

## RESEARCH ARTICLE

# Investigating Storm Impacts on Springs in a Karst Region Using Oxygen and Hydrogen Isotopes

Yang Wang<sup>1,2</sup>  | Riley G. Thomason<sup>1,2</sup> | Ming Ye<sup>1</sup> 

<sup>1</sup>Department of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, Florida, USA | <sup>2</sup>Geochemistry Program, National High Magnetic Field Laboratory, Tallahassee, Florida, USA

**Correspondence:** Yang Wang (ywang4@fsu.edu)

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## ABSTRACT

Groundwater contamination is a growing concern in many regions around the world. Karst aquifers are particularly vulnerable to contamination because surface runoff can rapidly enter the subsurface through sinkholes and conduits. This study analysed time-series oxygen and hydrogen isotope data collected before and after Hurricane Idalia to assess storm impacts on two nearby springs with different discharge rates—Sally Ward Spring (~0.6 m<sup>3</sup>/s) and Wakulla Spring (~13 m<sup>3</sup>/s)—in a karst region of North Florida in the US. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of rainwater from Hurricane Idalia (event water hereinafter) were  $-15.2\text{‰}$  and  $-108.5\text{‰}$ , respectively, considerably lower than those of normal rainfall in the region ( $\delta^{18}\text{O} = -4.1\text{‰} \pm 1.6\text{‰}$  and  $\delta^2\text{H} = -20.2\text{‰} \pm 12.2\text{‰}$ ), providing a distinct tracer for storm-derived water. Event water appeared at Sally Ward Spring within one day and again at 12–19 and ~30 days post-storm, while it took 10–12 days to appear at Wakulla Spring. These relatively short transit times are in general agreement with previous dye-tracer-based estimates, reflecting rapid flows through sinkholes and conduits. Isotopic mass balance calculations, however, reveal that event water contributed no more than ~7% and ~1% of the discharge at Sally Ward Spring and Wakulla Spring, respectively. These results demonstrate that despite the marked differences in hydrodynamics, discharge at both springs is dominated by pre-event aquifer water, even following a major storm. The data further suggest that surface water bodies (e.g., lakes and ponds) within the springshed are important groundwater sources, contributing a substantial amount (> 20%) of water to base flow at both springs. These findings highlight the complex recharge dynamics of the karst aquifer system and the limited direct contribution of event water to spring discharge. This study also demonstrated that the unique isotopic signatures of tropical cyclones can serve as powerful natural tracers in regional hydrological investigations.

## 1 | Introduction

Groundwater is a critical natural resource that supports the livelihoods of billions of people and diverse ecosystems worldwide (Jasechko and Perrone 2021; Rohde et al. 2024). However, the quantity and/or quality of groundwater resources in many regions are declining due to overextraction, pollution and climate change (Jasechko and Perrone 2021). In Florida, the Floridan aquifer—a large and highly productive groundwater system—is the primary source of drinking water for most Floridians; it

also provides water for industrial and agricultural uses in the state (United States Geological Survey, n.d.). The Floridan aquifer is a karst aquifer system where recharge from precipitation and other surface water sources (e.g., lakes) can occur relatively rapidly through sinkholes and conduits in limestone, and more slowly through the matrix of underlying aquifers (Ahmed et al. 2021; Ford and Williams 2007). Since groundwater and surface water in karst areas are hydraulically connected through many sinkholes, lakes, sinking river and streams, conduits in underground limestone and springs, the aquifer is especially

susceptible to contamination from surface water (White 1993; Katz et al. 1997; Hartmann et al. 2021). This is because the direct and rapid recharge through sinkholes and underground cavities and conduits to the subsurface, as well as resurgence through springs, can contribute to both chemical and biological contamination of water supplies (Hartmann et al. 2021; Katz et al. 1997; White 1993).

North Florida is home to numerous sinkholes and springs. Springs are the points of discharge for groundwater that integrates waters spatially and temporally from various parts of the aquifer, and thus provide a window into regional groundwater quality (Ahmed et al. 2021; Katz 2004). As in many parts of the world (e.g., Burg and Heaton 1998; Hartmann et al. 2021), increased urban and agricultural development, along with other human activities, has affected the quality of spring waters in this region (FDEP-SP 2026; Katz et al. 2009; Katz 2004; Katz et al. 2001; Katz et al. 1999; McGlynn and Deyle 2018; Spellman et al. 2022; Spellman et al. 2024; Spellman et al. 2025). Analyses of chemical and isotopic tracers (CFC-11, CFC-12, CFC-13, SF<sub>6</sub>, <sup>3</sup>H and <sup>3</sup>He) in water from major springs in North and Central Florida have yielded apparent groundwater ages that often differ by more than 1–2 decades, even within the same spring (Happell et al. 2006; Katz 2004). Transit times estimated using the tracer data and models suggest that impacts on recharge water quality may take several years to ~60 years or more to manifest at these springs (Katz 2004; Happell et al. 2006). In contrast, dye tracer studies have revealed extremely rapid solute transport through conduit systems to springs, on the order of days to weeks (Kincaid et al. 2005, 2007; Kincaid 2006; Kincaid and Werner 2008). Such rapid transit times potentially allow contaminants in surface water to reach the springs quickly. A recent study of a large sinkhole lake in North Florida, using stable oxygen and hydrogen isotopes in conjunction with a dye tracing experiment, demonstrated that lake water drained through a sinkhole on the lakebed was detected at a spring located 32 km downgradient within about 3–5 weeks during a dry season (Ahmed et al. 2021).

Although these studies have provided valuable insights into regional hydrodynamics, the wide range of estimated transit times and the discrepancies among tracer-derived ages make it difficult to reliably assess how long pollutants take to move through the spring system, or how transit time may vary with hydrologic conditions. It remains unclear how karst characteristics affect the partitioning of storm water recharge between advective and dispersive mechanisms. Improved understanding of surface-water–groundwater interactions (e.g., recharge pathways, mixing dynamics and transit times) can inform spring-shed management and support strategies to protect groundwater and spring water quality.

Natural abundances of oxygen and hydrogen isotopes in water have been widely used to investigate water sources, mixing processes and hydraulic connections between sinkhole lakes and karst springs (e.g., Ahmed et al. 2021; Clark and Fritz 1997; Criss et al. 2001; Katz et al. 1995; Klaus and McDonnell 2013; Sklash et al. 1976; Walton-Day and Poeter 2009). Previous studies have shown that precipitation associated with tropical cyclones, including both hurricanes and tropical storms, is considerably depleted in the heavy oxygen and hydrogen isotopes <sup>18</sup>O and

<sup>2</sup>H relative to normal summer precipitation (Jahan et al. 2021; Lawrence 1998; Lawrence and Gedzelman 1996; Odezulu 2011; Sun et al. 2022). These abnormally low stable isotope ratios could potentially serve as natural tracers for investigating recharge pathways, groundwater transit times and the influence of storm runoff on springs.

This research uses stable isotopes in tropical cyclone precipitation and spring waters to address the following questions: Can the isotope signature of tropical cyclones be detected in spring waters following a tropical cyclone? If so, how long does it take for storm-derived event water to reach the springs? What fraction of spring discharge consists of event water following the storm? These questions have implications for understanding the potential impacts of large storm events and associated surface runoff on the water quality of groundwater and karst springs. The results from this study provide new insight into not only source contributions to spring discharge but also the impact of karst characteristics on the partitioning of storm water recharge between advective and dispersive flows.

## 2 | Study Area

Two freshwater springs, Sally Ward Spring and Wakulla Spring, in the Woodville Karst Plain (WKP) in North Florida (Figure 1) were selected for this study. The WKP is located in the eastern Florida panhandle, bordering the Gulf of Mexico (Figure 1). It is bounded to the north by the Cody Scarp (an ancient shoreline), to the west by the Apalachicola Lowlands, and to the east by the Steinhatchee River (Hendry and Sproul 1966). It is a gently sloping lowland that extends from south of Tallahassee to the Gulf of Mexico and a subzone of the Ocala Karst District (Hendry and Sproul 1966; Rupert 1988). The WKP is underlain by a thin (< 8 m thick) layer of unconsolidated and undifferentiated Pleistocene quartz sand and shell beds. This thin layer of loose sediment and soil overlies a thick sequence of Oligocene and Miocene limestones (i.e., Suwannee Limestone and St. Marks Formation, respectively) that comprise the Upper Floridan Aquifer—a part of the Floridan Aquifer system that underlies almost the entire state of Florida and parts of Georgia, Alabama and South Carolina (Miller 1986; Rupert 1988). This region has a humid subtropical climate, with an average annual precipitation of 1494 mm based on the data for the period of 1991–2020 from Florida Climate Center (FCC 2026). The wet season extends from June through September, aligning with the early months of hurricane season, which runs from June 1 through November 30.

The WKP is a region of extensive karstification, containing numerous sinkholes, karst windows, sinking streams, swallets and springs (Hendry and Sproul 1966; Kincaid et al. 2005). The WKP has one of the longest and most extensive mapped karst conduit networks in the world (Xu and Hu 2021). Out of Florida's 27 first-magnitude springs, seven are in the WKP. Recharge to the Floridan aquifer within the WKP occurs by direct infiltration of precipitation through the variably thick sands and soil overlying the aquifer, drainage of precipitation through sinkholes and sinking streams, and groundwater flow from the north (Kincaid et al. 2005). Groundwater discharges from the Floridan aquifer through springs in the southern part of the region as well as submarine springs in the Gulf of Mexico (Kincaid et al. 2005).

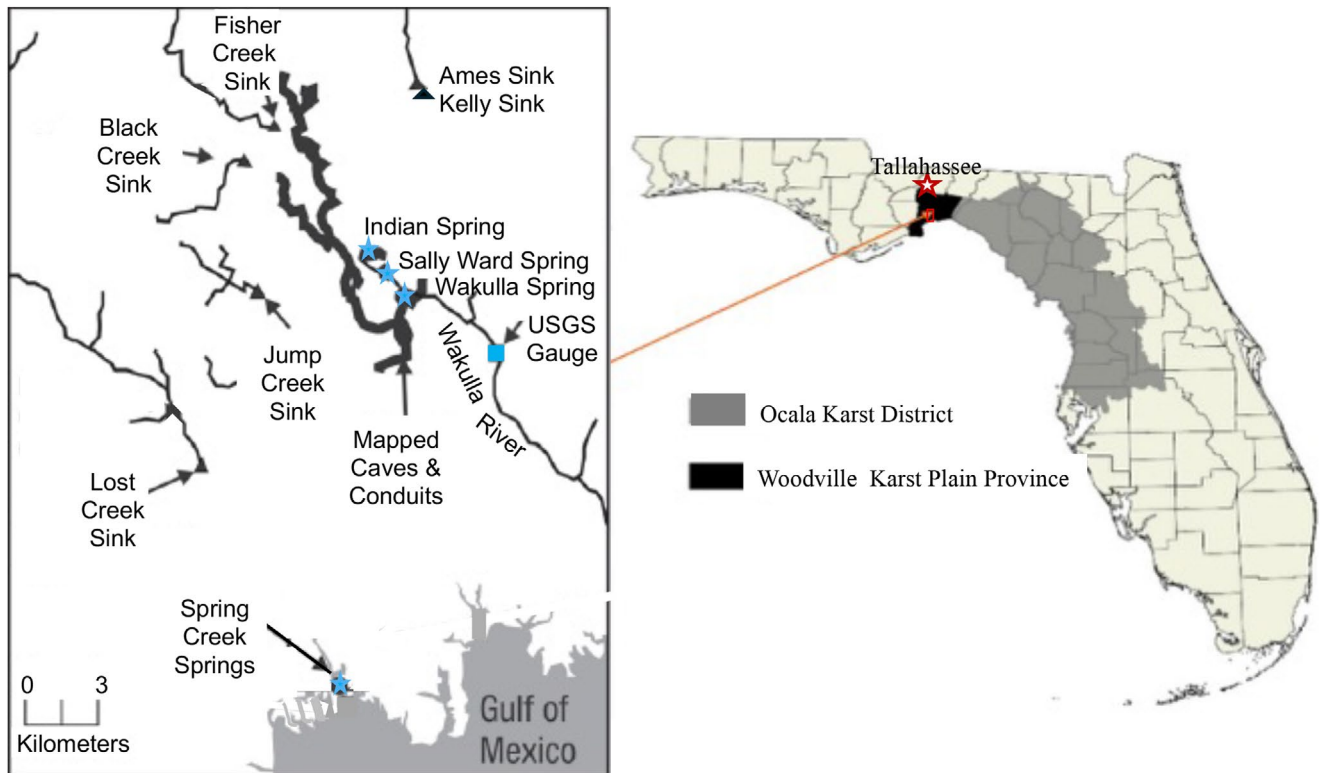


**FIGURE 1** | Map showing the locations of Sally Ward Spring and Wakulla Spring located in the Woodville Karst Plain within Ocala Karst District in Florida, US, along with local sinks mentioned in the text. Also shown are major mapped underground caves and conduits in the Woodville Karst Plain (Modified from McGlynn and Deyle 2018).

Both Sally Ward Spring and Wakulla Spring are in the Edward Ball Wakulla Springs (EBWS) State Park, 24 km south of Tallahassee, the capital of Florida (Figure 1). Wakulla Spring is a first-magnitude spring where approximately 300 million gallons of water flow out the spring each day, according to Florida Department of Environmental Protection (FDEP 2026). Groundwater discharging from Wakulla Spring flows through a network of conduits approximately 75 m below land surface. It is one of the largest and deepest freshwater springs in the world, with one of the longest and deepest cave systems (FDEP 2026). The discharge rate of Wakulla Spring fluctuated significantly from  $0.7 \text{ m}^3/\text{s}$  to  $54 \text{ m}^3/\text{s}$  in response to seasonal variations in rainfall (Kincaid 2006; Kincaid et al. 2005). Wakulla Spring is the headwater of the Wakulla River, which flows for ~16 km southeast merging to the St. Marks River and then to the Gulf of Mexico. Sally Ward Spring is a second-magnitude spring located ~1 km to the northwest of Wakulla Spring (Figure 1), with an average discharge rate of  $\sim 0.6 \text{ m}^3/\text{s}$ , ranging from  $0.06 \text{ m}^3/\text{s}$  to  $3.3 \text{ m}^3/\text{s}$ , recorded by the Northwest Florida Water Management District (NFWMD 2021). Discharge from the Sally Ward Spring flows down the Sally Spring run into the Wakulla River ~0.2 km downstream from the Wakulla Spring main vent (NFWMD 2021).

The springshed of Wakulla and Sally Ward Springs extends from the springs northward and westward into confined and poorly confined sections of the Floridan aquifer through Tallahassee and into southern Georgia (Kincaid et al. 2005). Dye tracing studies in the area have shown that multiple local

sinks within 12 km of EBWS State Park are directly connected to Wakulla Spring and Sally Ward Spring, with estimated transit times ranging from 10 to 23 days (Kincaid 2006; Kincaid et al. 2007). Dye tracing studies have also demonstrated hydraulic connections between Wakulla Spring and several lakes located 15–32 km north of the WKP, with estimated transit times ranging from 14 to 35 days (Kincaid et al. 2007; McGlynn and Deyle 2018).

### 3 | Materials and Methods

#### 3.1 | Sampling and Analytical Methods

Hurricane Idalia made landfall as a Category 4 storm on August 30, 2023, at Keaton Beach, North Florida, ~64 km southwest of EBWS State Park. The storm brought heavy rain along its path. Water samples were collected from Sally Ward and Wakulla Springs from August 28 to October 27, 2023. Stormwater from Hurricane Idalia was also collected in northeast Tallahassee, and monthly rainwater samples were collected from the same area from July through December 2023.

The spring water samples were collected in 1-L HDPE bottles from both springs every 2–4 days for 1 month and then weekly for an additional month. Before sample collection, each bottle was rinsed three times with spring water. The bottle was then filled with spring water from ~5 cm below the water surface, immediately capped, and placed in a cooler. The samples were

transported back to our lab, where 5 mL of each sample was transferred into a clean 5-mL borosilicate glass vial, tightly capped and stored in a refrigerator until isotope analysis.

Monthly rainwater samples were collected in a buried 1-L HDPE bottle fitted with a funnel above ground. The bottle contained a small amount of oil to prevent evaporation and was emptied once a month to obtain a monthly rain sample. A disposable pipette was used to carefully transfer 5 mL of the monthly rain sample into a clean 5-mL borosilicate glass vial. The sample vial was then tightly capped and stored in a refrigerator until isotope analysis.

Two water samples associated with Hurricane Idalia were also collected in clean 5-mL borosilicate glass vials shortly after the hurricane event. One sample was collected from an open container beneath a tree and represented rainwater from the hurricane (i.e., event water). The other was collected from a small drainage ditch on gently sloping, vegetated land adjacent to a road and likely represented a mixture of stormwater and soil water.

As storms tend to increase particulate matter (PM) in water through soil and sediment erosion caused by enhanced surface runoff and wind, and/or through the reactivation of cave sediments by increased recharge flow, the amount of PM in spring water was measured in this study and used as a proxy for the degree of storm impact on springs. PM was collected on a pre-combusted and pre-weighed 1.5-mm glass filter paper by filtering one 1-L bottle of spring water through the filter paper. The glass filter papers bearing the PM were dried in an oven at 70°C. After drying, they were weighed to determine the amount of PM in the spring water.

For stable isotope analyses, 500  $\mu$ L of each water sample was transferred using a high-precision pipette into a clean glass vial containing a platinum catalyst and capped. The vials containing the water samples and standards were flushed with helium containing either 2%  $H_2$  (for hydrogen isotope analysis) or 0.3%  $CO_2$  (for oxygen isotope analysis) and then allowed to react for 24 h. Headspace gas was introduced via an on-line, continuous-flow system (Finnigan GasBench II) into a Finnigan MAT DELTA plus XP Stable Isotope Ratio Mass Spectrometer at the National High Magnetic Field Laboratory for isotope analysis. The data were calibrated based on measurements of interspersed sets (beginning, every 12 samples, end) of three different lab water isotope standards (YW-ST-1:  $\delta^{18}O = -2.18$ ,  $\delta^2H = -11.6$ ; SLC-tap:  $\delta^{18}O = -16.2$ ,  $\delta^2H = -121.7$ ; QD:  $\delta^{18}O = -10.6$ ,  $\delta^2H = -35.8$ ) and are reported in standard  $\delta$  notation in the unit of per mil (‰) as  $\delta^2H$  and  $\delta^{18}O$  values in reference to the international standard VSMOW. The lab standards have been previously calibrated to the international standard VSMOW using IAEA reference materials VSMOW ( $\delta^{18}O = 0$ ,  $\delta^2H = 0$ ), LNW100 ( $\delta^{18}O = -19.64$ ,  $\delta^2H = -157.1$ ) and IAEA-04 ( $\delta^{18}O = -15.39$ ,  $\delta^2H = -114$ ). The analytical precision was  $\pm 0.1\%$  (1 $\sigma$ ) or better for  $\delta^{18}O$  and  $\pm 1\%$  (1 $\sigma$ ) for  $\delta^2H$  based on repeated analyses of lab standards processed along with the samples. These data were reported in a master's thesis (Thomason 2025) that is available online. Because of the high precision of  $\delta^{18}O$  measurements,  $\delta^{18}O$  values were used in this

study for estimating relative contributions of event water and surface water to spring discharge.

### 3.2 | Estimating Relative Contribution of Event Water to Spring Discharge

Detecting the storm signal in the spring water relies on the unique  $\delta^{18}O$  and  $\delta^2H$  signatures of rainfall associated with tropical cyclones. Tropical cyclones are known to produce precipitation with extremely negative  $\delta^{18}O$  and  $\delta^2H$  values when compared to normal thunderstorms (Lawrence 1998; Lawrence and Gedzelman 1996; Sun et al. 2022). This abnormally negative isotopic signature can be seen in surficial water bodies in areas impacted by tropical cyclones (Jahan et al. 2021; Lawrence 1998) and also in rain water from Hurricane Idalia collected in this study as shown in the following section. By comparing the isotopic values of the pre- and post-event spring water samples with those of rainwater associated with Hurricane Idalia, we estimated the transit times for the storm-derived event water to appear at the springs as well as the relative contribution of event water to spring water following hurricane Idalia.

Assuming that the spring water after a storm is a mixture of pre-storm groundwater and event water, the following isotope mass balance equations were used to determine the fraction of the spring discharge composed of event water after Hurricane Idalia:

$$\delta^{18}O_{Gw}F_{Gw} + \delta^{18}O_{Ew}F_{Ew} = \delta^{18}O_{Sp} \quad (1)$$

$$F_{Gw} + F_{Ew} = 1 \quad (2)$$

where  $\delta^{18}O_{Gw}$ ,  $\delta^{18}O_{Ew}$  and  $\delta^{18}O_{Sp}$  are the oxygen isotope compositions of pre-storm groundwater (i.e., pre-event spring water), event water, and spring water after event, respectively.  $F_{Gw}$  and  $F_{Ew}$  are the fractions of pre-event groundwater and event water, respectively, in spring water.

By solving the above equations, we can obtain the following:

$$F_{Ew} = (\delta^{18}O_{Gw} - \delta^{18}O_{Sp}) / (\delta^{18}O_{Gw} - \delta^{18}O_{Ew}) \quad (3)$$

Using the above equation and the measured  $\delta^{18}O_{Gw}$ ,  $\delta^{18}O_{Ew}$  and  $\delta^{18}O_{Sp}$  values, the mixing fraction of event water in the spring water ( $F_{Ew}$ ) was estimated.

### 3.3 | Estimating Relative Contribution of Surface Water Sources to Spring Discharge

We assumed that pre-event spring water (i.e., pre-storm groundwater) was a mixture of rainwater and surface water (from lakes, ponds and wetlands), both of which had entered the Floridan aquifer over time prior to Hurricane Idalia. Following the derivation of Equation (3), the relative contribution of surface water to the pre-Idalia discharge was estimated using the following isotope mass-balance equation:

$$F_{Sw} = (\delta^{18}O_{Rn} - \delta^{18}O_{Gw}) / (\delta^{18}O_{Rn} - \delta^{18}O_{Sw}) \quad (4)$$

where  $\delta^{18}\text{O}_{\text{Rn}}$  is the long-term average oxygen isotope composition of regional rainfall;  $\delta^{18}\text{O}_{\text{Gw}}$  and  $\delta^{18}\text{O}_{\text{Sw}}$  are the average oxygen isotope compositions of pre-storm spring water and surface water bodies, respectively.  $F_{\text{Sw}}$  is the fraction of spring water derived from surface water sources (e.g., lakes, ponds and wetlands) through sinkholes.

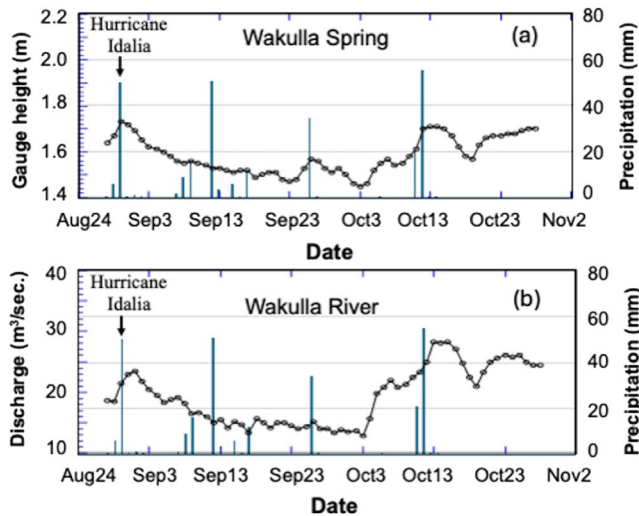


**FIGURE 2** | Daily rainfall amounts recorded at Tallahassee International Airport (<https://climatecenter.fsu.edu/>), along with (a) daily average gauge heights recorded at the USGS monitoring station at Wakulla Spring (<https://waterdata.usgs.gov/monitoring-location/USGS-02327000>) and (b) daily average discharges of Wakulla River measured at a USGS monitoring station located ~3.2 km downstream from Wakulla Spring ([https://waterdata.usgs.gov/nwis/inventory/?site\\_no=02327022](https://waterdata.usgs.gov/nwis/inventory/?site_no=02327022)).

## 4 | Results

### 4.1 | $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of Rainwater and Spring Water

Hurricane Idalia delivered more than 50 mm of rainfall to the study area on August 30, 2023 (Figure 2). Large rainfall events can cause rapid increases in spring water level and discharge because karst aquifer systems are highly sensitive to rainfalls (Xu and Hu 2021). This sensitivity is evident in the spring gauge height (water level) records, in which nearly all major rainfall events resulted in increased gauge height, with the sole exception of the rainfall event on September 12 (Figure 2a). Because no weather station is located in the EBWS State Park, the rainfall record was obtained from the nearest station at Tallahassee International Airport (TIA), approximately 23 km north of the springs. This station recorded nearly as much rain on September 12 as during Hurricane Idalia (Figure 2), while our rain collector located ~15 km north of TIA recorded only 30 mm of total rainfall in September (Table S1). Therefore, the discrepancy between spring discharge and rainfall records reflects spatial variability in rainfall, with the September 12 event primarily affecting localised areas in and around TIA.

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of rain samples collected in Tallahassee from July 2023 through December 2023 ranged from  $-15.2\text{‰}$  to  $-1.7\text{‰}$  and  $-108.5\text{‰}$  to  $-7.2\text{‰}$ , respectively, with the lowest values associated with Hurricane Idalia (Figure 3a; Table S1). The data confirm previous observations (Lawrence and Gedzelman 1996; Lawrence 1998; Odezulu 2011; Jahan et al. 2021), showing that precipitation from Hurricane Idalia was considerably more depleted

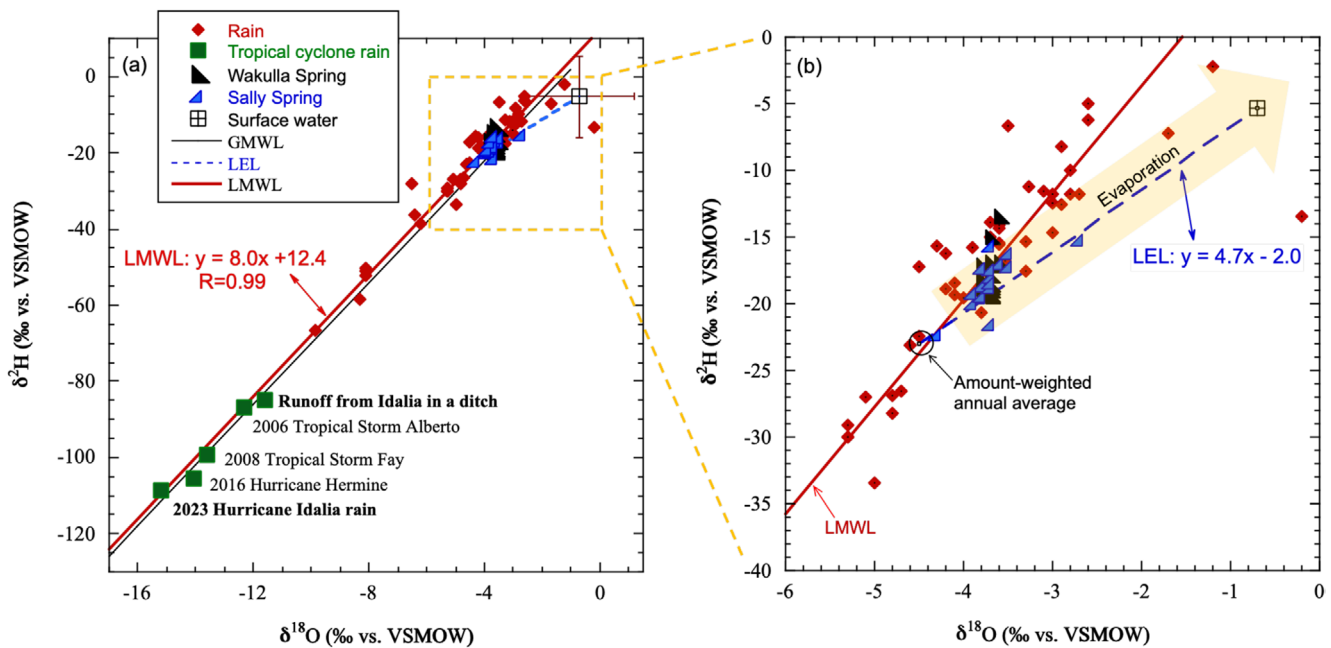


**FIGURE 3** |  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of spring water samples collected from Sally Ward Spring and Wakulla Spring between August 28 and October 27, 2023. Hurricane Idalia passed through the study area on August 30, 2023. Also shown are  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of monthly rain during the period of 2006–2023, along with rain (and runoff) associated with tropical cyclones that passed through the study area and the mean composition (and  $\pm 1\sigma$  as error bars) of surface water bodies (i.e., lakes, ponds, sinks) in the region. LEL, average local evaporation line, defined as the line connecting the amount-weighted annual average precipitation composition (2006–2023) to the mean isotopic composition of surface water bodies. GMWL, global meteoric water line (Craig 1961). LMWL, local meteoric water line.

in  $^{18}\text{O}$  and  $^2\text{H}$  than normal rains in the area (Figure 3a; Table S1). Combining the rainwater isotope data that we previously collected over a nearly 4-year period (5/2006–12/2009) (Odezulu 2011) from Tallahassee and the new data produced in this study yielded an amount-weighted annual mean  $\delta^{18}\text{O}$  value of  $-4.5\text{‰}$  and  $\delta^2\text{H}$  value of  $-23.1\text{‰}$  for precipitation in the study area for the period of 2006–2023. Unweighted averages of monthly precipitation  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values for the same period are  $-4.1\text{‰} \pm 1.6\text{‰}$  ( $1\sigma$ ,  $n = 48$ ) and  $-20.2\text{‰} \pm 12.2\text{‰}$  ( $1\sigma$ ,  $n = 48$ ), respectively. Linear regression of all rainwater isotope data yielded the following Local Meteoric Water Line (LMWL) shown in Figure 3:

$$\delta^2\text{H} = 8.0 \delta^{18}\text{O} + 12.4 \quad (5)$$

which is similar to the Global Meteoric Water Line (i.e.,  $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ ) (Craig 1961).

Water samples from the two springs show much smaller isotopic variabilities than local rains (Figure 3a). The samples from Sally Ward Spring had  $\delta^{18}\text{O}$  values ranging from  $-4.3\text{‰}$  to  $-2.7\text{‰}$  and  $\delta^2\text{H}$  values from  $-22\text{‰}$  to  $-15\text{‰}$  during the study period (Figure 4; Table S2). The samples from Wakulla Spring showed an even smaller isotopic variability during the same period, with  $\delta^{18}\text{O}$  values ranging from  $-3.8\text{‰}$  to  $-3.6\text{‰}$  and  $\delta^2\text{H}$  values from  $-19\text{‰}$  to  $-15\text{‰}$  (Figure 5; Table S3), which are within the range ( $-5.1\text{‰}$  to  $-2.7\text{‰}$  for  $\delta^{18}\text{O}$  and  $-29\text{‰}$  to  $-16\text{‰}$  for  $\delta^2\text{H}$ ) previously observed for the spring in 2012 and 2013 (Rau 2016).

As shown in Figure 3, water samples from both springs plot either on or near the LMWL. This indicates that the groundwater is primarily recharged by local rainfall (Clark and Fritz 1997). This is not surprising from a hydrologic perspective. The springshed is estimated to cover approximately 975 miles<sup>2</sup> ( $2.53 \times 10^9 \text{ m}^2$ ) (FDEP 2026). The amount of annual rainfall ( $\sim 1494 \text{ mm}$ ) is equivalent to 996 648 million gallons of water falling on the springshed each year, which is more than 3300 times the average daily discharge at Wakulla Spring. If only 12% of the annual rainfall first recharges the aquifer and then discharges at Wakulla Spring, it would be enough to sustain the average discharge at the Wakulla Spring for a year. However, Figure 3 shows that most samples plot slightly below the LMWL, suggesting the influence of evaporation. This is because evaporation preferentially removes isotopically lighter water molecules into vapour phase, enriching the remaining water in heavier isotopes  $^{18}\text{O}$  and  $^2\text{H}$  (Gonfiantini 1986). As a result, the isotopic values of evaporated water fall below the LMWL, along an evaporation line with a slope typically between 2 and 5 depending on local relative humidity, in a  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  plot (Clark and Fritz 1997; Gat 1996), providing a diagnostic feature for identifying the influence of evaporated surface waters on groundwater system.

## 4.2 | Response of Sally Ward Spring to Hurricane Idalia

Water samples collected one day after Hurricane Idalia from Sally Ward Spring showed a marked decrease in both  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , accompanied by a sharp increase in PM content (Figure 4a–c), reflecting a rapid response to the storm. The decrease in isotopic

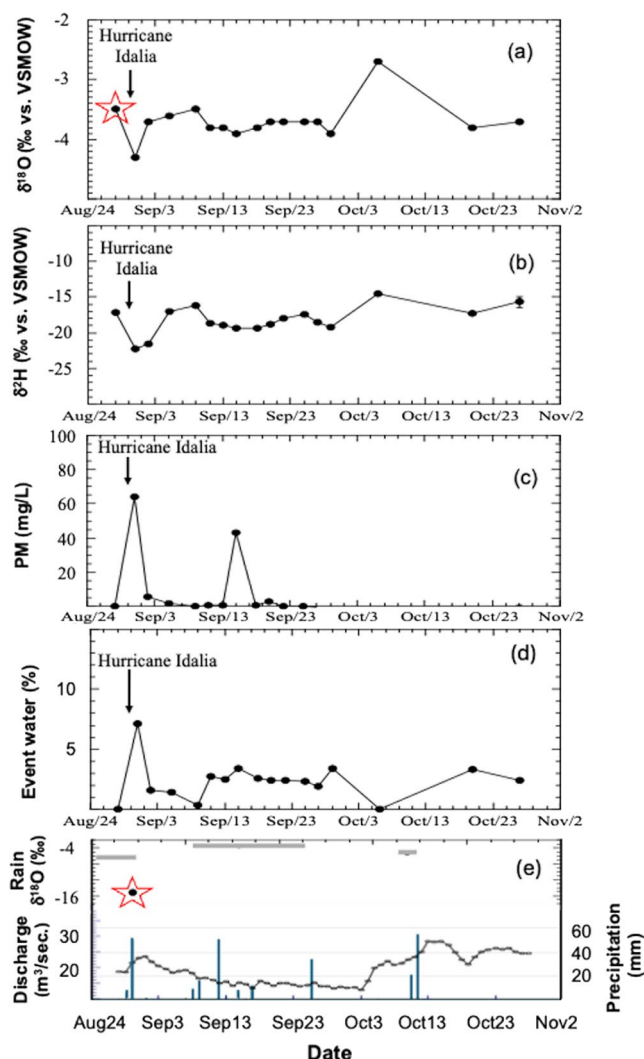


**FIGURE 4** | Temporal variations of  $\delta^{18}\text{O}$  (a),  $\delta^2\text{H}$  (b) and PM (c) of water samples collected from Sally Ward Spring before and after Hurricane Idalia passed through the area, along with relative contribution of event water to discharge (d) estimated using an isotopic mass balance model. Also shown in (e) are the  $\delta^{18}\text{O}$  values of rainwater (event water) from Hurricane Idalia (solid black dot) and amount-weighted monthly precipitation (grey bars), together with the daily precipitation amount recorded at Tallahassee International Airport and the daily average discharges of the Wakulla River measured at the USGS monitoring station. Red stars in (a) and (e) highlight the endmember  $\delta^{18}\text{O}$  values used in the isotopic mass balance model to calculate the percentage of event water in spring water following the hurricane.

values is consistent with an influx of isotopically light event water, while the PM peak reflects an increased input of particles driven by strong winds, cave sediment reactivation and enhanced surface runoff. Over the following 5–9 days, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of the spring water rose back to pre-storm levels, while PM content decreased to pre-storm levels. Approximately 12 days after Idalia, both  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values declined to below pre-storm levels, reaching a second minimum between September 11 and 18, about 12–19 days after Idalia passed through the area. They then rose gradually towards pre-storm levels before declining again to another low point on September 29, about 30 days after the hurricane (Figure 4a,b).

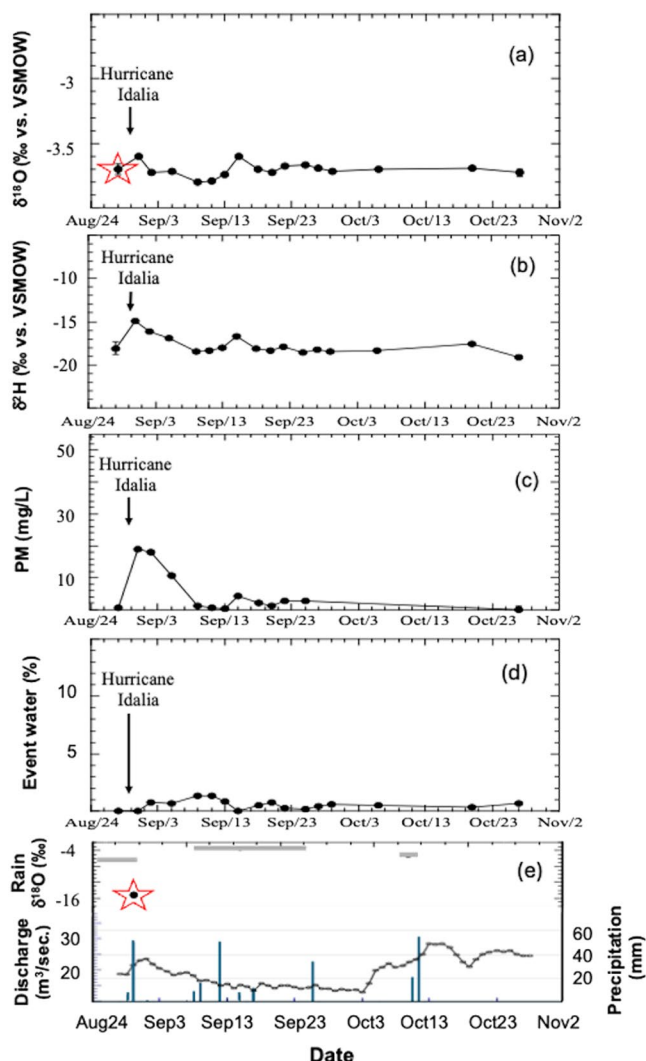


**FIGURE 5** | Temporal variations of  $\delta^{18}\text{O}$  (a),  $\delta^2\text{H}$  (b) and PM (c) of water samples collected from Wakulla Spring before and after Hurricane Idalia passed through the area, along with relative contribution of event water to discharge (d) estimated using an isotopic mass balance model. Also shown in (e) are the  $\delta^{18}\text{O}$  values of rainwater (event water) from Hurricane Idalia (solid black dot) and amount-weighted monthly precipitation (grey bars), together with the daily precipitation amount recorded at Tallahassee International Airport and the daily average discharges of the Wakulla River measured at the USGS monitoring station. Red stars in (a) and (e) highlight the endmember  $\delta^{18}\text{O}$  values used in the isotopic mass balance model to calculate the percentage of event water in spring water following the hurricane.

Two heavy rainfall events ( $>30\text{mm}$ ) were recorded at TIA in September (on the 12th and 26th). As noted previously, the early September event appears to have affected only areas in and around TIA and had no influence on spring discharge (Figure 2). The elevated PM content in the sample collected after this event (Figure 4c) is likely due to increased atmospheric deposition caused by enhanced winds. Similarly, the late September event had only small impacts on spring water level and discharge (Figures 2 and 4e). The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of September rainwater were  $-3.6\text{‰}$  and  $-14\text{‰}$ , respectively, which are generally higher than those of the spring water in the same month ( $-3.73\text{‰} \pm 0.10\text{‰}$  and  $-18.6\text{‰} \pm 1.4\text{‰}$  for  $\delta^{18}\text{O}$  and

$\delta^2\text{H}$ , respectively). Given these considerations, it is unlikely that the September rain events were responsible for the observed decreases in spring-water isotope values. Thereafter,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values increased in early October following a dry period and decreased in late October, approximately 8 days after a large rain event (Figure 4).

A dye-tracing study estimated a transit time of approximately 14 days for water from Ames Sink (Figure 1) to reach Sally Ward Spring (Kincaid and Werner 2008). Transit times from other local sinkholes and swallets to Sally Ward Spring have not been investigated. It has been reported that there was a hydrologic connection between Sally Ward Spring and Indian Spring—a smaller spring  $\sim 1.6\text{km}$  northwest of Sally Ward Spring (Figure 1)—via a wetland slough during heavy rains (NFWFMD 2021). Under normal conditions, Sally Ward Spring and Indian Spring are hydrologically isolated. However, during periods of excessive rainfall, the wetland slough between the two springs became inundated, allowing surface water to flow into Sally Ward Spring (NFWFMD 2021).

The pronounced drop in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values (by  $1\text{‰}$  and  $5\text{‰}$ , respectively) observed one day after Hurricane Idalia indicates a transit time of about 1 day for event water to first emerge at Sally Ward Spring (Figure 4). This rapid response most likely reflects input from storm runoff delivered through adjacent wetlands and nearby sinking streams to the spring. The second and third minima in spring  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values during September, which cannot be explained by local rainfall events as noted above, are consistent with mixing of runoff water from Idalia, suggesting longer transit times of 12–19 days and 30 days, respectively. These estimates are in line with the 14-day transit time from Ames Sink (Figure 1) determined by a dye-tracing study (Kincaid and Werner 2008) and reflect relatively fast flows of storm runoff through various sinks and conduits in the area.

Using Equation (3) and the measured  $\delta^{18}\text{O}$  value of the pre-storm spring sample ( $-3.5\text{‰}$ , collected 2 days before the storm) and Idalia rainwater ( $-15.2\text{‰}$ ), we estimated the proportion of event water in spring discharge (Figure 4d). Although Sally Ward Spring water was predominantly pre-event water, event water accounted for  $\sim 7\%$  of the spring water 1 day after the storm. The relative amount of event water in the spring water declined over the following days but increased again to  $\sim 3\%$  at 12–19 days and once more at  $\sim 30$  days after the hurricane.

### 4.3 | Response of Wakulla Spring to Hurricane Idalia

Gauge height at Wakulla Spring peaked  $\sim 10\text{h}$  after Hurricane Idalia made landfall in the early morning of August 30, whereas Wakulla River discharge, recorded at the USGS monitoring station  $\sim 3.2\text{km}$  downstream from the spring, peaked 2 days later on September 1 (Figures 2 and 5e). Unlike Sally Ward Spring, samples collected 1 day after the storm from Wakulla Spring—a much larger spring—showed a minor increase in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , along with a pronounced rise in PM content, relative to conditions 2 days before the storm (Figure 5a–c). Over the following 9–12 days,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and PM in the spring

water gradually declined to slightly below pre-storm levels, or to pre-storm levels in the case of PM.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  returned to pre-storm values 3 days later on September 13. These parameters then remained relatively stable for the rest of the study period (Figure 5). Although a large rain event occurred in October, bringing more rain to the area than Hurricane Idalia and resulting in increased spring discharge, the reduced sampling frequency in late September and October prevents assessment of its impact on the  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and PM in spring water (Figure 5).

The small isotopic spike observed at Wakulla Spring 1 day after the storm was unexpected but can be reasonably explained. Although the wide scatter in isotopic values of rainfall is substantially reduced by mixing during infiltration through the unsaturated zone into the aquifer (Clark and Fritz 1997), the isotopic composition of groundwater within the Floridan aquifer is not spatially uniform. This heterogeneity is evidenced by variations in the isotope ratios of spring waters (Figures 3–5; Rau 2016), reflecting both temporal and spatial differences in the isotopic composition of recharge. Surface water bodies (e.g., lakes and ponds) are typically enriched in  $^{18}\text{O}$  and  $^2\text{H}$  relative to local meteoric water due to evaporation (Gonfiantini 1986). Therefore, the observed post-storm increase in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  at Wakulla Spring suggests that early discharge following the storm contained a slightly greater contribution from evaporated surface water sources. This pattern is most likely caused by increased recharge flows pushing out older groundwater that had been partially derived from lakes and other surface water bodies. The higher PM content in the post-storm sample reflects an influx of particles due to enhanced erosion by strong winds, enhanced surface runoff, and/or cave sediment reactivation.

The lowest isotopic values occurred in samples collected 10–12 days after Hurricane Idalia (Figure 5), suggesting a transit time of about 10–12 days for event water to emerge at Wakulla Spring. The weak storm signal ( $\sim 0.2\%$  decrease in  $\delta^{18}\text{O}$  compared to pre-storm samples) can be explained by a low event-water-groundwater mixing ratio, as revealed by isotopic mass-balance calculations discussed below. Rau (2016) estimated a similar transit time of 9 days, also based on  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  changes in spring water following Tropical Storm Debby in 2012. Tropical Storm Debby brought more than 10 times as much rainfall as Hurricane Idalia to the study area and caused a 1.2‰ drop in spring  $\delta^{18}\text{O}$ , relative to pre-storm level, 9 days after the storm. Unfortunately, Rau (2016) did not measure the isotopic composition of rainfall from that storm and thus could not evaluate the contribution of Debby rainfall to spring discharge. The estimated transit time of 10–12 days is also similar to the dye-tracer travel times from some of the local sinks to Wakulla Spring (Figure 1): 9.5 days from Fisher Creek Sink, 10.3 days from Black Creek Sink, and approximately 20–23 days from Kelly and Ames Sinks (Kincaid and Werner 2008). Isotopic mass-balance calculations show that water at Wakulla Spring consisted almost entirely of pre-event water stored in the aquifer, recharged by previous rains and other surface sources, with event water from Hurricane Idalia accounting for  $\leq 1\%$  of the spring water following Hurricane Idalia (Figure 5d).

## 5 | Discussion

The stable isotope data indicate that Sally Ward and Wakulla Springs respond differently to storm events, despite proximity of their spring vents. Although both springs display much smaller isotopic variability than rainfall, Sally Ward Spring shows a larger range of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values relative to Wakulla Spring (Figures 3–5). Following Hurricane Idalia, event water was detected at Sally Ward Spring within 1 day, as evidenced by a significant decrease in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values, and it contributed up to  $\sim 7\%$  of the spring flow 1 day after the storm (Figure 4d). The proportion of event water then declined rapidly but increased again to  $\sim 3\%$  at 12–19 days and once more around 30 days after the hurricane, indicating multiple flow paths. In contrast, no clear signal of event water was detected at Wakulla Spring until approximately 10–12 days after the storm, when event water accounted for about 1% of the spring discharge (Figure 5d). These observations indicate that Sally Ward Spring is more sensitive to the influence of storm runoff than Wakulla Spring, which is a much larger system with discharge rates more than 22 times greater than those of Sally Ward Spring. The difference in storm response between the two springs may also reflect differences in their source areas within the aquifer (e.g., shallow vs. deep sections), resulting from differences in their connections to sinks and the complex underground conduit networks within the springshed. The high sensitivity of Sally Ward Spring to storms is also supported by the PM data, which show much higher ( $> 3$  times higher) PM concentrations in water from Sally Ward Spring than in water from Wakulla Spring collected 1 day after the hurricane (Figures 4c and 5c). This suggests that smaller springs are more vulnerable to the impacts of storm runoff than larger springs.

Previous studies have used various chemical and isotopic tracers to examine groundwater flow patterns and mixing water fractions in the Wakulla Spring watershed (e.g., Compare and Ye 2025; Katz 2001; Katz 2004; Katz et al. 2001; Katz et al. 2004; Katz et al. 1997; Osmond et al. 1971; Osmond et al. 1968). By examining variations in uranium isotopic composition in water samples from different sections of the Floridan Aquifer in North Florida, Osmond et al. (1968) suggested that most of the water at Wakulla Spring was recharged south of the Cody Scarp (i.e., within the WKP). Based on analyses of  $^3\text{H}$  and U isotopes, Osmond et al. (1971) estimated that water discharging from Wakulla Spring was a mixture of water from shallow (35%) and deep (65%) parts of the aquifer. Apparent ages of groundwater discharging from Wakulla Spring, derived from measurements of  $\text{SF}_6$ , are about 7–9 years (Katz 2004). Whereas, apparent ages of water from Wakulla Spring, calculated from  $^3\text{H}$  and  $^3\text{He}$  concentrations, are about 32–45 years (Katz 2004; Katz et al. 2004) and 50 years (Happell et al. 2006). The mean transit times estimated for groundwater discharging from Wakulla Spring, using isotopic and chemical tracers in conjunction with lumped-parameter flow models, range from 50 to 80 years (Katz et al. 2004). These apparent ages and transit times estimated based on analyses of  $\text{SF}_6$ ,  $^3\text{H}$  and  $^3\text{He}$  concentrations in spring water samples likely reflect the slower movement of groundwater through the aquifer matrix in the watershed.

Dye-tracing studies conducted in the Wakulla springshed showed much shorter transit times from some of the local sinks (Figure 1) to Wakulla Spring and Sally Ward Spring, varying from approximately 10 to 23 days (Kincaid and Werner 2008). These much faster transit times determined in dye-tracing experiments are in general agreement with the transit times derived from the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  time-series data, reflecting faster flows through sinks and conduits. These rapid flows, however, accounted for only a small proportion of the discharges at both springs, as indicated by the isotopic mass balance calculations.

Both springs showed elevated PM concentrations following Hurricane Idalia. The USGS monitoring stations at Wakulla Spring and on Wakulla River recorded increased water level and discharge lasting for 3–5 days (Figure 2), consistent with enhanced recharge and aquifer discharge. However, isotopic mass balance calculations indicate that runoff from Hurricane Idalia contributed no more than ~7% and ~1% of total flow at Sally Ward Spring and Wakulla Spring, respectively. These results show that discharges at both springs are dominated by pre-event water stored in the aquifer, even following a major storm. This implies that most of the event water from the storm infiltrated through soil pores to recharge the aquifer, replenishing the regional storage of groundwater that flows slowly through the aquifer matrix down the hydraulic gradient. Some of the event water also flowed as surface runoff into lakes, ponds and other low-lying areas to replenish surface water sources that recharge the aquifer. This also explains the longer transit times estimated from analyses of  $\text{SF}_6$ ,  $^3\text{H}$  and  $^3\text{He}$  (Happell et al. 2006; Katz 2004; Katz et al. 2004) and helps to reconcile the discrepancies in transit times estimated using different tracers. Our findings highlight the complexity of surface water and groundwater interactions in karst aquifer systems.

For the study period, both springs have essentially the same average isotopic values:  $-3.7\text{‰} \pm 0.3\text{‰}$  ( $\delta^{18}\text{O}$ ) and  $-18.1\text{‰} \pm 1.9\text{‰}$  ( $\delta^2\text{H}$ ) for Sally Ward Spring, and  $-3.7\text{‰} \pm 0.1\text{‰}$  ( $\delta^{18}\text{O}$ ) and  $-17.9\text{‰} \pm 1.0\text{‰}$  ( $\delta^2\text{H}$ ) for Wakulla Spring. These values are higher than the long-term amount-weighted annual mean  $\delta^{18}\text{O}$  ( $-4.5\text{‰}$ ) and  $\delta^2\text{H}$  ( $-23.1\text{‰}$ ) values for precipitation in this region. This, together with the observation that most spring-water samples plot slightly below the LMWL in Figure 3, suggests that (1) evaporation occurred prior to infiltration or (2) both springs received a significant portion of their recharge from evaporated surface-water bodies such as lakes, swallets and ponds.

North Florida has many shallow lakes, ponds and wetlands, where surface water can drain rapidly into the aquifer through sinkholes in lake beds and percolate slowly into the aquifer through pores in the underlying sediments. Although sourced from local precipitation, these surface water bodies are typically enriched in  $^{18}\text{O}$  and  $^2\text{H}$ , relative to local rains, due to evaporation (Ahmed et al. 2021; Bugna et al. 2020; Jahan et al. 2021; Katz et al. 1997; Odezulu 2011). Previous dye tracing studies have demonstrated hydraulic connections between Wakulla Spring and some of the lakes north of the WKP, including Lake Jackson (35-day travel time), Lake Lafayette (30–35 day travel time) and Lake Munson (14–22 days) in Tallahassee (Kincaid et al. 2007; McGlynn and Deyle 2018). Both Lake Jackson (~16 km<sup>2</sup>) and Lake Lafayette (~7.4 km<sup>2</sup>) are among the ‘Disappearing Lakes’ that are known

to drain periodically through sinkholes on their lake beds (Lammers 2021). Such dry-down events allow relatively rapid recharge of the aquifer by large volumes of lake water periodically, shifting the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of groundwater and thus spring water to higher values temporarily. The  $\delta^{18}\text{O}$  value of pre-event discharge was  $-3.7\text{‰}$  at Wakulla Spring and  $-3.5\text{‰}$  at Sally Ward Spring during the study period. The average  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of lakes, ponds and sinks in North Florida are  $-0.7\text{‰} \pm 1.9\text{‰}$  ( $\pm 1\sigma$ ,  $n = 109$ ) and  $-5\text{‰} \pm 11\text{‰}$  ( $\pm 1\sigma$ ,  $n = 106$ ) (Figure 3 and Table S4). Assuming that pre-event spring water was a mixture of water originating from direct infiltration of local rainfalls, with  $\delta^{18}\text{O}$  of  $-4.5\text{‰}$  (i.e., long-term amount-weighted average value for precipitation in the area), and water derived from evaporated surface water bodies (i.e., lakes, ponds and swallets) with  $\delta^{18}\text{O}$  of  $-0.7\text{‰}$ , mass-balance calculations (using Equation (4)) suggest that the relative contribution of surface water bodies to the pre-Idalia discharge (i.e., base flow) was ~22% at Wakulla Spring and ~26% at the Sally Ward Spring (Figure 6). Rau (2016) reported an average  $\delta^{18}\text{O}$  value of  $-3.3\text{‰}$  for the base flow at Wakulla Spring in 2012 and 2013. Assuming the same end-member values, these higher isotopic values would suggest a greater proportion (~32% on average) of the base flow originated from surface water bodies in the watershed.

Our study demonstrates that the unique isotopic signatures of tropical cyclones can serve as effective natural tracers in regional hydrological investigations. Compared to dyes and other chemical tracers, stable oxygen and hydrogen isotopes are not affected by absorption or degradation. Furthermore, when source endmembers can be identified, isotopic mass-balance analysis allows quantitative assessment of mixing ratios and the relative contributions of different sources, which is difficult to achieve using dye tracers. Our approach is applicable to any region that may be impacted by tropical cyclones. Although PM increased at both springs after the storm, we caution against using PM as a surrogate for isotope data, as PM can be influenced by processes other than storm-driven inputs, such as sediment reactivation within the karst system and atmospheric deposition.

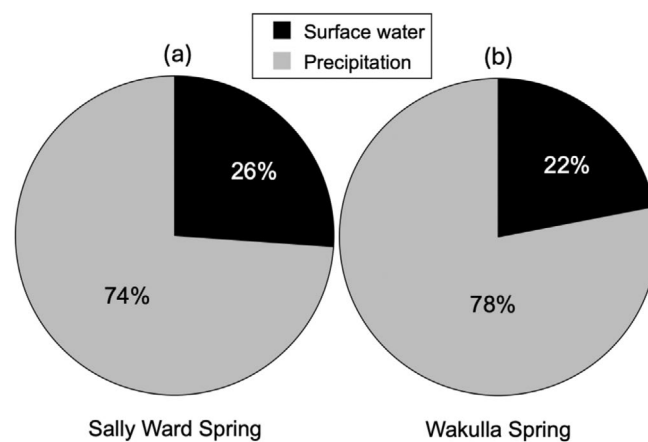


**FIGURE 6** | Relative contributions of surface water sources and direct rainwater infiltration over a longer period to pre-storm discharge at Sally Ward Spring (a) and Wakulla Spring (b), estimated using an isotopic mass balance model, the average  $\delta^{18}\text{O}$  values of precipitation (for the period of 2006–2023) and surface water bodies, and the  $\delta^{18}\text{O}$  values of spring-water samples collected before Hurricane Idalia.

## 6 | Conclusions

Stable isotope analyses of water samples from Sally Ward Spring, Wakulla Spring, and precipitation in North Florida reveal distinct hydrologic responses to Hurricane Idalia and provide new insights into groundwater recharge and flow dynamics in this karst aquifer system. Precipitation associated with Hurricane Idalia was highly depleted in  $^{18}\text{O}$  and  $^2\text{H}$  relative to typical regional rainfall, consistent with previous observations of tropical cyclone precipitation and confirming its utility as an effective hydrologic tracer.

Storm-derived event water was detected at Sally Ward Spring within 1 day of the hurricane, whereas a clear signal of event water did not appear at Wakulla Spring until approximately 10–12 days later. Additional pulses of event water were detected at Sally Ward Spring approximately 12–19 days and ~30 days after the storm. These observations indicate that Sally Ward Spring and Wakulla Spring exhibit markedly different hydrodynamic responses to large storm events, despite the close proximity of the two springs. The relatively short transit times of many days to weeks are generally consistent with prior dye-tracing results, reflecting fast flow through sinking streams and underground conduits. However, isotopic mass-balance calculations indicate that discharge at both springs is overwhelmingly dominated by pre-event water stored within the aquifer, even following a major storm. Elevated PM concentrations and increased spring discharge following the hurricane reflect aquifer's sensitivity to intense rainfall and increased recharge. Isotope data further indicate that surface waters, including lakes and ponds, are an important source of groundwater, contributing a substantial portion (> 20%) of base flow at both springs. Together, these results underscore the complexity of groundwater flow and storage in the karst aquifer system and the importance of pre-event groundwater in sustaining spring discharge.

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### Data Availability Statement

All relevant data are within the manuscript and its [Supporting Information](#) files.

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## Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Table S1:**  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of storm and monthly rain samples from Tallahassee in North Florida. **Table S2:**  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  values, percent of event water and particle content of water samples collected from Sally Ward Spring before and after Hurricane Idalia. **Table S3:**  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  values, percent of event water and particle content of water samples collected from Wakulla Spring before and after Hurricane Idalia. **Table S4:**  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of surface water bodies in North Florida.