ via RuBisCO, the initial carbon fixation is accomplished via the enzyme PEP carboxylase, which is more kinetically efficient at carbon fixation especially under low atmospheric CO_2 concentrations. However, the initial 4-carbon acid produced via PEP carboxylase fixation is decarboxylated in specialized bundle sheath cells, where a second step of carbon fixation via RuBisCO is required. This uniquely allows C-4 plants to increase the concentration of CO_2 inside the mesophyll cells (a carbon concentrating mechanism) and thereby suppress photorespiration by RuBisCO. Because nearly all the CO_2 in the mesophyll cells is fixed, C-4 plants discriminate less against $^{13}CO_2$ than C-3 plants. This two-stage carbon fixation of C4 plants comes at the loss of requiring more energy than C-3 photosynthesis, so is generally less efficient. The exceptions are hot and water-stressed growing conditions, or low atmospheric CO_2 concentrations—conditions under which the net loss of carbon to photorespiration reduces the efficiency of C-3 plants to the point that C-4 plants have the advantage of greater water-use efficiency (Hatch, 1987).

With this in mind, particulate and dissolved organic matter deposited in the water-saturated conditions of the Everglades is expected to be C-3-dominant and have $\delta^{13}C$ values close to that of C-3 vegetation. However, agricultural production in water-stressed uplands and drained regions adjacent to the Everglades is used for many C-4 crops, and is believed to provide localized C-4-derived inputs via runoff, which could increase the $\delta^{13}C$ values of organic matter derived from these drained agricultural regions or uplands.

Purpose and Goals

This paper provides data from a ten-month, monitoring study during 2007. The data come from water samples collected at three sites: Palma Vista Cave, a small cave within Palma Vista Hammock; a shallow well in the bedrock within Palma Vista Hammock; and Taylor Slough to the east of Palma Vista Hammock (Figure 1a). The data consist of hydrologic and geochemical observations. More specifically, the data provide insight into the variation of rainfall, water levels, basic water chemistry, primary cations and anions, and stable isotopes of oxygen, hydrogen, and carbon.

Our specific purposes in collecting these data are fourfold: 1) to better characterize the relative response of water levels in the slough and the hammock to precipitation events; 2) to observe seasonal trends in water chemistry and relate those trends to the local climate; 3) to identify, using stable isotopes, the transport pathways for near-surface waters within this portion of the

Everglades ecosystem; and 4) to quantify the exchange of waters between the surface and the shallow subsurface.

These data supplement the findings of Price and Swart (2002) during a study of similar scope. The differences between our respective studies are reflected in the geographic scale and data resolution. Price and Swart's study was wider ranging and longer term. 46 wells and 23 surface-water sites were sampled over a more than 3,000 km^2 region throughout the east-central Everglades between 1997 and 1999. Samples were collected on a monthly basis and many sites were not sampled during the course of the study. This study, in contrast, is much narrower in scope with a greater sampling frequency. All three sites are within an area of 5 km^2 and each site was sampled every two weeks.

Samples and Analyses

The data comprise 22 sets of water samples collected every two weeks beginning on March 29, 2007 and ending on January 16, 2008. Each set consists of samples from: 1) precipitation (P); 2) surface waters collected at the USGS gauging station at the bridge over Taylor Slough (TS) (National Water Information Service [NWIS] station ID 252404080362401); 3) water within Palma Vista Cave (PVC); and 4) water drawn from the nearby shallow well (PVW) in Palma Vista Hammock (both the cave and well share NWIS station ID 252312080371901).

To supplement these samples, hourly water-level measurements were collected during the course of the study using piezometers at both the TS and PVW sites. Hourly measurements of precipitation amount were collected using a rain gauge at the TS site.

Precipitation waters were collected for analysis using a funnel and a 2 m length of 1 cm tygon tubing. The tubing was snugly inserted through a plastic seal and extended to the bottom of a plastic reservoir to minimize evaporation from the water surface in the reservoir back through the tube; the tubing and reservoir were shaded and shielded by aluminum foil and insulation to further reduce evaporation between sample collections. Samples of the precipitation were poured into a 60-mL glass bottle, sealed, and kept at 4 °C until the time of analysis for δD and δ^{18}O. The remaining water in the collection reservoir was removed after each sample.

Surface waters from the slough, the well, and the cave were consistently drawn from 30 cm depth using a peristaltic pump. Three well volumes were purged from the well prior to sample collection. The sample suite at each site that are presented in this paper include:

1) A one-liter bottle of water filtered through a 0.45 μm membrane collected for analysis of dissolved organic carbon (DOC) δ^{13}C and C:N ratios, fixed with 30% HCl to prevent further bacterial production, and covered in Parafilm to eliminate headspace;

2) a sealed 60-mL glass bottle of filtered water collected for δD and δ^{18}O analyses;

3) a 125-mL opaque bottle of filtered, non-acidified water collected for nitrate and total nitrogen analyses;

4) a 250-mL bottle of filtered, non-acidified water to analyze for dissolved major cations and anions;

5) a 250-mL bottle of filtered and acidified water to analyze for dissolved metals;

6) a 250-mL bottle of unfiltered water to analyze for suspended solids; and

7) a 250-mL bottle of unfiltered and acidified water to analyze for total metals.

Additionally, during each sampling interval we collected field measurements of pH, specific conductance (SpC), dissolved oxygen (DO), temperature, and total alkalinity at TS, PVC, and PVW. Moreover, two YSI datasondes were deployed during the period 9/18/2007 through 10/10/2007 to collect field parameters every 15 minutes. At TS, an OSM 600 collected SpC data. At PVW, an OSM-600XLS collected temperature and pH in addition to SpC.

The majority of the geochemical analyses were conducted at the National Water Quality Lab (NWQL) in Denver, CO. Data from these analyses are publically available from the NWIS database. All stable isotope measurements are reported in standard δ-notation:

$$\delta = \left({}^{R_{sample}}\!/_{R_{std}} - 1 \right) \times 1000$$

where R is the ratio of heavy to light isotope. Analyses of δD and $\delta^{18}O$ were conducted by the Reston Stable Isotope Lab (RSIL), Reston, VA, and reported with respect to the international VSMOW standard.

Analysis of carbon isotopes and C:N ratios were conducted at the University of South Florida Department of Geology in Tampa, FL. Dissolved organic matter was physically separated from each sample by filtration and evaporative concentration. Stable isotope analyses of organic matter were carried out using a Delta V gas-source isotope ratio mass spectrometer (IRMS) coupled to a Costech elemental analyzer, and analyzed for $\delta^{13}C$, %C, and %N, with ratios of %C and %N used to calculate C:N. Stable isotopes were standardized to Fergie CN (containing sucrose, KNO_3, Si, and kaolinite), and B2155 (protein).

RESULTS

Figure 2 is a compilation of a hyetograph, water level data, and field measurements (temperature, pH, specific conductance, and dissolved oxygen). In the hyetograph, moisture sources (tropical wave, frontal system, local convention, tropical convection) are indicated for major events as well as the principle wind direction as identified from daily radar animations. The MSD is clearly present during mid- to late-August. Generally speaking, the values for all except for pH appear to follow similar trends, or at least follow what appears to be an annual

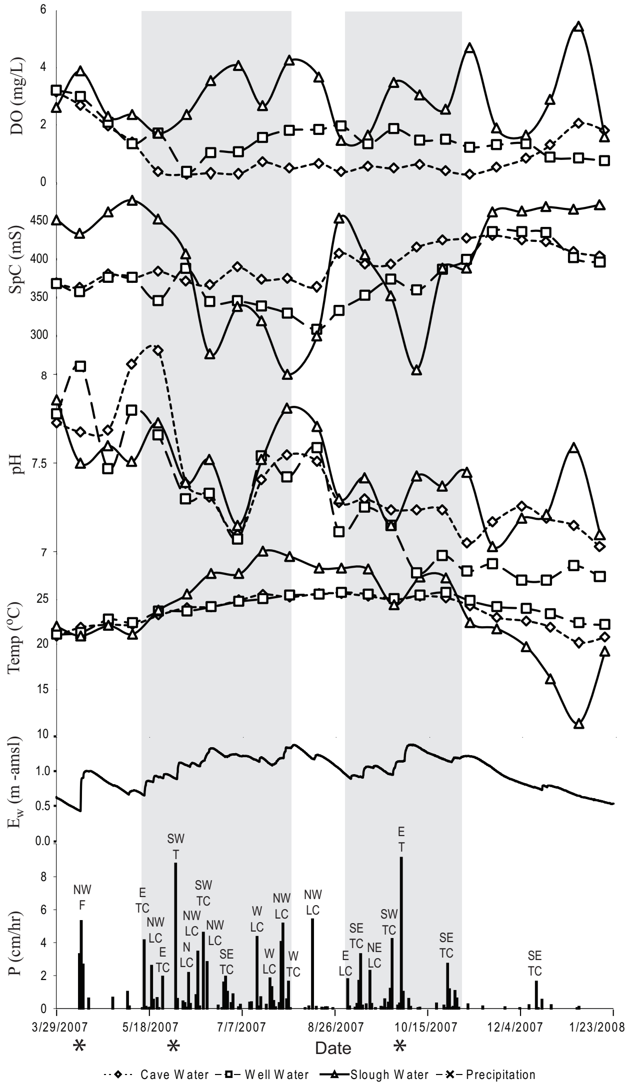


Figure 2. A compilation time-series plot of a hyetograph (P) and water level (Ew) data at Taylor Slough, and field measurements of temperature (T), pH, specific conductance (SpC), and dissolved oxygen (DO) at all three sampling sites. Precipitation events that exceed a rate of 2 cm/hr also include information about type and motion of the precipitation as indicated by Doppler radar (F – frontal, LC – local convection, TC – tropical convection, T- tropical system; N – north, NW – northwest, E – East, NE – northeast, S – south, SW – southwest, SE – southeast). Grey bars indicate the wet season. Asterisks indicate precipitation events that are particularly meaningful to the discussion

cycle. In all cases, the surface water of the slough experiences the greatest excursions, whereas the cave and well waters remain relatively stable and mutually similar.

Figure 3 is the shorter-term, higher-resolution data. In these data, temperature, pH, and conductivity all respond to individual rain events, shown by an immediate increase in water level. These data also reveal other fine structures in the data such as daily variations in slough-water SpC due to solar insolation; diurnal fluctuations in water level from tidal forces as the piezometer was not vented; and a sharp, temporary excursion in well-water SpC and pH during a precipitation event on 9/25.

Figure 4 is a Piper diagram relating principle cations, Ca, Mg, and Na+K, with principle anions, Cl, SO_4, and HCO_3, for all samples. These same data, with other cations and anions are presented in time-series format in Figure 5. There are similar trends in many of the parameters to those of the field measurements in Figure 2. As before, the slough waters experience the greatest excursions during the rainy season and the well and cave waters remain relatively stable throughout the year. There are, however, notable exceptions to this trend. For example, total nitrogen, sulfate, and potassium experience a spike in the slough water sample collected on 4/11. This sample immediately follows the first major rainfall of the year (Figure 5). The samples from the well and the cave do not reveal a similar spike on this day. However, the dissolved iron in the well water dramatically increases at the beginning of the rainy season in May and remains high until after the dry season begins in November. The dissolved iron in the cave water remains low except for an anomalously high spike of 318 µg/L on 8/29 during the mid-summer drought (Figure 5). The charge balances are within 1.3% for this sample and less than 5% for all samples.

In Figure 6, data from isotopic analyses, D_{ex}, C:N ratios, and pCO_2 are presented. In general, the values of δD and $\delta^{18}O$ track not only each other at all three sites but also precipitation. Precipitation samples have the greatest variability, followed by slough water, which again experiences more fluctuation than either the well or the cave waters. The most depleted values of δD and $\delta^{18}O$ in precipitation and slough water occur following Tropical Storm Barry on 6/1 and 6/2 and following an unnamed tropical low on 9/25. The average values of δD (-1.3‰) and $\delta^{18}O$ (-0.5‰) in the slough water are considerably greater than for the

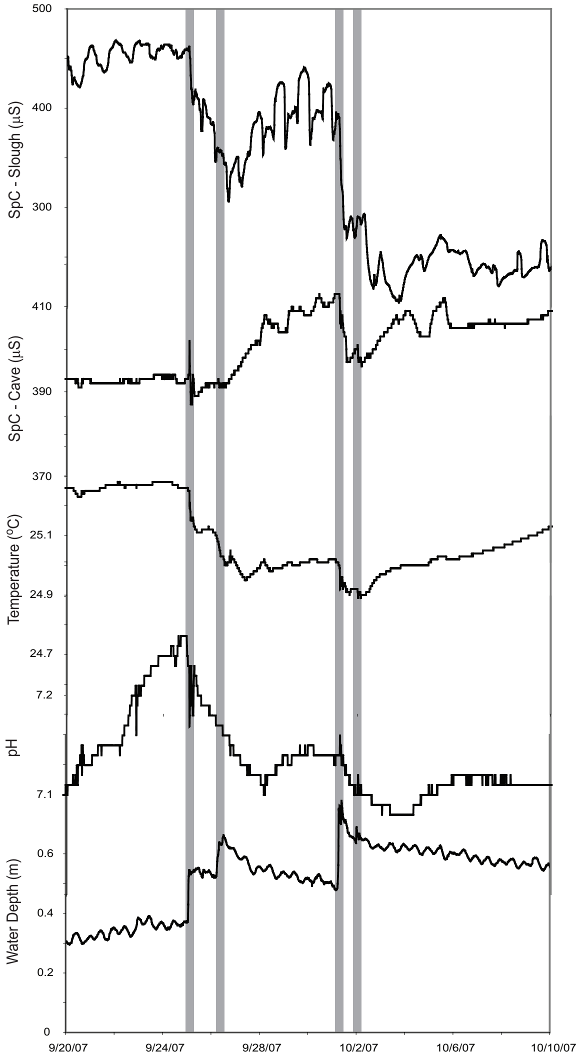


Figure 3. Shorter-term, higher-resolution data at Palma Vista Cave and Taylor Slough that include water level at the cave, pH in the cave, temperature in the cave, specific conductance (SpC) in both the cave and the slough. Grey bars indicate the specific precipitation events.

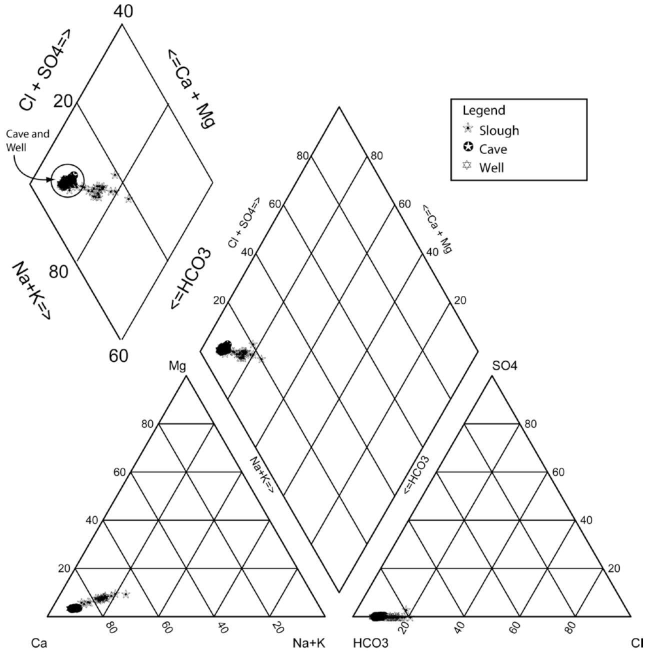


Figure 4. Piper plot of major cations and anions from data at all three sampling locations. Detail inset in upper left shows tight clustering of cave and well data.

well (-11‰, -2.2‰) or the cave (-12‰, -2.4‰). The average values of D_{ex} for precipitation are 8 between the beginning of the study and 8/29 and 13/1 for the remainder of the study. The D_{ex} data reaches a low of -1.3 on 8/17.

Values of D_{ex} in the samples of precipitation have a distinct seasonal variation divided by the MSD in late-August (Figure 6). From the start of the study until the MSD, values of D_{ex} average 8.2 with a trend toward lower values and a minimum value of -1.25 on 8/17. After the MSD, values of D_{ex} remain consistently above 10 with an average of 13.1 and a maximum value of 19.1 on 1/16.

The values of $\delta^{13}C_{DOC}$ at the three sites range between -22.6 and -28.0‰ (Figure 6). Average values of $\delta^{13}C_{DOC}$ from the cave and the well were nearly identical, measuring -26.7 and -26.3‰, respectively; however, the well was more enriched between April and August 2007 compared to later in the study by approximately 1‰. $\delta^{13}C_{DOC}$ values are consistently ^{13}C-enriched in the slough (-24.7‰ average) compared to the cave and the well. Large fluctuations in $\delta^{13}C_{DOC}$ at the cave began in late August, with peak values on 8/29, 10/10, and between 12/6 and 12/19. With the exception of the sample on 8/29, these $\delta^{13}C_{DOC}$ peaks coincided with peaks at the well.

C:N ratios were highest at the cave, averaging approximately 19.8:1, with the highest ratios occurring from summer to fall (Figure 6). Average C:N ratios at the well and slough were approximately 14.8:1 and 15.4:1, respectively, and peaked in spring to early summer, although ratios at the well were generally lower than the slough.

DISCUSSION

Water-level changes are rapid simultaneous, and of similar magnitude in Taylor Slough (Figure 2). When it rains, that precipitation is instantly manifested as an increase of water level – either by direct addition to surface waters, as is the case for the slough, or by rapid percolation through a thin vadose zone of very porous and solution-modified rock, as is the case for the cave and the well. In fact, on 12/06 at the cave, a one-liter application of water on the surface was heard dripping into the cave pool after only three minutes when the soil was dry and after approximately 15 seconds when the soil was saturated. The water is likely being channeled via syndepositional burrow networks or root-generated macropores.

Not only does rain immediately affect water levels in the Everglades, the water chemistry of these $Ca\text{-}HCO_3$ waters also changes (Figure 3). For example, water in the slough experienced reduction of more than 100 µS in SpC in less than two hours during a major precipitation event on 10/1 (Figure 3). That same event reduced the SpC in the well by 15 µS. At broader time scales, the addition of rainwater during the rainy season oxygenates the water and dilutes the dissolved solids in the slough water, which in turn reduces the total alkalinity (Figures 2 and 5).

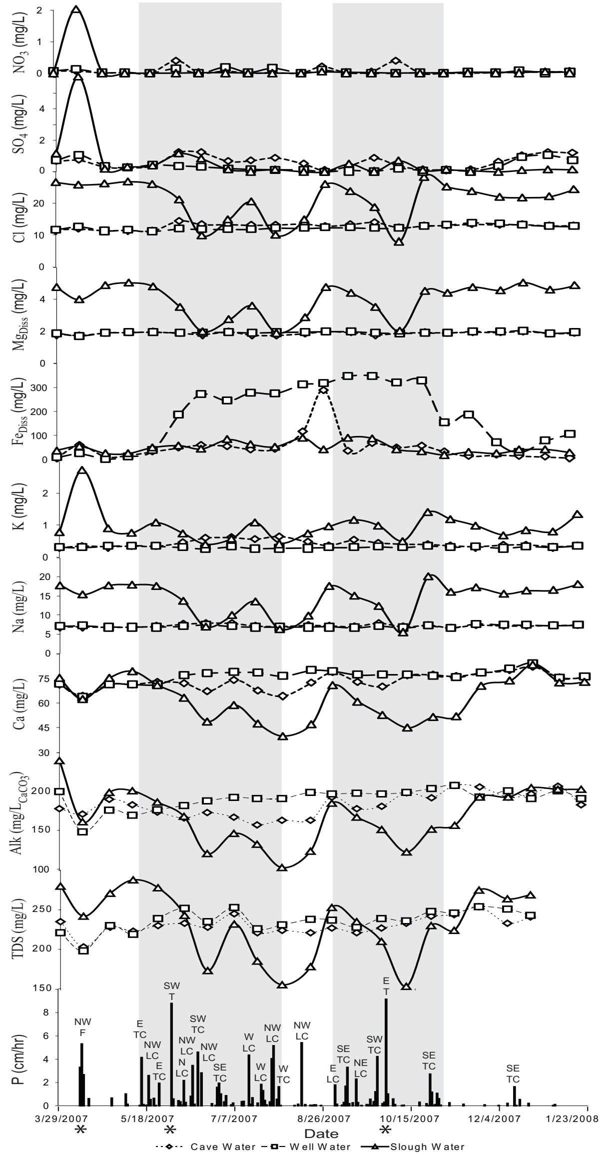


Figure 5. Compilation time-series plot of a hyetograph (P), total dissolved solids (TDS), total alkalinity (Alk), major cations (Ca, Na, K, Fe, Mg), and major anions (Cl, SO_4, NO_3). Precipitation events that exceed a rate of 2 cm/hr also include information about type and motion of the precipitation as indicated by Doppler radar (F – frontal, LC – local convection, TC – tropical convection, T- tropical system; N – north, NW – northwest, E – East, NE – northeast, S – south, SW – southwest, SE – southeast). Grey bars indicate the wet season. Asterisks indicate precipitation events that are particularly meaningful to the discussion.

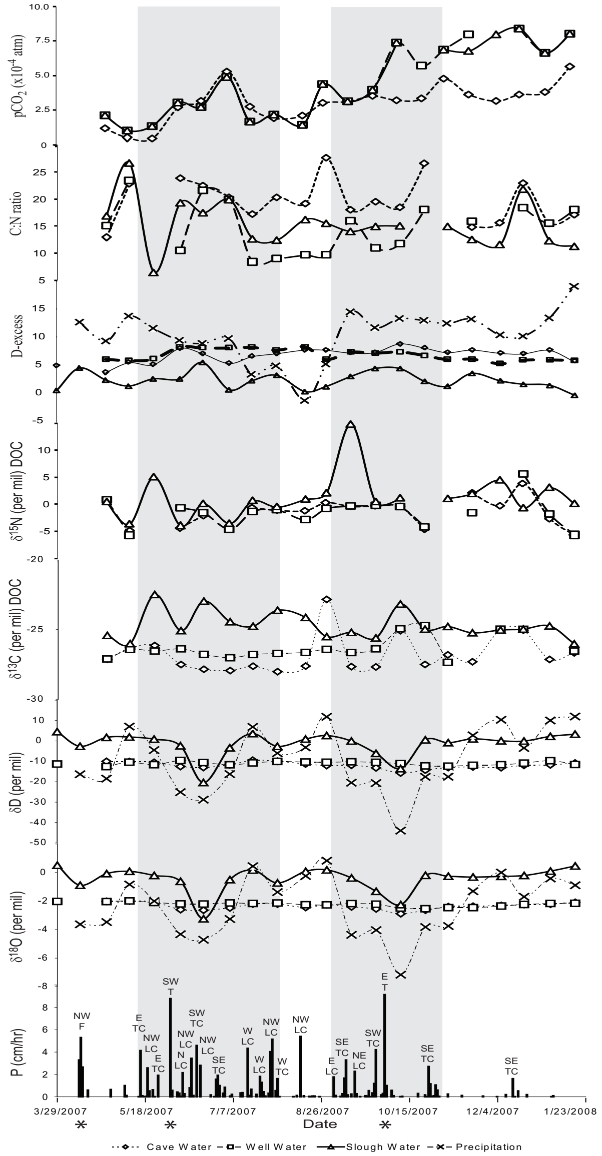


Figure 6. Compilation time-series plot of a hyetograph (P), ratios of stable isotopes ($\delta^{18}O$, δD, $\delta^{13}C$, $\delta^{15}N$), D excess, C:N ratio, and pCO_2. Precipitation events that exceed a rate of 2 cm/hr also include information about type and motion of the precipitation as indicated by Doppler radar (F – frontal, LC – local convection, TC – tropcial convection, T- tropical system; N – north, NW – northwest, E – East, NE – northeast, S – south, SW – southwest, SE – southeast). Grey bars indicate the wet season. Asterisks indicate precipitation events that are particularly meaningful to the discussion

Compared to the slough, neither the well nor the cave water vary significantly from the dry season to wet season; these waters tightly cluster on the Piper diagram (Figure 4). Furthermore, this Piper diagram reveals that slough waters can have Na and Mg concentrations elevated above the cave and well. These samples occur during the dry season (Figure 5). Na in the slough, for example, averages 16 mg/L during winter and spring compared to an average of 7.2 mg/L in both the cave and the well (Figure 5). A similar pattern exists for Mg, with a dry season average in the slough of 4.5 mg/L and 1.7 mg/L in the cave and the well, respectively. Chloride, and to a lesser extent K, have the same annual pattern. The concentrations of Ca in the slough, while following the same trend as the other dissolved solids, have values in the dry season roughly equivalent to that of the cave and well and more diluted values during the wet season (Figure 5). Simple concentration of surface waters due to evapotranspiration (ET) and a mixing of surface water and one or more external sources such as precipitation, canal water, and deep groundwater drive these observed patterns of dissolved solids in the slough compared to the cave and well. Determining the relative proportions of external sources without concurrent end member comparisons is difficult.

Moisture sources

With vast expanses of open water, lush vegetation, and warm subtropical conditions, it comes as no surprise that evapotranspiration (ET) rates are very high in the Everglades. In fact, German (2000) measured rates of ET that ranged between 108 cm/yr, at a site where the water level is below the land surface to 146 cm/yr at a site with exposed water and no emergent vegetation. This translates to more than 75% of average precipitation, with the unevaporated balance contributing to runoff and infiltration to groundwater.

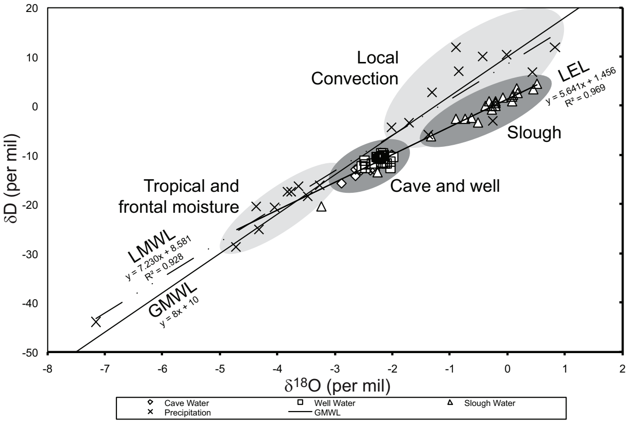


Figure 7. Plot of δD versus δ¹⁸O for samples of precipitation, surface water from the slough, and shallow groundwater from the cave and well. The global meteoric water line (GMWL), local meteoric water line (LMWL), and local evaporation line (LEL) are shown along with regressions. The LEL connects samples from the slough, the cave, and the well to precipitation samples from frontal and tropical systems, which have a distinct isotopic signature from samples of precipitation that come from local convection.

A plot of δD versus δ^{18}O clearly reveals the effects of ET at our field site (Figure 7). The LMWL of precipitation samples in the Everglades is δD = 7.2(δ^{18}O)+ 8.6 (R^2 = 0.93) and has a similar slope and intercept to the GMWL. Points on the LMWL cluster into two principle groups: 1) samples with a δD range of -6 to +12‰ and a δ^{18}O that ranges between -2 and +1 ‰ which are associated principally with local convection, and 2) samples with a δD range of -29 to -16‰ and δ^{18}O that ranges between -5 and -3‰ which are generally associated with tropical moisture or the passage of frontal systems (Figures 6 and 7).

The time-series data of precipitation Dex (Figure 6) further distinguish between moisture sources for precipitation. During the late spring and summer of 2007, and before the MSD, precipitation samples registered values of D_{ex}<10. It is likely that these samples reflect continental moisture with a significant component provided by transpiration and carried by the Westerlies or moisture generated by local ET and convection. Samples with $D_{ex}>10$ cluster in the fall and winter, after the MSD, and appear to be associated with evaporated maritime moisture carried along the Trade Winds.

A least squares fit using the samples from the well, the cave, and precipitation samples from tropical or frontal system produces a LEL with a slope of 5.6 and a R^2 of 0.97 (Figure 7), an indication of significant evaporation (Gonfiantini, 1986). The LEL fit demonstrates an additional, and important, point about Everglades hydrology. Samples from the slough, enriched in D and ^{18}O via ET, evolved along the LEL from shallow groundwater in the hammocks that include the well and the cave. These waters in the hammocks themselves evolved along the LEL from tropical and frontal moisture sources, not localized convection. Whereas local convection is frequent, yet isolated and of short duration, tropical and frontal systems are infrequent, but widespread and long lasting. Florea and Vacher (2007) demonstrated the importance of tropical and frontal systems to aquifer recharge in west-central Florida. The same principle applies in the Everglades. Tropical and frontal systems in the spring and fall, respectively, add new water to the flow system. Local convection recycles the available water, a statement supported by values of $D_{ex}<10$ gathered during the parts of the wet season dominated by local convection (Figure 6). A further point the data illustrates is that shallow groundwater in the hammocks and pine rocklands, depleted in D and ^{18}O (Figure 6), recharges the surface water in the slough, which is enriched in the heavier isotopes. Mixing of surface water in the slough with shallow groundwater in the hammocks appears limited. The limited geochemical changes in the cave and well compared to the slough (Figure 5) further illustrate this point. This finding supports that of Price and Swart (2006), who demonstrated that the shallow groundwater in the pine rocklands recharges Taylor Slough downstream of our field site.

Sources of dissolved solids

While our δD and $\delta^{18}O$ data as well as those of Price and Swart (2006) suggest that surface waters in Taylor Slough evolve via ET alteration of shallow groundwater, our data regarding dissolved solids provide evidence that at least part of the surface waters in the study area have their source in the agricultural area to the north and east, outside of ENP. For example, the lowest concentrations of Na, Mg, K, and Cl in the slough are equivalent to the median value at the cave and well (13 mg/L for Cl – Figure 5). These low concentrations in the slough occur during the wet season, when frequent rains dilute the total dissolved solids. In contrast, elevated concentrations of these ions in the slough (27 mg/L for Cl) are the likely result of a combination of evaporation and source waters with higher original concentrations of these solutes with the relative proportion of these two phenomenon being hard to discern.

The lower average values of total dissolved solids in the cave and the well (Figure 5) point toward less influence by evaporation; a point illustrated by the lower average temperature and higher average relative humidity in the hammock and the fact that evaporation is greatly reduced in shallow groundwater compared to surface water. Collectively, the ion data in this study and that of Price and Swart (2006) support the isotope data that demonstrate that the direction of shallow groundwater flow is from the hammock and pine rocklands to the slough.

The time-series data of SO_4, K, and NO_3, reveal an interesting event. The highest values of each occur in the sample from the slough on 4/11, which immediately follows the first major rainfall of the year (Figure 5). Following Orem (2004), we attribute the SO_4 to runoff of agricultural sulfur used as soil amendment along with N and K in the agricultural areas to the north and east of Everglades National Park. This SO_4 may enter Taylor Slough via the S-322 pump station on the L-31W canal 3 km to the northeast of the sampling site (Figure 1a) and concentrate in the soil via ET during the dry season. At the end of the dry season, when low water levels expose these soils, the first major precipitation event in the Everglades liberates the SO_4. We furthermore feel that this process explains the similar spikes in both K and NO_3.

The $\delta^{13}C_{DOC}$ data also demonstrate a potential influence of source waters external to Everglades National Park. Vegetation at all three localities is C-3-dominant, and is more apparent in the $\delta^{13}C_{DOC}$ at the cave and the well (Figure 6). The $\delta^{13}C_{DOC}$ in the slough is slightly more enriched, a sign that the slough waters could be subject to inputs that might include organic material from agricultural runoff and C-4 vegetation.

C:N ratios at the cave are highest, indicating DOC here is composed of refractory organic tissues such as lignin in various stages of decomposition. Because the cave is open to the C-3 dominated forest above, it can be assumed the primary source of DOC here is attributed to plant detritus falling and/or washing in from the surface. The ratios at the slough and well were lower than the cave, supporting one or more of the following three scenarios: 1) DOC in comes from sources containing more labile organic tissues, such as aquatic macrophytes and algae; 2) DOC is in the more advanced stages of decomposition, with inherently low C:N ratios, and 3) carbon is rapidly recycled/remineralized by organisms, lowering its proportion relative to nitrogen. Though we can assume that Scenarios 1 and 3 are more important at the slough due to the availability of sunlight and relatively high rates of primary productivity relative to the well, and that the well is governed by Scenario 2 as organic detritus is transported to it from the cave, these hypotheses should be tested with further geochemical analyses. By comparing the rate of organic C and N inputs to accumulation/burial rates in the sediments, we can estimate the volume of C and N recycled/remineralized through various geochemical processes at each site. Combining these data with that collected in this study as well as $\delta^{15}N$ and additional ion analyses (including NH_4^+ and PO_4^{3-}) can pinpoint the occurrence of specific geochemical processes influencing C and N flux at these sites, including, but not limited to, ammonification, denitrification, and phosphate reduction (Brenner et al., 2006; Troxler and Richards, 2009).

Calculated pCO_2 values become progressively higher in the winter months as surface productivity slows down, supporting scenario 2 (Figure 6), which. Calculated pCO_2 values at the slough demonstrate the same trend, suggesting that identical processes are occurring; however, because C:N ratios at the slough are slightly higher and $\delta^{13}C_{DOC}$ is slightly more enriched, DOC sources themselves are not identical between the two locations and may come from a wider variety of sources in the slough water. For example, C:N ratios might increase due to the widespread growth of woodier plants such as sawgrass, which is supported by similar trends in %C between the slough and cave during the summer months. At the same time, $\delta^{13}C_{DOC}$ might increase from slightly more enriched sources of DOC from agricultural areas to the north and east of Everglades National Park.

Conclusions

This study reveals a dynamic geochemical environment in the surface water of Everglades National Park that is sensitive to dilution from rainfall and input from external sources. Shallow groundwater, on the other hand, remains geochemically stable during the year. Of particular influence to the geochemistry of surface waters are large-scale, external sources of moisture such as tropical systems in the late summer and fall, and occasional frontal systems in the late winter and spring.

Stable isotopes of hydrogen and oxygen in samples of precipitation fit to a LMWL with a similar slope and intercept to the GMWL. These same samples clearly subdivide into two groups representing types of precipitation, those less depleted in the heavier isotope that represent local convection and those strongly depleted in the heavier isotope derived from tropical or frontal systems. An analysis of D_{ex} during the study reveals two sources of moisture separated by the Mid Summer Drought during late August: samples with $D_{ex}<10$ in the late spring and summer that represent moisture influenced by transpiration that are derived from continental sources from frontal systems conveyed by the Westerlies or local convection, and samples with $D_{ex}>10$ in the late summer and fall that represent moisture that are derived from evaporated maritime sources, such as tropical systems, brought onshore by the Trade Winds.

Stable isotopes of dissolved organic carbon suggest that C-3 vegetation dominates the organic matter in the surface water and shallow groundwater in Everglades National Park. C:N ratios in the cave samples indicate that the organic primarily originate from input from woody material, while a lower C:N ratio in the nearby well indicates that woody debris entering the cave further decomposes in transit to the well. C:N ratios in surface waters are of similar value to that in the well, but when combined with the stable isotope data, they suggest a blend of organic not present at the cave and well. When viewed in concert with the pCO_2 and geochemical data, specifically SO_4, NO_3, and K, there appears to be some input from C-4 vegetation in the agricultural areas to the north and east of Everglades National Park.

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