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Evaluating Complex Hydrogeological Settings in a Constructed Wetland: An Isotopic/Chemical Mass Balance Approach

Olesya Lazareva · Thomas Pichler

Abstract The objective of this study was to investigate the hydrogeological conditions of an artificial wetland, with four possible sources of water: (1) ground water, (2) industrial waste water, (3) seepage from a water body to the north, and (4) seepage from a water body to the south. The wetland was designed to improve the quality of municipal effluent and industrial wastewater. To evaluate and separate the impact of wetland processes from those due to dilution with water from "clean" sources (i.e., rain water or ground water), a combined isotope/chemical mass-balance approach was employed. The δD, $\delta^{18}O$, and Na were monitored for 18 months. Based on the data, the variation of individual proportions of each water type in the wetland and monitor wells was calculated. The isotopic composition of water in the wetland varied throughout the study period changing along the wetland flow path. The wetland contained mainly wastewater (88%–100%) during normal operations; however, hurricanes and inconsistent pumping added low conductivity water directly and triggered enhanced groundwater inflow into the wetland of up to 78%. Finally, the composition of water in monitor wells was mostly groundwater dominated; however seepage from a water body to the north was detected.

Keywords Florida · Stable isotopes · Waste water treatment · Fluid mixing

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Introduction

Investigation of complex hydrogeological conditions of wetland systems can be challenging. The isotopic composition of oxygen and hydrogen can provide important information about the source of water, i.e., for the actual H_2O molecules rather than dissolved constituents. Applications range across the whole spectrum of hydrogeological and hydrological studies, including hydrothermal systems (McCarthy et al. 2005; Pichler 2005a), aquifer recharge (Gonfiantini et al. 1998), groundwater-surface interaction (Baskaran et al. 2009), contamination studies (Pichler 2005b), but the water cycle (Craig 1961), delineating the source of water is particularly important for managing this resource in areas with limited water supply. The quantification of groundwater inflow into wetlands and lakes in Florida, for example, is an important component in the water balance equation (Sacks 2002). Groundwater input can differ significantly depending on the topographic settings, type of soil, depth to bedrock, vegetation, fractures, climate, and the anthropogenic activity, affecting water levels and quality (Kendall and Coplen 2001). Estimating this term can be very complicated, but quantification is possible using a chemical and isotope mass-balance method (Stauffer 1985; Krabbenhoft et al. 1990; Winter 1995; Sacks 2002). The isotope mass-balance method for estimating the water balance of lakes and wetlands has been used extensively (Dincer 1968; Krabbenhoft et al. 1994; Michaels 1995; Yehdegho et al. 1997; Hunt et al. 1998) and successfully applied in central Florida (Sacks 2002).

The major objective of this study was to investigate the complex hydrogeological settings of a constructed wetland in central Florida under a variety of meteorological conditions with respect to temperature, rainfall, and humidity using an the isotope/chemical mass-balance approach. Particularly, it was important to evaluate and separate the impact of wetland processes from those simply due to dilution with water from

"clean" sources (i.e., rain water or ground water). The purpose of this wetland was to improve the chemical composition of municipal effluent, industrial waste water, and surface runoff (Lazareva and Pichler 2010). The wetland was located in a closed phosphate mine and thus contributed to the reclamation of phosphate mines (EPA 1993). Phosphate mining in central Florida is widely distributed and annually disturbs about 15 to 25 km^2 of land through generation of clay settling areas, open mine pits, phosphogypsum stacks, and tailing sand deposits (FIPR). Florida law requires reclamation of previously mined phosphate lands into lakes, wetlands, pasture, and agricultural lands.

The monitoring of δD and $δ^{18}O$ was used (1) to evaluate possible groundwater input into six monitor wells installed along the wetland flow path; (2) to differentiate potential sources of water in the wetland, and (3) to understand the possible factors controlling the fluid mixing in the wetland and monitor wells. The values of $δ^{18}O$ and δD were used in combination with previously published Na data (Lazareva and Pichler 2010). This approach proved necessary due to the complex hydrogeological framework at the site, which resulted in four possible sources of water to the wetland: (1) ground water, (2) industrial waste water, (3) seepage from a water body to the north, (4) seepage from a water body to the south.

Site Description

The constructed wetland /filter basin treatment system was located in an area used during phosphate mining for clay settling and sand tailings at the Hines Energy Complex, Polk County, Florida (27°48′N latitude and 81°52′W longitude) (Fig. 1) (Lazareva and Pichler 2010). The system was established in 1999 and used for the experimental treatment of industrial wastewater from the Hines Energy electric power generating plant (cooling water), and tertiary treated effluent from the city of Bartow. Rain and excess surface water runoff provided additional water. The surface flow wetland was approximately 1,500 m long, varied in water depth from 0.5 to 2 m and was constructed in a U-shape (Fig. 1). The area of the wetland was about 12,250 m^2. The wetland was not lined. Its vegetation was allowed to evolve naturally and consisted of both native and non-native species. Generally, water from the Hines Energy Complex cooling pond (CP) was pumped into the wetland at different rates depending on the season from 5,012 to 6,757 L/day in the rainy seasons of 2006 and 2007 and 9,255 L/day in the dry season of 2006. The residence time of water in the wetland was approximately 120 days (Lazareva and Pichler 2010). The wetland was surrounded by two bodies of water: N-15 to the north and SA-8 to the south (Fig. 1). These previously mined and reclaimed phosphate lands are now a water-cropping system to capture, store, and reuse stormwater (PEF 2004).

The hydrogeological framework can be subdivided into the Floridan Aquifer System (FAS), the Intermediate Aquifer System (IAS) or Intermediate Confining Unit, and the Surficial Aquifer System (SAS) (Miller 1986). The Upper FAS is a continuous sequence of carbonate rocks of high porosity and permeability approximately 600 m thick (Miller 1986). From lowermost to uppermost, it is composed of the Paleocene—Eocene Avon Park Formation, the Eocene Ocala Limestone, and the Oligocene Suwannee Limestone. The FAS is confined above by the IAS, which consists of interbedded clays, sand beds, carbonates, and phosphorite of the Lower Oligocene—Miocene Hawthorn Group and the Lower Pliocene Tamiami Formation. It reaches a maximum thickness of 400 m (Scott 1988; Scott 1990; Brewster-Wingard et al. 1997; Missimer 1997). The overlying unconfined Pleistocene—Holocene SAS is about 30 m thick and comprised of unconsolidated to poorly indurated sands, sandy clays, carbonates, and reworked phosphorite grains (Gilboy 1985; Sacks and Tihansky 1996).

Methods

Water Sampling

Monitoring was carried out for 18 months in order to evaluate wetland performance under a variety of meteorological and hydrologic conditions. This was deemed necessary to separate wetland-induced changes in water chemistry from those due to dilution by runoff, groundwater or seepage from nearby water bodies (N-15 and SA-8; Fig. 1). Water sampling began in April 2006 and finished in October 2007 (Lazareva and Pichler 2010). For the isotope part of the study monthly water samples were obtained from the cooling pond (CP), wetland water from a pump (WP), wetland water from surface (WS), water bodies to the north and south of the wetland, N-15 and SA-8, and several samples from the effluent discharge (EF) (Fig. 1). To evaluate possible seepage from N-15 and SA-8 into the wetland, six monitor wells (MWs) were installed along the flow path and sampled monthly. In total, 192 water samples were collected and analyzed (Table 1). In order to investigate the potential change in isotopic signature along the wetland flow path, 18 samples within the surface water were collected and analyzed. The wetland transects were performed on April 24, May 15, and June 27, 2006, respectively.

Water Analysis

For this part of the study, water samples were filtered through a 0.45 μm membrane and placed into 30 mL HDPE bottles. Values of $δ^{18}O$ and δD were determined at the University of South Florida stable isotope laboratory using a Finnegan Delta V 3 keV Isotope Ratio Mass Spectrometer and a Gasbench II preparation device. For oxygen isotope determination, 200 μL
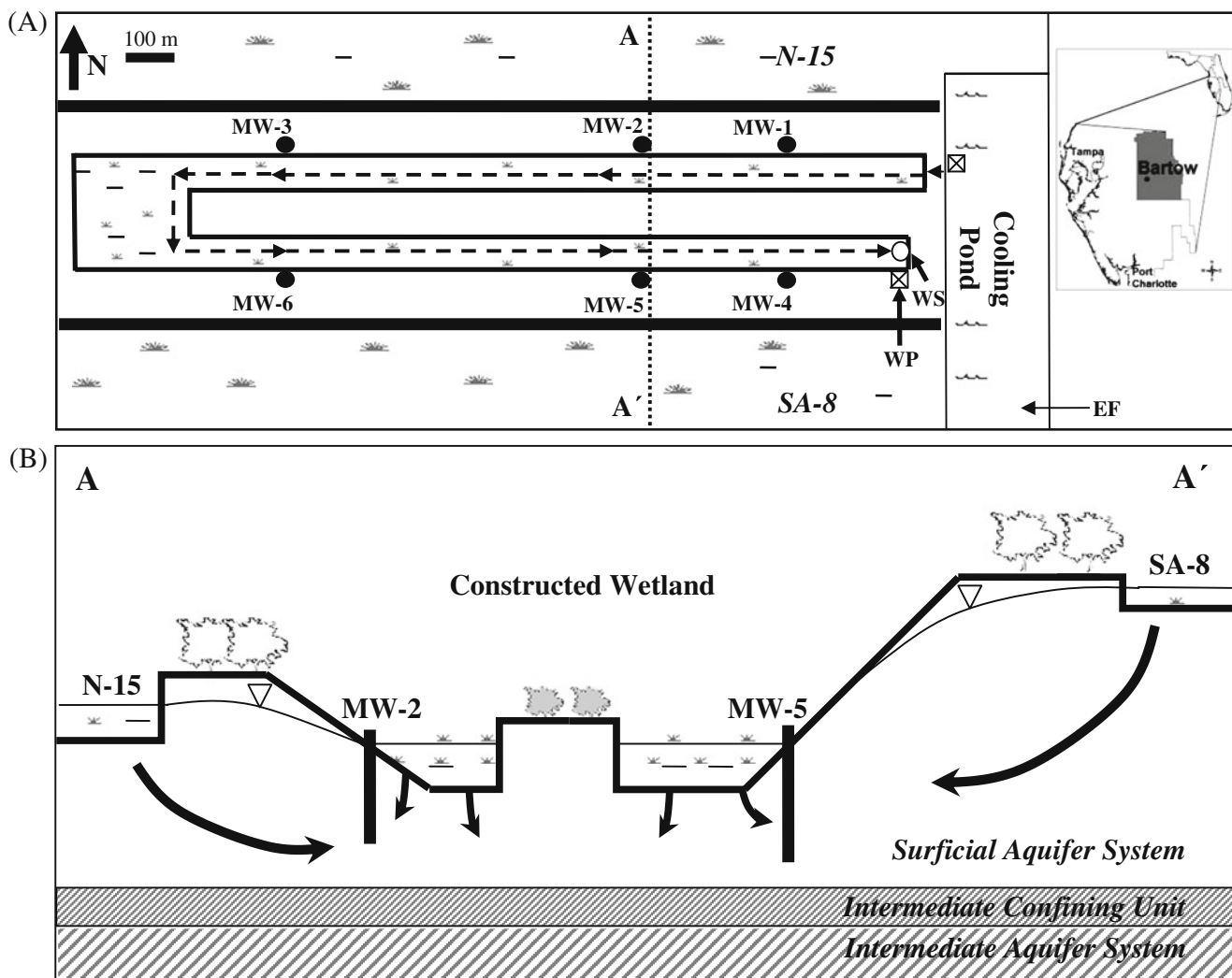
Fig. 1 **a** Map of the study area including water transfer system from the cooling pond to the U-shaped constructed wetland; **b** Cross-section along transect A—A Note water sampling locations: MW-1 to MW-6 = monitor wells; *WP* = wetland water from pump; *WS* = wetland water from surface; *EF* = effluent; N-15 and SA-8 = water bodies to the north and south of the wetland. Arrows represent possible groundwater flow paths. Vertical dimensions are not to scale

of sample was equilibrated with 0.3% CO_2 in He mixture for 24 h at 25°C. Prior to hydrogen isotope analysis, 20 mL of sample were reacted for 24 h with 1 g of Cu wire to remove dissolved sulfides and to reduce the effects of H_2S gas on the Pt catalyst during the H_2 equilibration. Following this treatment, 200 μL of sample were equilibrated with a 1% H_2 and He mixture for 10 minutes. Both oxygen and hydrogen isotope measurements were compared to the Vienna Standard Mean Ocean Water (VSMOW) standard and reported as $\delta^{18}O$ and δD. The average standard deviations for $\delta^{18}O$ and δD measurements were 0.1‰ and 1.0‰, respectively.

Precipitation measurements (amount of rainfall) were performed by the staff from the Hines Energy Complex weather station. Surface water-level measurements were done by Schreuder Inc. and meteorological data was available from the nearby Frostproof Station of the Florida Automated Weather Network (FAWN).

Results

Precipitation Measurements

Daily precipitation was recorded at the Hines Energy Complex weather station from May 1, 2006 to October 31, 2007. Due to periodic variations in precipitation and temperature of the study area two different seasons could be distinguished: the dry season from November to April, and the rainy or wet season from May to October. The highest levels of rainfall (up to 123 mm) were detected during the hurricanes Ernesto and Alberto, in June and September 2006. The mean monthly rainfall ranged from 0 to 11 mm. Total seasonal precipitation during the dry season of 2006 was 324 mm, while the rainy seasons of 2006 and 2007 varied between 917 and 782 mm, respectively (Lazareva and Pichler 2010).

Table 1 Minimum, maximum, mean, median and standard deviation values of $\delta^{18}O$ and δD in all sampling locations

Location	$\delta^{18}O$					δD					
	Min	Max	Mean	Med	STD	Min	Max	Mean	Med	STD	N
CP	4.42	5.98	5.18	5.02	0.46	20.2	29.0	24.4	24.1	2.7	18
EF	−1.74	−1.67	−1.71	−1.73	0.04	−9.2	−8.3	−8.8	−8.7	0.5	3
WP	−2.31	5.62	2.47	2.54	2.16	−10.6	29.3	12.0	12.4	11.2	19
WS	−2.31	5.69	2.59	3.10	2.45	−10.7	28.5	13.0	15.4	11.9	14
MW-1	−4.18	4.95	−2.51	−2.93	2.08	−24.9	24.2	−12.9	−14.7	11.0	19
MW-2	−2.93	1.03	−1.85	−2.27	1.07	−15.6	4.6	−9.6	−10.8	5.5	20
MW-3	−3.66	4.15	−0.50	−0.93	2.39	−19.2	20.6	−3.0	−3.1	12.3	17
MW-6	−4.15	−2.51	−3.12	−3.13	0.31	−23.8	−12.5	−16.1	−15.6	2.5	18
MW-5	−4.12	−2.19	−3.01	−2.90	0.57	−23.8	−2.5	−14.5	−15.8	5.4	17
MW-4	−4.63	−0.53	−2.82	−2.76	1.00	−27.8	−1.4	−14.0	−14.2	7.2	18
SA-8	1.97	3.94	2.92	3.19	0.71	10.4	19.9	14.6	14.3	3.4	11
N-15	0.03	2.84	1.51	1.46	0.76	−1.9	12.9	7.3	6.9	4.0	18

CP- cooling pond; EF—effluent; WP—wetland water from pump; WS—wetland water from surface; MW-1 to MW-6—monitor wells arranged according to the wetland flow path; SA-8 and N-15—water bodies to the north and south of the wetland.

Surface Water-Level Measurements

The monitoring of surface water-level elevations above National Geodetic Vertical Datum (NGVD) showed that the SA-8 had a higher level (51.6–52.5 m) compared to the N-15 (49.9–50.7 m) and the cooling pond (CP) (49.0–49.3 m) (Fig. 2). The elevation of wetland water surface (WS) ranged from 49.7 to 50.8 m with the lower levels in April–May 2007. Records showed that at the end of April the CP pump was turned off and the WS was lowered approximately 1 m for maintenance purposes. After one month the CP pump was turned back on and the wetland treatment system became again operational.

Isotopic Composition

The complete chemical composition of water samples from all locations was reported previously by Lazareva and Pichler (2010) and Lazareva (2010).

Wetland Water

During the 18-month period of the study, the δD and $\delta^{18}O$ composition of wastewater in the cooling pond (CP) was relatively constant and ranged from 20.2‰ to 29.0‰ and 4.4‰ to 6.0‰, respectively (Table 1). The isotopic composition of treated effluent (EF) discharging into the CP ranged from −8.3‰ to −9.2‰ for δD and −1.67‰ to −1.74‰ for $\delta^{18}O$. These values were close to the Upper Floridan groundwater line reported by Swancar and Hutchinson (1995). In contrast to the CP, the isotopic composition of wetland water collected from a pump (WP) at the end of the flow path showed seasonal variation. The δD and $\delta^{18}O$

values at the WP ranged from −10.6‰ to 29.3‰ and −2.31‰ to 5.62‰, respectively. The δD and $\delta^{18}O$ of the wetland water from surface (WS) were very similar to the WP and ranged from −10.7‰ to 28.5‰ and −2.31‰ to 5.69‰, respectively. The most depleted isotope values at the WP corresponded to hurricanes Ernesto and Alberto, in June and September 2006. The wetland transect was carried out three times within about two months. The first transect was performed on April 24, 2006. The $\delta^{18}O$ and δD values along the wetland were relatively heavy, ranging from 0.33‰ to 3.16‰ and from 3.6‰ to 17.1‰, respectively. It was noticeable that at the beginning of the wetland $\delta^{18}O$ and δD were depleted by 3.88‰ and 17.3‰ compared to the CP. The second transect, performed on May 15, 2006 showed a slow isotopic depletion along the wetland flow path where $\delta^{18}O$ and δD ranged from 0.60‰ to 4.09‰ and from 5.5‰ to 19.4‰, respectively. The third transect, performed after hurricane Alberto (June 27, 2006), demonstrated even higher depletion of $\delta^{18}O$ and δD varying between −0.02‰ to 3.25‰ and −3.1‰ to 14.5‰, respectively. It was interesting to note that a distinctive depletion of $\delta^{18}O$ and δD from 4/28 to 6/27 was evident between 1,300 and 2,700 m but reversed between 0 and 1,300 m of the wetland flow path (Fig. 3).

Figure 4 shows a high correlation between δD and $\delta^{18}O$ at the WP with the trendline equation of $\delta D = 5.1 \ \delta^{18}O – 0.6$ ($R^2 = 0.98$). Kendall and Coplen (2001) reported that the local meteoric water line for Florida was $\delta D = 5.4 \ \delta^{18}O + 1.3$ ($R^2 = 0.96$). The regression equation for the Upper Floridan groundwater line published by Swancar and Hutchinson (1995) was $\delta D = 5.4 \ \delta^{18}O + 1.5$ ($R^2 = 0.97$). The distribution of δD and $\delta^{18}O$ for the WP is very similar to the reported water lines but slightly lower in slope and intercept. The lower slope and intercept was caused by the pumping of the CP
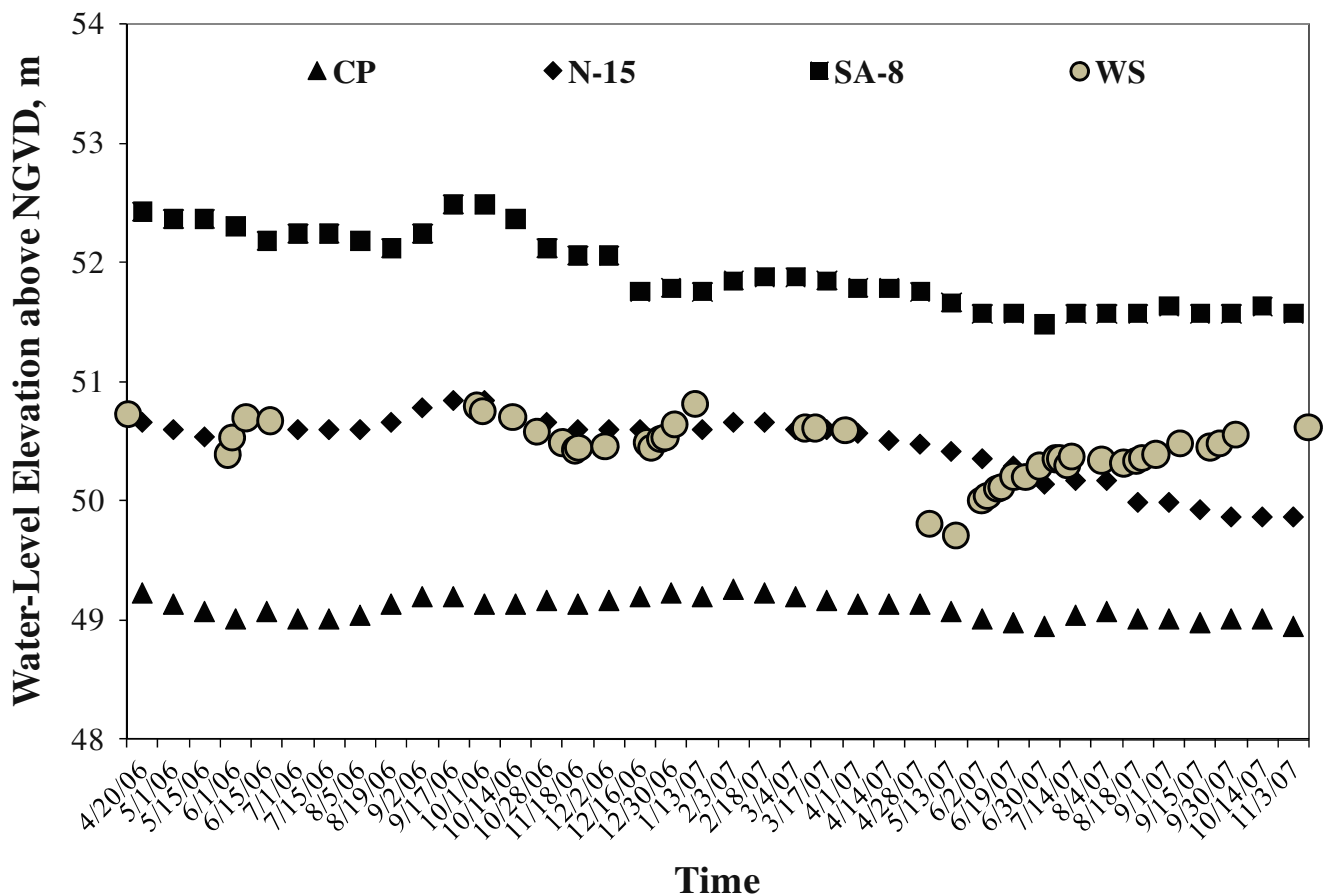
Fig. 2 Water-level elevations at the CP, WS, N-15 and SA-8 above National Geodetic Vertical Datum (NGVD) Note: CP = cooling pond; N-15 and SA-8 = water bodies to the north and south of the wetland; WS = wetland water surface

water into the wetland due to evaporative enrichment. The trendline for CP is δD=4.9 δ^{18}O–0.97 (R^2=0.68). Generally, the offset to the right from the local meteoric water line reflects the influence of evaporation (Craig and Gordon 1965; Gat 1996). Evaporation from an open surface reservoir causes nonequilibrium enrichment of δ^{18}O in the remaining water due to the differences in gaseous diffusion rates for δ^{18}O and δD, particularly under low humidity conditions (Craig and Gordon 1965; Kendall and McDonnell 2006). As a result the slope of the meteoric water line drops below 8. In addition to humidity, the slope of evaporation loss depends on a number of environmental factors such as solar radiation, temperature, and wind speed (Clark and Fritz 1997). The average relative humidity of the study area from April 2006 to October 2007 was 74.6% (FAWN). At this humidity the slope of a local meteoric water line should be close to 5 (Gat 1996; Gonfiantini et al. 1998; Kendall and Coplen 2001).

Monitor Wells, SA-8 and N-15

To evaluate possible seepage of water from N-15 and SA-8 into the wetland, six monitor wells (MWs) installed along the flow path were analyzed (Fig. 1). The δD and δ^{18}O in MW-1, MW-2 and MW-3 ranged from −24.9‰ to 24.2‰ and from −4.19‰ to 4.95‰, respectively (Fig. 4, Table 1, Appendix 2). For MW-1, the δD and δ^{18}O values had a highly defined peak in June–August 2007 as a result of pumping operation. The CP pump was turned off in April and May for maintenance purposes and restarted in June, which caused the change of isotopic signature in MW-1 due to its proximity to the CP. The δD and δ^{18}O values in MW-4, MW-5, and MW-6 showed less variation and ranged from −27.8‰ to −1.4‰ and −4.63‰ to −0.53‰, respectively, and plotted closely to −18.0‰ for δD and −3.70‰ for reported δ^{18}O in the Intermediate Aquifer (Sacks and Tihansky 1996) (Fig. 4). The δD and δ^{18}O values in N-15 varied between −1.9‰ to 12.9‰ and 0.03‰ to 2.84‰, respectively. The δD and δ^{18}O in SA-8 were from 10.4‰ to 19.9‰ and 1.97‰ to 3.94‰, respectively (Fig. 4). Generally, of all wells MW-3 had the most distinctive isotopic composition compared to the groundwater value and was probably more influenced by the seepage from N-15 or WP (Fig. 4). The analysis of variance (ANOVA) using the δ^{18}O and δD values was applied to examine the difference in isotopic signature between MWs, WP, SA-8 and N-15 (Fig. 5). For the first group of samples (MW-1 to MW-3,
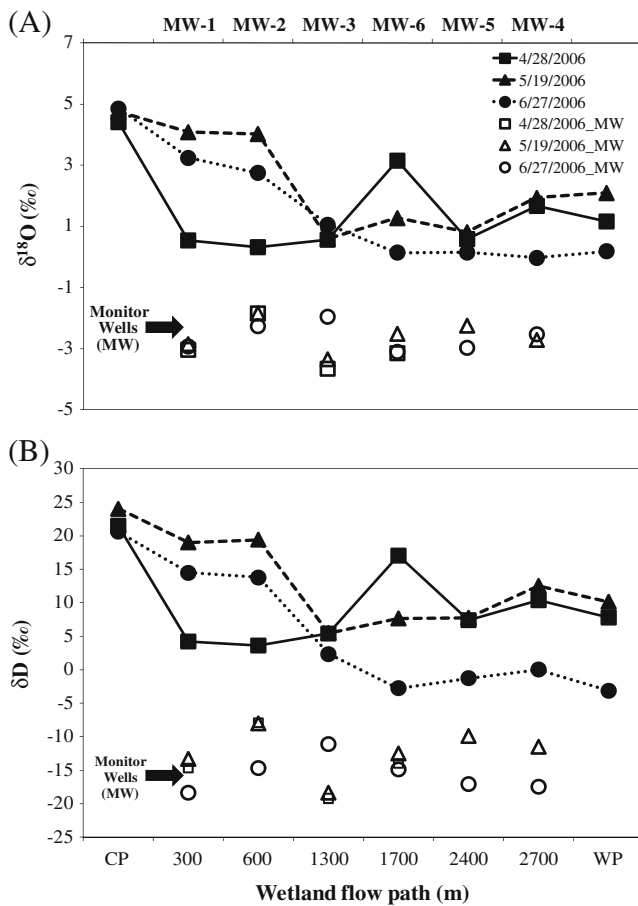
Fig. 3 Evaluation of wetland surface water isotopic composition along the flow path Note: CP = cooling pond; WP = wetland water from pump, MW = monitoring wells

WP and N-15), the F ratio (26.3 and 24.3 for $\delta^{18}O$ and δD, respectively) was significantly larger than the critical value (2.5), indicating a statistically significant difference within the data set. The variance for MW-3 had the highest value (5.7 and 151.9 for $\delta^{18}O$ and δD, respectively) indicating the influence from other sources of water. For the second group of samples (MW-4 to MW-6, WP, and SA-8), the F ratio (104.8 and 75.6 for $\delta^{18}O$ and δD, respectively) was much larger than the critical value.

Discussion

The concentrations of Na in conjunction with $\delta^{18}O$ values, as well known conservative tracers (Siegel and Glaser 1987; Siegel and Glaser 2006), were used in the isotope/chemical mass-balance approach to differentiate potential sources of water in the wetland and monitor wells and to understand factors controlling the flow of seepage water into the wetland. The concentration of Cl, which can also be used as a tracer, was not used due to the possible non-conservative behavior of Cl in wetland waters (Viers et al.
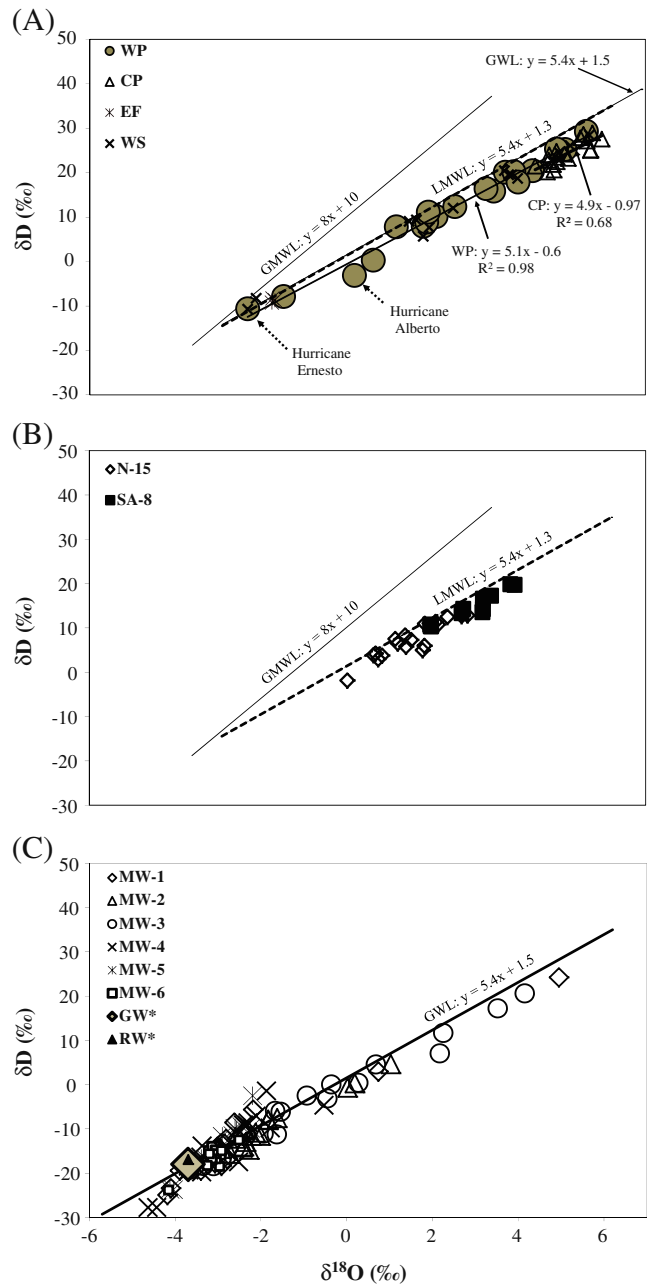
Fig. 4 δD vs $\delta^{18}O$ for the wetland **a**, SA-8 and N-15 **b**, and monitoring wells **c** Note: WP = wetland water from pump; WS = wetland water from surface; CP = cooling pond; EF = effluent; N-15 and SA-8 = water bodies to the north and south of the wetland; MW-1 to MW-6 = monitoring wells; GW* = Floridan ground water from the Intermediate Aquifer (well ROMP 45, Sacks and Tihansky 1996); RW* = rain water (Kish et al. 2009). Local meteoric water line (LMWL) is from Kendall and Coplen (2001). Global meteoric water line (GMWL) is from Craig (1961). Upper Floridan Aquifer groundwater line (GWL) is from Swancar and Hutchinson (1995)

2001). Varner et al. (1999) reported that wetlands can be a substantial source of methyl chloride (CH_3Cl) emission to the atmosphere. The flux of this compound is biologically mediated and greatly depends on temperature and vegetation density. Also, Cl can be incorporated into plant tissues (Alloway 1992; White and Broadley 2001) or adsorbed

Fig. 5 Average and variance of δ^{18}O **a** and δD **b** estimated by ANOVA at MW-1 to MW-6, N-15, SA-8, CP and WP Note: MW-1 to MW-6 = monitoring wells arranged according to the wetland flow path; N-15 and SA-8 = water bodies to the north and south of the wetland; CP = cooling pond, and WP = wetland water from pump

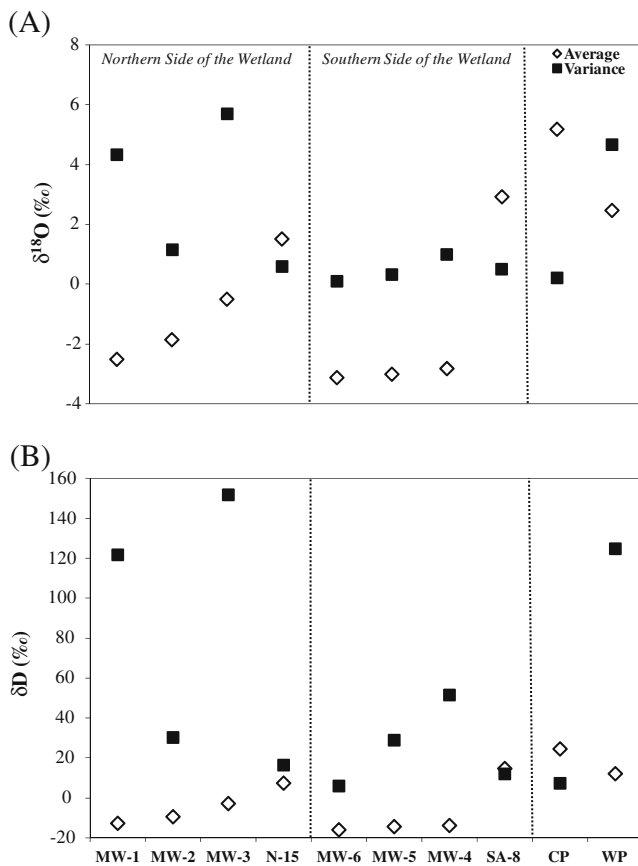**Fig. 6** Four and three end-members for the WP **a**, monitoring wells MW-1 to MW-3 **b**, and MW-4 to MW-6 **c** used for the mass-balance approach Note: WP = wetland water from pump; CP = cooling pond; GW = Floridan ground water from the Intermediate Aquifer System (well ROMP 45 from Sacks and Tihansky 1996); N-15 and SA-8 = water bodies to the north and south of the wetland; Error bars = standard deviation

onto soil or mineral surface through a non-specific adsorption (Altman 1994; Katou et al. 1996).

Water Composition in the Wetland

The composition of wetland water can be described by a mixture of four possible sources including: (1) Floridan ground water from the Intermediate Aquifer System (ROMP 45 from Sacks and Tihansky 1996), (2) cooling pond water, (3) a water body to the north (N-15), and (4) a water body to the south (SA-8) of the wetland (Fig. 6A). The groundwater and rainwater sources were combined in one as "GW" because the local meteoric water line had a tendency to approach the Upper Floridan groundwater line (Swancar and Hutchinson 1995; Kendall and Coplen 2001; Kish et al. 2009).

When these water sources are considered as end-members to the wetland water (i.e., have unique chemical composition compared to the mixture), it is possible to estimate mixing proportions between them waters using a mass-balance approach (e.g., Christophersen and Hooper 1992; Clark and Fritz 1997; Doctor et al. 2006). For this study, the following linear mass-balance equations were applied to the northern and southern sides of the wetland to describe the final composition of wetland water. *Northern side*: The three-component mass-balance approach used two parameters (δ18O and Na) and three equations to determine each variable. Assuming that the wetland water was a result of mixing groundwater (GW), cooling pond water (CP) and N-15, the following equation could be

used to assess the individual contributions from each source:

$$m_{WP} = m_{GW} + m_{CP} + M_{N-15} = 1 \quad (1)$$

Making a substitution of Eq. (1) into the isotopic mass-balance equation for $\delta^{18}O$,

$$m_{WP}*\delta^{18}O_{WP} = m_{GW}*\delta^{18}O_{GW} + m_{CP}*\delta^{18}O_{CP} + m_{N-15}*\delta^{18}O_{N-15} \quad (2)$$

and substitution of Eq. (1) into the chemical mass-balance equation for Na:

$$m_{WP}*Na_{WP} = m_{GW}*Na_{GW} + m_{CP}*Na_{CP} + m_{N-15}*Na_{N-15} \quad (3)$$

followed by a combination of the Eqs. 1, 2, and 3 to determine the proportion or mass of each water source in the wetland water

$$m_{CP} = \frac{Na_{N-15}*\left(\delta^{18}O_{WP} - \delta^{18}O_{GW}\right) + Na_{GW}*\left(\delta^{18}O_{N-15} - \delta^{18}O_{WP}\right) + Na_{WP}*\left(\delta^{18}O_{GW} - \delta^{18}O_{N-15}\right)}{Na_{N-15}*\left(\delta^{18}O_{CP} - \delta^{18}O_{GW}\right) + Na_{GW}*\left(\delta^{18}O_{N-15} - \delta^{18}O_{CP}\right) + Na_{CP}*\left(\delta^{18}O_{GW} - \delta^{18}O_{N-15}\right)}$$

$$m_{N-15} = \frac{\delta^{18}O_{WP} - \delta^{18}O_{GW} + \left(\delta^{18}O_{GW}*m_{CP}\right) - \left(m_{CP}*\delta^{18}O_{CP}\right)}{\delta^{18}O_{N-15} - \delta^{18}O_{GW}}$$

$$m_{GW} = 1 - m_{WP} - m_{N-15}$$

Southern side: The mass-balance equations for the southern side of the wetland were analogous to the combination of Eqs. 1, 2, and 3 listed above with the substitution of N-15 for SA-8.

Evaluation of the final percentage of four water sources present in the wetland was calculated using average values of $\delta^{18}O$ and Na from the CP, N-15, and SA-8 and was based on the following:

$$V_{CPn} = V_{CPs} = 1L$$

$$V_{CPn}*m_{CPn} + V_{CPs}*m_{CPs} = V_{CP}*m_{CP} = (V_{CPn} + V_{CPs})*m_{CP}$$

$$m_{CP} = \frac{V_{CPn}*m_{CPn} + V_{CPs}*m_{CPs}}{(V_{CPn} + V_{CPs})}$$

Therefore, $m_{CP} = \frac{m_{CPn} + m_{CPs}}{2}$.

Similarly to the equation above, $m_{GW} = \frac{m_{GWn} + m_{GWs}}{2}$; $m_{N-15} = \frac{m_{N-15n} + 0}{2}$, and $m_{SA-8} = \frac{0 + m_{SA-8s}}{2}$ subscripts for the m_{CPn}, m_{CPs}, m_{GWn}, m_{GWs}, m_{N-15s}, and m_{SA-8n} indicate the

mass or percentage of each end-member in the wetland water calculated for the northern (*n*) and southern (*s*) sides.

Water Composition in Monitor Wells

Similarly to the wetland water described above, the water composition in the monitor wells was a mixture of three possible sources (Fig. 6b and c):

MW-1, 2 and 3; (1) ground water (GW), (2) wetland water (WP), and (3) N-15; and
MW-4, 5 and 6; (1) ground water (GW), (2) wetland water (WP), and (3) SA-8.

Based on these assumptions the following linear mass-balance equations were applied to evaluate the proportions of different waters present in the monitor wells:MW-1 to MW-3:

$$m_{Well} = 1$$

$$m_{Well} = m_{GW} + m_{WP} + m_{N-15}$$

$$1 = m_{GW} + m_{WP} + m_{N-15}$$

$$m_{well}*\delta^{18}O_{Well} = m_{GW}*\delta^{18}O_{GW} + m_{WP}*\delta^{18}O_{WP} + m_{N-15}*\delta^{18}O_{N-15}$$

$$m_{well}*Na_{Well} = m_{GW}*Na_{GW} + m_{WP}*Na_{WP} + m_{N-15}*Na_{N-15}$$

$$m_{WP} = \frac{Na_{N-15}*\left(\delta^{18}O_{Well} - \delta^{18}O_{GW}\right) + Na_{GW}*\left(\delta^{18}O_{N-15} - \delta^{18}O_{Well}\right) + Na_{Well}*\left(\delta^{18}O_{GW} - \delta^{18}O_{N-15}\right)}{Na_{N-15}*\left(\delta^{18}O_{WP} - \delta^{18}O_{GW}\right) + Na_{GW}*\left(\delta^{18}O_{N-15} - \delta^{18}O_{WP}\right) + Na_{WP}*\left(\delta^{18}O_{GW} - \delta^{18}O_{N-15}\right)}$$

$$m_{N-15} = \frac{\delta^{18}O_{Well} - \delta^{18}O_{GW} + \left(\delta^{18}O_{GW}*m_{WP}\right) - \left(m_{WP}*\delta^{18}O_{WP}\right)}{\delta^{18}O_{N-15} - \delta^{18}O_{GW}}$$

$$m_{GW} = 1 - m_{WP} - m_{N-15}$$

MW-4 to MW-6: The mass-balance equations for MW-4 to MW-6 were similar to the above with the substitution of N-15 for SA-8.

The final calculated composition of the wetland water from pumping station (WP) is shown in Appendix 1 and Fig. 7. It clearly demonstrates the changes in the WP quality throughout the duration of the study reflecting the influence of dry/rainy seasons and pumping operations. At the beginning of the monitoring, the wetland consisted of a mix of waters from the SA-8, N-15, GW, and CP. During the period of April–July 2006 the composition of the wetland water had the following changes: input of N-15 decreased from 50% to 20%, contribution from SA-8 dropped from 37% to 9%, GW increased from 8% to 41%, and the CP increased up to 30%. However, between August and September 2006 the CP inflow dropped to 22% but the GW input increased up to 78%. According to the operational data, before the end of September 2006 the pumping of the CP water into the wetland had maintenance and power issues and was periodically turned off. In addition, the considerable GW inflow was impacted by heavy rainfall during two hurricanes in June-early September 2006, which added low conductivity water directly and triggered enhanced groundwater input into the wetland (Criss and Winston 2003).

Later, during the dry season (November 2006–April 2007) the WP contained mostly the CP water (88%–100%) and minor inflows of GW (<12%) that were caused by short mechanical problems. During the second rainy season (May–October 2007) the CP water inflow remained high (87%–100%). However, the maintenance/power issues and a significant rainfall in August–October caused the GW seepage to increase up to 13%. Assessment of the wetland surface water along the flow path on April 28, May 19, and June 27, 2006 indicated a distinct decrease in isotopic signature from the input (CP) to the output (WP) (Fig. 3). According to the mass-balance calculations for April 28 and May 19, the wetland water was composed of 47%–50% of N-15, 31%–37% of SA-8, 18%–8% of GW, and 4%–5% of the CP waters (Fig. 7). At the same time, the mass-balance estimation for June 27 showed that the wetland water consisted of 41% of GW, 28% of N-15, 18% of CP, and 13% of the SA-8 waters. Therefore, the decrease in isotopic fractionation of 1.91‰ for $\delta^{18}O$ and 13.2‰ for δD coincided with the drastic GW input and direct rainfall into the wetland after the strong hurricane Alberto in June 2006.

The calculated proportions of three end-members in MW-1 to MW-6 estimated by the isotope/chemical mass-balance approach are shown in Appendix 2. The
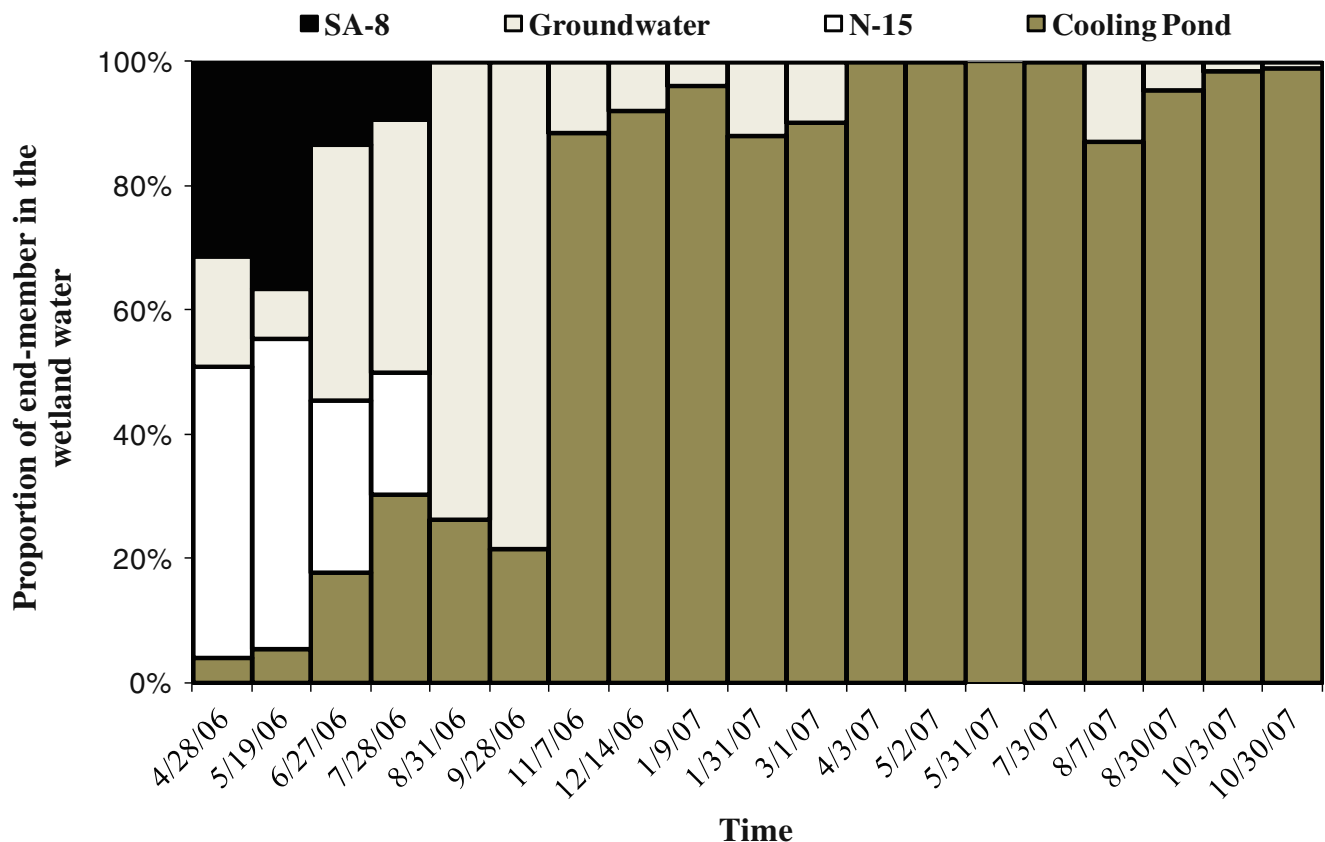

Fig. 7 The calculated mass of each end-member in the wetland using an isotope/chemical mass-balance approach

composition of MW-1 to MW-3 was substantially affected by the seepage from the N-15 with the highest levels at MW-2 and MW-3 (up to 91%). The estimated GW inflow varied from 0% to 100% decreasing from MW-1 to MW-3. The highest input from the WP (up to 100%) was to MW-3 in August–October 2007. The composition of MW-4 to MW-6 was mostly controlled by the GW inflow (40%–100%). The estimated seepage from the SA-8 was <28% with increasing inflow from MW-5 to MW-4. The highest inflow from the WP (<42%) was to MW-6 (except one MW-4 sample from 10/30/07).

The influence of each end-member on the composition of MWs could be caused by several factors such as (1) lithologic settings of the study area causing a variability in porosity and permeability; (2) total depth of MWs; (3) hydrologic gradient; (4) proximity of N-15 and SA-8 to the wetland; and (5) periodic variations in precipitation (dry/rainy season). The lithology of MWs cores along the wetland was relatively uniform and sediments were composed of light-tan to brown poorly to well-sorted fine sands or silts with occasional grey clay nodules. The brown color was due to the presence of organic material. Generally, clay content was higher at MW-4 to MW-6 compared to MW-1 to MW-3. At the same time, of all wells MW-3 had more medium-fine sands at the top 1.5 m. The monitoring of water-level elevations showed that the SA-8 had a higher level compared to N-15, CP, and the wetland (Fig. 2). However, the isotope/chemical mass-balance method showed that the seepage from SA-8 was substantially lower than from N-15. The higher inflow of N-15 into MWs could be due to a closer location to the wetland compared to SA-8. In addition, MW-1 to MW-3 were shallower than MW-4 to MW-6 and were less affected by the GW inflow but more affected by the N-15 dilution. The total depths of MW-1 to MW-3, and MW-4 to MW-6 were 3 and 4 m, respectively. As a result, the deeper wells could generally have a higher input of GW. Despite the fact that the inputs from N-15 and SA-8 were detected in MWs, they were not identified in the wetland once the treatment system became fully operational potentially indicating a water loss from the wetland. Sacks (2002) used the isotope mass-balance method for estimating the water balance of lakes in central Florida and reported that the majority of lakes in upland areas of Polk and Highlands Counties had from medium to high groundwater inflows with 25%–50% and > 50% of total inflow, respectively. The inflows depended on topography, humidity, air and lake-surface temperatures, lake depth, distance downward to the Upper Floridan Aquifer (thickness of the Surficial Aquifer and Intermediate Confining Unit), and fraction of wetlands.

Conclusions

The combined isotope/chemical mass-balance approach to evaluate the hydrogeological settings in the constructed wetland demonstrated the following:

1. Stable isotopes of hydrogen (δD) and oxygen ($\delta^{18}O$) in combination with geochemical data were useful tools to discriminate major sources of water in the constructed wetland and monitor wells (MWs).
2. Composition of water in the wetland varied throughout the period of the study.
3. Depletion of isotopic composition along the wetland flow path.
4. Wetland was mostly composed of wastewater (88%–100%) during normal pumping operations; however, hurricanes and inconsistent pumping added low conductivity water directly and triggered enhanced groundwater inflow into the wetland of up to 78%.
5. Composition of water in MWs was mostly groundwater dominated; however water in MW-1 to MW-3 was periodically induced by the seepage from a water body to the north.
6. The possible factors controlling the fluid mixing in MWs could be due to: (1) lithologic settings of the study area causing a variability in porosity and permeability; (2) total depth of MWs; (3) hydrologic gradient; (4) proximity of the water bodies to the north and south (N-15 and SA-8) of the wetland; and (5) periodic variations in precipitation (dry/rainy season).
7. Seepage from water bodies surrounding the wetland were not identified in the wetland water once the system became operational potentially indicating a water loss from the wetland.

The investigation using a combined isotope/chemical mass-balance approach was very important to evaluate complex hydrogeological settings in a constructed wetland. Potentially, this approach can be successfully implemented across the whole spectrum of hydrological and hydrogeological studies.

Appendix 1

Table 2 Chemical and isotopic data of waters used for the mass-balance approach

Sample	Date	$\delta^{18}O^*$	δD^*	Na'	Sample	Date	$\delta^{18}O^*$	δD^*	Na'	Sample	Date	$\delta^{18}O^*$	δD^*	Na'	Sample	Date	$\delta^{18}O^*$	δD^*	Na'	mCP	mGW	mN-15	mSA-8
CP	4/28/06	4.42	21.5	67.9	N-15	4/28/2006	2.09	11.4	28.2	SA-8					WP	4/28/06	1.17	7.8	17.3	4	18	47	31
	5/19/06	4.75	24.0	67.7		5/19/2006	2.70	12.7	31.3							5/19/06	2.10	10.1	20.1	5	8	50	37
	6/27/06	4.86	20.6	69.3		6/27/2006	1.79	5.0	25.7							6/27/06	0.19	−3.1	25.4	18	41	28	13
	7/28/06	5.11	24.2	72.3		7/28/2006	1.83	6.0	27.0							7/28/06	0.63	0.3	32.4	30	41	20	9
	8/31/06	4.70	20.2	69.8		8/31/2006	0.03	−1.9	18.8							8/31/06	−1.47	−7.9	24.3	26	74	0	0
	9/28/06	4.74	22.8	72.2		9/28/2006	0.75	3.0	22.0							9/28/06	−2.31	−10.6	19.6	22	78	0	0
	11/7/06	no sample				11/7/2006	1.21	6.5	26.9							11/7/06	3.45	15.9	67.1	88	12	0	0
	12/14/06	4.84	21.8	73.1		12/14/2006	1.52	7.3	27.7		12/14/2006	1.97	10.8	13.3		12/14/06	4.36	20.5	71.4	92	8	0	0
	1/9/07	4.93	23.5	74.0												1/9/07	3.27	16.4	70.0	96	4	0	0
	1/31/07	4.92	24.8	72.0		1/31/2007	1.15	7.5	27.1		1/31/2007	1.98	10.4	13.7		1/31/07	3.72	20.1	67.8	88	12	0	0
	3/1/07	4.93	22.5	76.3		3/1/2007	1.38	8.3	28.7		3/1/2007	1.99	10.4	14.0		3/1/07	3.92	20.2	69.3	90	10	0	0
	4/3/07	5.19	23.2	86.3		4/3/2007	1.84	11.0	30.0		4/3/2007	2.70	13.3	14.5		4/3/07	5.12	25.2	78.3	100	0	0	0
	5/2/07	5.48	27.9	81.6		5/2/2007	2.37	12.5	29.6		5/2/2007	3.39	17.3	15.3		5/2/07	4.92	25.3	81.8	100	0	0	0
	5/31/07	5.55	28.6	82.3		5/31/2007	2.84	12.9	29.8		5/31/2007	3.84	19.9	15.0		5/31/07	5.62	29.3	93.5	100	0	0	0
	7/3/07	5.76	29.0	87.7		7/3/2007	2.15	10.8	28.6		7/3/2007	3.94	19.7	15.6		7/3/07	4.02	17.9	78.5	100	0	0	0
	8/7/07	5.72	25.1	82.4		8/7/2007	1.40	5.8	25.1		8/7/2007	3.20	16.6	15.8		8/7/07	1.80	8.0	61.5	87	13	0	0
	8/30/07	5.98	27.6	87.1		8/30/2007	0.84	3.8	24.1		8/30/2007	3.19	13.6	15.3		8/30/07	1.88	8.9	67.5	95	5	0	0
	10/3/07	5.71	25.0	86.2		10/3/2007	0.69	4.2	23.2		10/3/2007	3.20	14.3	15.5		10/3/07	1.92	11.1	71.3	99	1	0	0
	10/30/07	5.63	27.1	86.9		10/30/2007	0.64	3.9	24.7		10/30/2007	2.74	14.3	15.6		10/30/07	2.54	12.4	72.5	99	1	0	0

CP = cooling pond; *SA-8* and *N-15* = water bodies to the north and south of the wetland; *WP* = wetland water from pump; *GW* = ground water (based on well ROMP 45 data from Sacks and Tihansky 1996); (*) = values in ‰; (') = values in mg/L; *m* = mass or percentage of each end-member in the WP; Na values from Lazareva, Pichler (2010)

Appendix 2

Table 3 Chemical and isotopic data of the monitor wells (MW-1 to MW-6) used for the mass-balance approach

Sample	Date	δ18O*	δD*	Na'	mWP	mN-15	mGW	Sample	Date	δ18O*	δD*	Na'	mWP	mSA-8	mGW
MW-1	4/28/06	−3.04	−14.7	15.2	24	0	79	MW-4	4/28/06	no sample					
	5/19/06	−2.85	−13.3	9.7	2	14	84		5/19/06	−2.71	−11.5	15.4	19	0	81
	6/27/06	−2.92	−18.4	5.5	0	15	85		6/27/06	−2.52	−17.5	7.2	0	18	82
	7/28/06	−2.79	−16.9	6.8	0	17	83		7/28/06	−2.80	−14.6	7.8	2	12	86
	8/31/06	−4.10	−23.4	3.6	0	0	100		8/31/06	−4.63	−27.8	2.5	0	0	100
	9/28/06	−3.89	−19.4	3.8	0	0	100		9/28/06	−3.69	−18.5	3.2	0	0	100
	11/7/06	−3.69	−19.7	5.9	0	0	100		11/7/06	−3.68	−19.3	4.9	0	0	100
	12/14/06	−3.33	−18.2	5.6	0	7	93		12/14/06	−3.37	−13.9	5.3	0	5	95
	1/9/07	−3.07	−17.8	5.5	0	12	88		1/9/07	−2.80	−15.0	12.8	13	1	85
	1/31/07	−2.62	−8.6	7.1	0	21	79		1/31/07	−1.87	−1.4	7.4	0	28	72
	3/1/07	−2.18	−5.7	6.6	0	29	71		3/1/07	−2.11	−7.1	12.7	11	14	75
	4/3/07	−2.55	−12.1	6.4	0	22	78		4/3/07	−2.32	−9.1	11.9	10	12	78
	5/2/07	−2.81	−12.3	7.4	0	17	83		5/2/07	−2.30	−8.6	11.8	10	12	78
	5/31/07	0.74	2.9	30.4	25	56	19		5/31/07	−2.41	−9.1	11.5	9	11	80
	7/3/07	4.95	24.2	71.4	100	0	0		7/3/07	−3.40	−16.3	20.1	32	0	68
	8/7/07	−3.01	−14.0	4.8	0	13	87		8/7/07	−3.38	−19.8	5.0	0	5	95
	8/30/07	−2.93	−13.3	4.8	0	15	85		8/30/07	−4.43	−27.8	15.1	24	0	76
	10/3/07	−4.18	−24.9	5.1	5	0	95		10/3/07	−1.78	−9.8	22.9	34	0	66
	10/30/07	−3.40	−19.4	6.0	0	6	94		10/30/07	−0.53	−4.7	36.1	60	0	40
MW-2	4/28/06	−1.83	−7.9	16.7	12	21	66	MW-5	4/28/06	no sample					
	5/19/06	−1.83	−8.0	16.1	10	24	66		5/19/06	−2.24	−9.9	14.0	14	9	77
	6/27/06	−2.27	−14.7	9.0	0	27	73		6/27/06	−2.97	−17.0	11.7	12	0	88
	7/28/06	−2.43	−14.2	8.7	0	24	76		7/28/06	no sample					
	8/31/06	−2.72	−15.6	6.5	0	19	81		8/31/06	−4.04	−23.8	5.3	0	0	100
	9/28/06	−2.93	−14.5	7.7	0	15	85		9/28/06	−3.68	−18.5	5.7	0	0	100
	11/7/06	−2.59	−12.2	9.5	0	21	79		11/7/06	−3.12	−17.2	13.3	16	0	84
	12/14/06	−2.35	−12.9	8.3	0	26	74		12/14/06	−2.75	−14.8	14.8	18	0	82
	1/9/07	−2.40	−14.0	8.3	0	25	75		1/9/07	−2.84	−15.8	7.4	1	12	87
	1/31/07	−2.38	−9.9	8.5	0	25	75		1/31/07	−2.19	−2.5	4.3	0	23	77
	3/1/07	−2.38	−10.4	9.2	0	25	75		3/1/07	−2.44	−9.5	7.1	0	19	81
	4/3/07	−2.38	−10.2	10.1	0	25	75		4/3/07	−2.65	−11.5	8.9	4	12	84
	5/2/07	2.12	−10.8	11.9	0	30	70		5/2/07	−2.57	−10.4	7.7	1	16	83
	5/31/07	−2.22	−11.6	10.6	0	28	72		5/31/07	−2.60	−9.9	9.7	6	11	83
	7/3/07	−1.62	−7.6	12.9	0	40	60		7/3/07	−2.90	−11.7	9.8	7	6	87
	8/7/07	−2.01	−11.6	11.0	0	32	68		8/7/07	−3.39	−16.8	7.0	2	3	95
	8/30/07	0.02	−0.7	16.1	0	71	29		8/30/07	−4.12	−23.7	7.5	5	0	95
	10/3/07	1.03	4.6	19.5	0	91	9		10/3/07	−3.28	−16.8	8.6	5	1	93
	10/30/07	0.19	0.3	17.0	0	75	25		10/30/07	−3.33	−17.4	7.0	2	4	94
MW-3	4/28/06	−3.66	−19.2	5.7	0	1	99	MW-6	4/28/06	−3.14	−14.0	24.8	42	0	58
	5/19/06	−3.35	−18.4	6.0	0	7	93		5/19/06	−2.51	−12.5	15.7	19	0	81
	6/27/06	−1.94	−11.1	10.1	0	34	66		6/27/06	−3.11	−14.9	21.2	34	0	66
	7/28/06	−0.93	−2.5	13.6	0	53	47		7/28/06	no sample					
	8/31/06	−3.11	−18.4	9.2	4	7	89		8/31/06	−4.15	−23.8	9.0	9	0	91
	9/28/06	−1.54	−6.1	12.7	0	41	59		9/28/06	−3.22	−14.9	19.7	31	0	69
	11/7/06	−1.67	−5.9	13.5	0	39	61		11/7/06	−3.16	−17.2	24.3	41	0	59
	12/14/06	0.27	0.4	22.6	3	72	24		12/14/06	−2.93	−16.0	24.6	41	0	59

Table 3 (continued)

Sample	Date	δ18O*	δD*	Na'	mWP	mN-15	mGW	Sample	Date	δ18O*	δD*	Na'	mWP	mSA-8	mGW
	1/9/07	−0.45	−3.1	28.4	34	22	44		1/9/07	−2.96	−18.5	24.1	40	0	60
	1/31/07	−0.36	0.1	26.4	26	33	41		1/31/07	−3.14	−14.0	19.6	30	0	70
	3/1/07	no sample							3/1/07	−3.06	−14.8	23.5	39	0	61
	4/3/07	0.68	4.6	31.4	29	50	21		4/3/07	−3.04	−16.8	23.4	39	0	61
	5/2/07	−1.63	−11.2	12.0	0	40	60		5/2/07	−3.06	−14.8	24.6	42	0	58
	5/31/07	−2.91	−16.3	7.1	0	15	85		5/31/07	−3.06	−15.6	24.8	42	0	58
	7/3/07	no sample							7/3/07	−3.14	−17.1	22.0	36	0	64
	8/7/07	4.15	20.6	65.6	100	0	0		8/7/07	−3.14	−16.8	21.4	35	0	65
	8/30/07	2.17	7.1	67.1	100	0	0		8/30/07	−3.25	−18.3	22.3	37	0	63
	10/3/07	2.25	11.7	63.3	100	0	0		10/3/07	−3.20	−15.7	23.9	41	0	59
	10/30/07	3.52	17.3	82.7	100	0	0		10/30/07	−2.92	−15.0	16.9	23	0	77

WP = wetland water from pump; *GW* = groundwater (based on well ROMP 45 data from Sacks and Tihansky 1996); SA-8 and N-15 = water bodies to the north and south of the wetland; (*) = values in ‰; (′) = values in mg/L; *m* = mass or percentage of each end-member in MW; Na values from Lazareva and Pichler (2010)

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