

1 **Seasonal variation and influence factors of river water isotopes in the**
2 **East Asian monsoon region: A case study in Xiangjiang River basin**
3 **spanning 13 hydrological years**

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9 **ABSTRACT:** Seasonal variation and influencing factors of river water isotopes were
10 investigated in the Xiangjiang River basin, located in the East Asian monsoon region.
11 This investigation involved comprehensive sampling of daily precipitation and river
12 water with 5-day interval, as well as observing hydrometeorological factors spanning
13 13 hydrological years from January 2010 to December 2022, combining with the
14 temporal and spatial correlation analyses based on linear regression and the isotopic
15 Atmospheric Water Balance Model. Key findings are as follows: River water $\delta^2\text{H}$
16 ($\delta^2\text{H}_R$) exhibited significant seasonal variation, with the most positive and negative
17 values occurring in the spring flood period and summer drought period, respectively,
18 in alignment with those observed in precipitation. The correlations of the $\delta^2\text{H}_R$ with
19 corresponding hydrometeorological factors with a 5-day interval were commonly
20 weak, due to the seasonality of precipitation isotopes and mixing of various water
21 bodies within the basin, but the changes in the runoff (ΔR) and $\delta^2\text{H}_R$ ($\Delta\delta^2\text{H}_R$) between
22 two contiguous samplings with 5-day or higher intervals showed significant responses
23 to the corresponding accumulated precipitation and evaporation. Prolonged rainless
24 intervals with high evaporation rates in 2013 and 2022, as well as significant

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25 precipitation events in major flood periods in 2011 and 2017, had a significant impact
26 on the $\delta^2\text{H}_R$ and runoff discharge. However, the most positive $\delta^2\text{H}_R$ values were
27 primarily influenced by precipitation input with the most enriched isotopes in the
28 spring flood period, while the moderately isotope-depleted precipitation during
29 limited wetness conditions led to the most negative $\delta^2\text{H}_R$. The spatial correlation
30 analysis between water isotopes and hydrometeorological factors at the observing site
31 and in the surrounding regions supported the representation of the Changsha site in
32 the Xiangjiang River basin. These results underscore the potential of $\Delta\delta^2\text{H}_R$ as a proxy
33 that reflects the seasonal variations in local environments, while caution is advised
34 when interpreting extreme isotopic signals in river water. Overall, this study provides
35 insights into the seasonal variation, extreme signal interpreting, and controlling
36 factors of $\delta^2\text{H}_R$ in the study area, which was valuable for paleoclimate reconstruction
37 and establishment of isotope hydrologic models.

38 **Keywords:** Stable isotopes; River water; Precipitation input; Evaporation; Seasonal
39 variation.

40 **1. Introduction**

41 River water is commonly recognized as a natural integrator of basin hydrological
42 processes, gaining insights into the effects of hydrometeorological factors like air
43 temperature, evaporation, precipitation input, and runoff discharge/water level (Yang
44 et al., 2020; von Freyberg et al., 2022). Stable isotopes of natural water possess
45 exceptional sensitivity and serve as remarkable recorders of environmental change,
46 for instance, water bodies undergo phase changes throughout the water cycle,
47 resulting in stable isotope fractionation—that is, an occurrence where light and heavy
48 stable isotope molecules are distributed unequally between phases (Scholl et al., 2015;
49 Xiao et al., 2022a). Generally, during water phase changes, light isotope molecules

50 tend to evaporate more readily than heavy isotope molecules, while heavy isotope
51 molecules preferentially condense compared to their lighter counterparts (Craig, 1961;
52 Dansgaard, 1964). The isotope fractionation contributes to variations in stable isotopic
53 compositions among different water bodies within the water cycle. For instance, the
54 stable river water isotopes primarily reflect the characteristics of precipitation, as
55 precipitation input acts as the primary water source (Sprenger et al., 2022; Wang et al.,
56 2023). Moreover, due to varying degrees of evaporative enrichment and mixing
57 processes experienced by different water bodies within a basin, the river water
58 isotopes markedly differ from those of the precipitation input and exhibit distinct
59 seasonality (Jiang et al., 2021; Sun et al., 2021; Das and Rai, 2022). This disparity
60 forms the basis for employing stable isotope techniques to investigate river water
61 generation processes in basins, while the stable isotope techniques were widely used
62 to indicate the water cycle processes (Boral et al., 2019; Xiao et al., 2020; Wu et al.,
63 2021), find extensive application in hydrometeorology modeling and diagnosis (e.g.,
64 Aggarwal et al., 2016; Sinha et al., 2019; Zhiña et al., 2022), and in the paleoclimate
65 reconstruction (e.g., Steinman et al., 2010; Jiménez-Iñiguez et al., 2022;
66 Emmanouilidis et al., 2022).

67 Extensive efforts have been made to investigate the extent of variations in river
68 water isotopes and examine the relationship between stable isotopes in river water and
69 specific environmental factors (e.g., Yang et al., 2020; Das and Rai, 2022; Ren et al.,
70 2023). Linear regression is an effective tool to build the empirical relationships
71 between hydrometeorological factors and river water isotopes, while numerous
72 empirical formulas have been developed and used for paleoclimate reconstruction and
73 interpretation based on these empirical relationships (Kendall and Coplen, 2001; Nan
74 et al., 2019). However, in regions where new water mixes thoroughly with old water,

75 the river water isotopes exhibit dampened signals, indicating that old water dominates
76 the composition of stream water and that the response of river water isotopes to
77 hydrometeorological factors is sluggish (Munoz-Villers and McDonnell, 2012;
78 Streletskiy et al., 2015). Moreover, extreme precipitation and drought events have
79 become more frequent under the background of global climate changes, as evidenced
80 in numerous regions worldwide (Nkemelang et al., 2018; Cook et al., 2018; Grillakis,
81 2019; Marengo et al., 2020; Cardoso et al., 2020). Furthermore, the scale effect and
82 spatial heterogeneity have always been a problem in hydrological model research
83 (Seyfried and Wilcox, 1995; Blöschl, 2006; Pechlivanidis et al., 2011; Devia et al.,
84 2015), for example, the representation of the observations at limited sampling sites in
85 the whole basin scale with a large area. These introduce additional complexities and
86 uncertainty in identifying the seasonal variation and influence factors of river water
87 isotopes on a basin scale, thus the interpreting of the extreme isotopic signals and the
88 variations in river water isotopes and the representing of the site observation based on
89 the spatial correlation analysis become necessary (Uchiyama et al., 2017; Boutt et al.,
90 2019; Saranya et al., 2020).

91 The East Asian monsoon region, characterized by complex water vapor sources,
92 substantial seasonal and inter-annual temperature and precipitation variations, as well
93 as frequent floods and seasonal droughts, further contributes to the hydrological
94 complexity in this region (Huang et al., 1998; Zhou et al., 2019; Wang et al., 2023).
95 Hence, long-term observations of river water and precipitation isotopes and
96 hydrometeorological factors, along with comprehensive analyses of the influencing
97 factors, are crucial to enhancing our understanding of how climate change impacts
98 hydrological regimes in basins within the East Asian monsoon region. Long-term
99 observations of water isotopes are crucial as they enable the capture of extreme

100 precipitation and drought events, facilitating an analysis of their influences on river
101 water isotopes, while also unveiling patterns of seasonal and inter-annual variation
102 (Rode et al., 2016; von Freyberg et al., 2022; Ren et al., 2023). However, the
103 long-term observations of river water isotopes with a high sampling frequency are
104 relatively challenging and rare due to logistical constraints (von Freyberg et al., 2017).

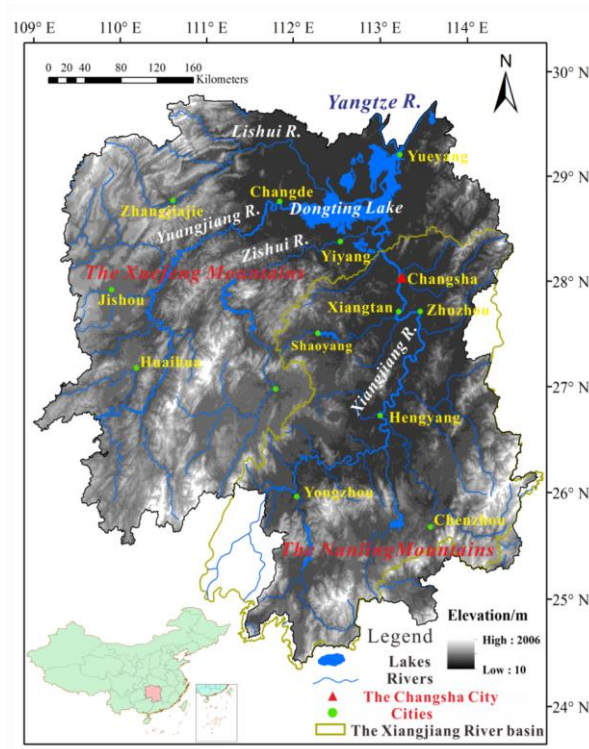
105 Therefore, in this study, the Xiangjiang River basin was selected as the study
106 area to investigate the seasonal variation and controlling factors of river water
107 isotopes under the influence of the monsoon. Extensive sampling of river water with
108 5-day interval and daily precipitation, along with the monitoring of
109 hydrometeorological factors, was conducted over 13 complete hydrological years
110 from January 2010 to December 2022, while the simple and multiple linear regression
111 was used to identify the temporal correlation between the hydrometeorological factors
112 and the river water isotopes, and the isotopic Atmospheric Water Balance Model
113 (iAWBM) was used to simulate the spatial distribution of the precipitation isotopes
114 and the hydrometeorological factors such as air temperature, evaporation, and
115 precipitation amount. This study aims to achieve the following objectives: (1) Identify
116 the factors influencing the seasonality of river water isotopes and assess the influences
117 of extreme drought and precipitation events; (2) Interpret the environmental
118 significance implied by the seasonality of river water isotopes; (3) Verify the
119 representation of the observation at the Changsha site in the Xiangjiang River basin.

120 **2. Study site**

121 The study area was situated in a typical East Asian monsoon region,
122 characterized by distinct climatic variations throughout the four seasons. On average,
123 the annual precipitation and evaporation were 1147 mm and 902 mm, respectively
124 (Xiao et al., 2022b). Notably, there is a significant seasonal disparity in precipitation,

125 with an average of 152 rainy days each year. The period from early March to mid-July
 126 experiences abundant precipitation due to the influence of the monsoon, whereas from
 127 mid-July to September, drought conditions prevail as a result of the subtropical
 128 high-pressure system. The average annual temperature in the region is 17.4 °C, and
 129 the duration of the plant growing period spans approximately 330 days.

130 The Xiangjiang River basin, originating in the Guangxi Zhuang Autonomous
 131 Region, encompasses a drainage area of 94,660 km². It stretches for 856 km
 132 northward across Hunan Province, passing through cities like Hengyang, Xiangtan,
 133 Zhuzhou, and Changsha (Fig. 1). The altitudinal range of the Xiangjiang River basin
 134 varies from 1902 to 10 m, with higher elevations in the southern region characterized
 135 by multiple terraces and valley landforms, while the northern part is relatively lower.
 136 The middle and lower reaches of the Xiangjiang River basin are predominantly hilly
 137 basins, surrounded by the Xuefeng Mountains and Nanling Mountains (Fig. 1).



138
 139 Figure 1. Map showing the location of the Hunan Province, China and the Changsha
 140

141 **3. Methods and materials**

142 **3.1 Water samples collection and analysis**

143 From January 2010 to December 2022, the collection of river water and
144 precipitation samples was conducted.

145 River water sampling took place 929 times at the center of Orange Island, with a
146 regular sampling interval of five days. Specifically, samples were obtained on the 1st,
147 6th, 11th, 16th, 21st, and 26th days of each month. The sampling depth of river water
148 was relatively deep to avoid the influences of human activity; moreover, this
149 operation can avoid the evaporation fractionation of surface water during the sampling
150 and ensure adequate mixes of the river water.

151 At the College of Geographic Science, Hunan Normal University, Changsha (Fig.
152 1, 112°56'28" E, 28°11'30" N), the sampling of precipitation and the measurements of
153 precipitation amount were conducted at the altitude of 55 m, adjacent to the Yuelu
154 Mountains, throughout the sampling period of this study (2010–2022). For
155 precipitation sampling, a siphon rain gauge was repurposed as a collector, consisting
156 of a 6-cm diameter funnel connected to a glass bottle via a plastic pipe. Both rainfall
157 and snowfall were collected and measured at 8:00 and 20:00 local time on the
158 precipitation day, and the volume-weighted value of the two samplings was used to
159 represent the precipitation isotopic values of the day, while the precipitation amount
160 of the day was calculated by the sum of the two samplings. Snowfall samples were
161 carefully packed in sealed plastic bags and transferred to the glass bottle, which was
162 later melted at room temperature, because the glass bottle is sealed and the collection
163 process is completed quickly, thus the evaporation of precipitation samples is
164 effectively prevented. A total of 1668 precipitation isotopic values were obtained over
165 1668 precipitation days. Furthermore, considering that the sampling interval for river

166 water was set at five days, and previous studies have indicated that it may take 3-5
167 days for precipitation (new water) to significantly contribute to river water (Yao et al.,
168 2016; Xiao et al., 2022a), the precipitation isotopes were volume-weighted in the
169 5-day interval within this study.

170 To ensure proper preservation, both the river water and precipitation samples
171 were transferred to clean, sealed, polyethylene bottles (30 ml) and stored in a
172 refrigerator at 0 °C. However, few precipitation and river water samples were lost,
173 resulting in some missing data. The isotopic composition of the samples was
174 determined using the off-axis integrated cavity output spectroscopy method,
175 specifically conducted with equipment from Los Gatos Research in the USA. The
176 stable isotopic values are represented by the δ (per mil) value of the sample relative to
177 Vienna Standard Mean Ocean Water (V-SMOW) as follows:

$$178 \quad \delta^2H \text{ or } \delta^{18}O = \left[\frac{R_{sample}}{R_{V-SMOW}} - 1 \right] \text{‰} \quad (1)$$

179 where R is the $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ ratio.

180 Comparison of the measured stable isotope values of 160 replicate samples of
181 ultrapure water and its standard composition (known $\delta^2\text{H} = -128\text{‰}$, $\delta^{18}\text{O} = -16.3\text{‰}$
182 V-SMOW) showed that the measurement precision was $< 1\text{‰}$ for $\delta^2\text{H}$ and $< 0.3\text{‰}$ for
183 $\delta^{18}\text{O}$ (Lis et al., 2008).

184 **3.2 Hydrometeorological observations**

185 The daily air temperature and evaporation data used in this study were obtained
186 from the National Meteorological Reference Station in Changsha (station code:
187 57687), specifically utilizing the large evaporator model E-601B. It is worth noting
188 that the evaporation recorded by the E-601B evaporator closely approximates the
189 actual evaporation experienced in small water bodies such as lakes and rivers. As such,

190 it reliably represents the quantity and temporal variations of evaporation within the
191 study area (Hua et al., 2019).

192 Daily runoff discharge data were obtained from the Xiangtan hydrological station
193 (station code: 61102000). Following the national standard “Code for liquid flow
194 measurement in open channels” (GB 50179-93, 1993) issued by the Ministry of Water
195 Resources of the People’s Republic of China, the daily discharge values are calculated
196 by applying the weighted average of intraday instantaneous discharge. This
197 calculation is based on water level observations and a specific stage-discharge curve.
198 As per the guidelines outlined in GB 50179-93, the relative errors in instantaneous
199 discharge measurements range from 2% for high water levels, 5% for normal water
200 levels, and 9% for low water levels. On average, the estimated annual discharge falls
201 within 5% of the actual value. To facilitate the comparison of runoff discharge with
202 precipitation and evaporation, the daily runoff discharge data (in m^3/d) are normalized
203 by dividing them by the basin area (in m^2) of the measuring cross-section.
204 Consequently, the runoff depth (in m/d or mm/d) and runoff discharge data (in m^3/d)
205 are computed and utilized in the subsequent analysis.

206 **3.3 Model analysis**

207 Because the samplings of precipitation and river water and the observation of
208 hydrometeorological factors were conducted at the Changsha site, it is necessary to
209 verify the representation of the Changsha site in the Xiangjiang River basin. For the
210 aims to support the foundation and reduce the uncertainty of this study, a spatial
211 correlation analysis was conducted between the Changsha site and the surrounding
212 regions based on data from 1979 to 2021, including precipitation isotopes,
213 precipitation amount, evaporation, and air temperature. The analysis employed the
214 simulated precipitation isotope data generated by the isotopic Atmospheric Water

215 Balance Model (iAWBM) as detailed by Zhang et al. (2015), which has a spatial
216 resolution of $1.5^{\circ} \times 1.5^{\circ}$, while the air temperature, evaporation, and precipitation
217 amount data from the ERA5 reanalysis dataset (<https://cds.climate.copernicus.eu>)
218 published by the European Centre for Medium-Range Weather Forecasts (ECMWF),
219 which has a spatial resolution of $1^{\circ} \times 1^{\circ}$. Overall, all the data employed in this spatial
220 correlation analysis was integrated into a 5-day interval.

221 For the aims of building the empirical relationships between the river water
222 isotopes and the hydrometeorological factors and to identify the controlling factor that
223 influences the river water isotopes, Multiple Linear Regressions (MLRs) were used to
224 build the prediction model of the river water isotopes. The variables include the
225 precipitation isotope and the hydrometeorological factors such as precipitation amount,
226 air temperature, evaporation, and runoff. Linear regression and a stepwise regression
227 method were applied in MLRs using SPSS for Windows Version 22.0 (SPSS Inc.,
228 SPSS Statistics 22.0). All the variables were taken as input variables and one or more
229 independent variables were retained in the prediction models.

230 **4. Results**

231 **4.1 Stable isotopic characteristics of precipitation and river water**

232 Table 1 presents the monthly average values of air temperature ($^{\circ}\text{C}$), precipitation
233 (mm), evaporation (mm), and runoff discharge (10^8 m^3), and the results illustrate the
234 uneven distribution of these factors throughout the year. Based on the monthly
235 patterns of these hydrometeorological factors (Table 1) and the previous findings (Qin
236 et al., 2006; Yao et al., 2016), four distinct runoff periods have been identified: the
237 rainless period, spring flood period, major flood period, and summer drought period.
238 The rainless period spans from October to the following February, characterized by
239 low air temperature, minimal precipitation, evaporation, and runoff discharge. In this

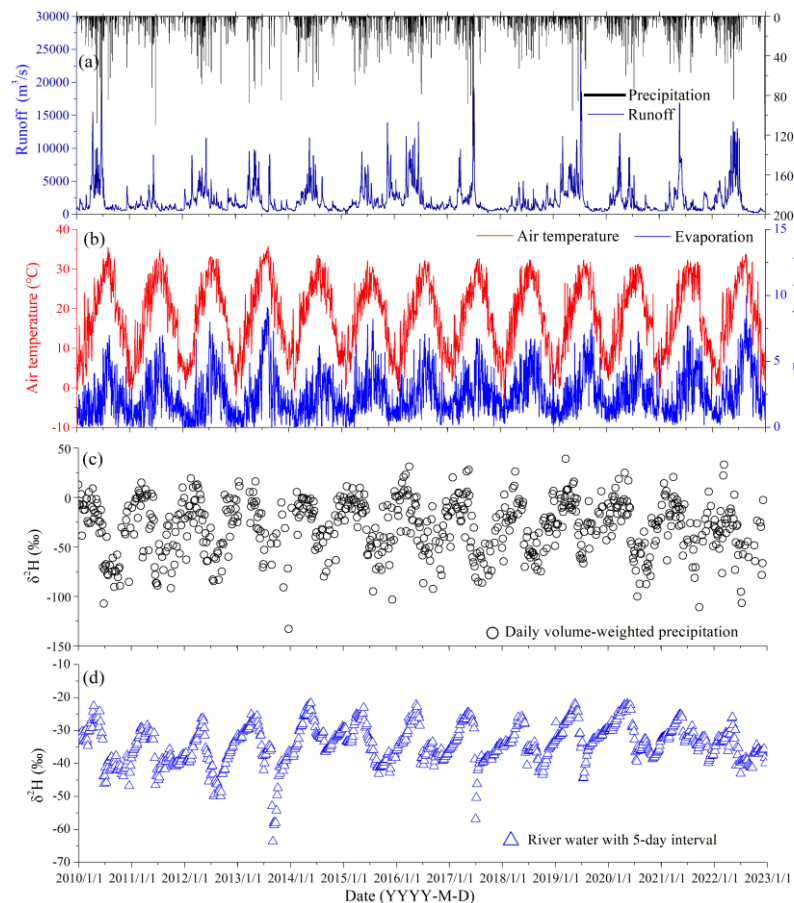
240 period, the runoff discharge exhibits slight fluctuations except for isolated peaks
 241 resulting from major rainfall events; The spring flood period, occurring in March and
 242 April, marks an increase in runoff discharge, this can be attributed to relatively higher
 243 precipitation amounts, as well as moderate air temperature and evaporation in spring;
 244 The major flood period, extending from May to mid-July, exhibits a rapid surge in
 245 runoff discharge, often reaching peak values due to intensive precipitation events; The
 246 summer drought period, spans from mid-July to September, while a significant
 247 decrease in runoff discharge is always observed. This decline can be attributed to high
 248 air temperature leading to increased evaporation in this period. Additionally, the
 249 scarcity of precipitation events and relatively low precipitation amounts contribute to
 250 the reduced runoff discharge in this period. Overall, the analysis highlights the
 251 seasonal variations in air temperature, precipitation, evaporation, and runoff discharge,
 252 leading to distinct runoff periods throughout the year.

253 Table 1. Monthly average air temperature (°C), precipitation (mm), evaporation
 254 (mm), and runoff discharge (10^8 m^3)

Month	Air Temperature °C	Precipitation mm	Evaporation mm	Runoff discharge $\times 10^8 \text{ m}^3$
Jan.	5.6	68.9	33.0	35.5
Fab.	7.6	82.3	33.8	35.7
March	12.7	150.0	46.4	65.1
April	17.8	145.6	60.8	85.5
May	22.2	230.6	71.9	111.7
June	26.1	212.3	80.6	115.0
July	29.4	156.7	132.4	71.9
Aug.	28.9	87.6	141.7	36.0
Sep.	24.8	84.2	105.3	26.8
Oct.	18.7	61.2	83.9	22.0
Nov.	13.6	82.7	53.9	38.1
Dec.	7.5	54.6	47.5	31.8

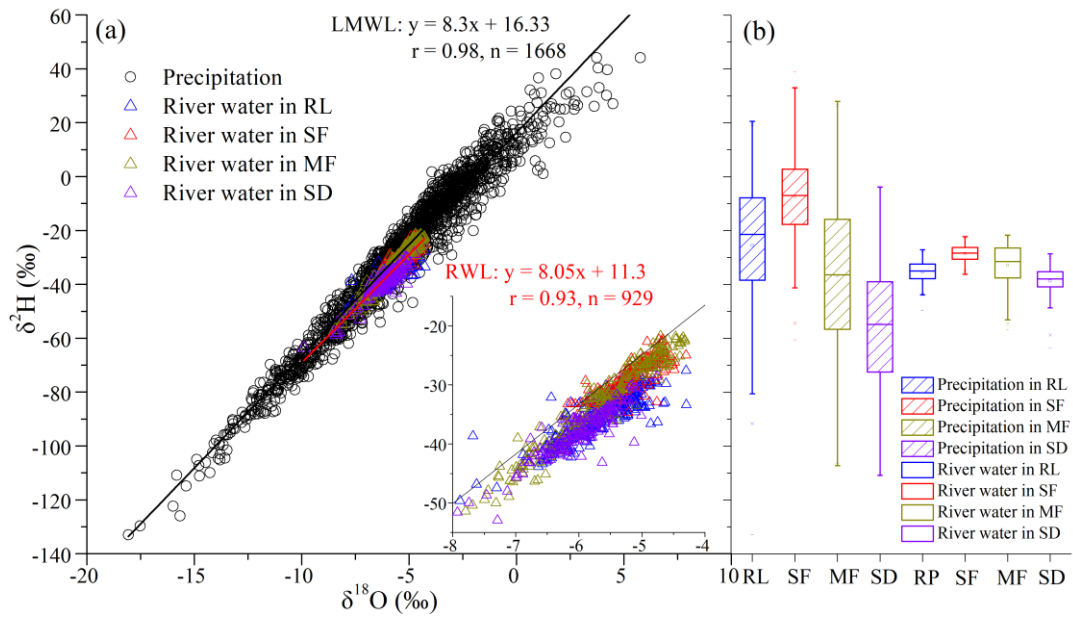
255 From 2010 to 2022, the 5-day volume-weighted precipitation $\delta^2\text{H}$ ($\delta^2\text{H}_P$)
 256 exhibited large seasonality throughout the year, as depicted in Fig. 2 and Fig. 3.

257 Notably, the 5-day volume-weighted $\delta^2\text{H}_P$ ranged from -133.0‰ to 39.1‰ , with a
 258 standard deviation of 27.6‰ . The 5-day volume-weighted $\delta^2\text{H}_P$ showed the maximum
 259 values in March, while the minimum values occurred in September (Fig. 2c).
 260 Furthermore, the 5-day volume-weighted $\delta^2\text{H}_P$ followed the following order: spring
 261 flood period > rainless period > major flood period > summer drought period (Fig. 3b).
 262 The seasonal variations in the precipitation isotopes primarily result from different
 263 vapor sources, upstream effects, circulation patterns, and local meteorological factors
 264 in different seasons (Zhou et al., 2019; Xiao et al., 2023). The $\delta^2\text{H}$ values of river
 265 water ($\delta^2\text{H}_R$) ranged from -63.7‰ to -21.7‰ , with a standard deviation of 6.1‰
 266 (Figs. 2 and 3).



267

268 Figure 2. Temporal variation of the daily runoff discharge and precipitation (a), daily
 269 air temperature and evaporation (b), daily volume-weighted precipitation $\delta^2\text{H}$ (c), and
 270 river water $\delta^2\text{H}$ with 5-day interval (d).



271

272 Figure 3. Stable isotope composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of daily volume-weighted
 273 precipitation and river water samples (a) and box plots of precipitation and river water
 274 $\delta^2\text{H}$ (b) in different periods (rainless period, spring flood period, major flood period,
 275 and summer drought period). LMWL (black solid line) and RWL (red solid line)
 276 represent the local meteoric water line and river water line based on all the
 277 precipitation and river water isotopic data from January 2010 to December 2022,
 278 respectively. The letters (RL, SF, MF, and SD) in the x-axis represent the rainless
 279 period, spring flood period, major flood period, and summer drought period,
 280 respectively.

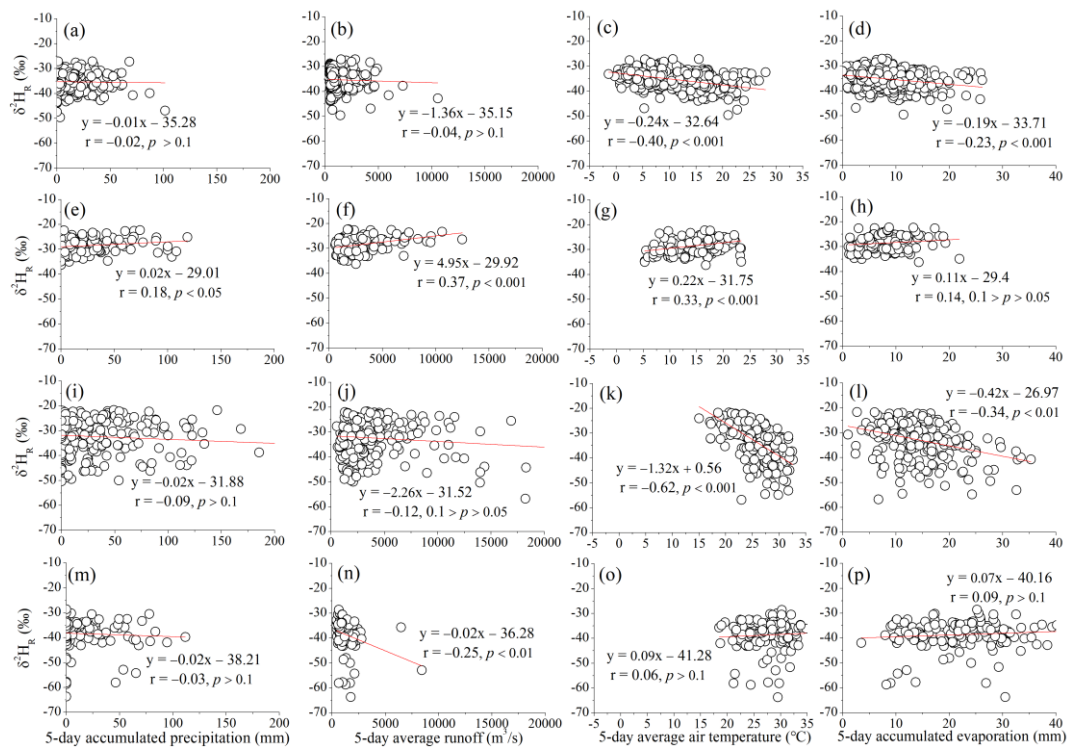
281 The magnitude of $\delta^2\text{H}_R$ was ranked as follows: spring flood period, major flood
 282 period, rainless period, and summer drought period (Fig. 3b). The most depleted and
 283 enriched isotopic values in river water in the sampling period occurred on September
 284 1, 2013, and May 21, 2014, respectively (Fig. 2). The seasonal variations in river
 285 water isotopes generally aligned with those observed in precipitation, indicating that
 286 river water directly derives from the precipitation input and is influenced by its
 287 isotopic composition. Moreover, the local meteoric water line (LMWL) and river

288 water line (RWL) have relatively close slopes of 8.3 and 8.05, respectively (Fig. 3a).
289 However, the $\delta^2\text{H}_R$ exhibited a relatively smaller range of variation and more
290 attenuated temporal pattern compared to the $\delta^2\text{H}_P$. This is likely due to the processes
291 that precipitation undergoes before recharging river water, such as evaporation and
292 mixing with older waters in the subsurface, which significantly reduce the variability
293 in $\delta^2\text{H}_R$ (Xiao et al., 2022a; 2023).

294 **4.2 Relationship between river water isotopes and various** 295 **hydrometeorological factors**

296 The relationships between the $\delta^2\text{H}_R$ and the corresponding 5-day accumulated
297 precipitation and evaporation and average runoff discharge and air temperature in
298 different periods are illustrated in Fig. 4. Based on the relationship between the 5-day
299 volume-weighted $\delta^2\text{H}_P$ and the corresponding accumulated precipitation in different
300 runoff periods (Fig. S1; left panel), it is evident that an “amount effect” is observed in
301 the precipitation isotopes across various runoff periods. Specifically, the increased
302 precipitation amounts consistently result in more isotope-depleted precipitation.
303 Furthermore, the $\delta^2\text{H}_R$ exhibits a positive correlation versus the corresponding 5-day
304 volume-weighted $\delta^2\text{H}_P$, with a correlation coefficient of 0.55 and $p < 0.001$ (Fig. S2).
305 This suggests that precipitation input is the primary factor influencing $\delta^2\text{H}_R$. However,
306 as shown in Fig. 4, the $\delta^2\text{H}_R$ exhibited relatively weak correlations with the
307 corresponding 5-day accumulated precipitations in the rainless period, major flood
308 period, and summer drought period, as indicated by low correlation coefficient values
309 and $p > 0.1$ (Fig. 4a, 4i, 4m). Although a positive correlation between $\delta^2\text{H}_R$ and the
310 corresponding 5-day accumulated precipitations in the spring flood period, their
311 correlation coefficients were not exceptionally high (Fig. 4e). The weak correlation
312 between the $\delta^2\text{H}_R$ and precipitation amount or runoff discharge can be attributed to the

313 expansive area and water reserves in the Xiangjiang River basin—that is, after
 314 precipitation falls in the basin and the new input precipitation within 5 days may
 315 influence the $\delta^2\text{H}_R$ to some extent, however, it tends to mix with old waters, such as
 316 groundwater, soil water, and river water consisting of a high proportion of older water
 317 components in the subsurface flowpaths (Xiao et al., 2023), thereby attenuating the
 318 impact of precipitation input and predominantly shape the river water isotopes.



319
 320 Figure 4. Relationships between the river water $\delta^2\text{H}$ and the corresponding 5-day
 321 accumulated precipitation (the first column), 5-day average runoff discharge (the
 322 second column), 5-day average air temperature (the third column), and 5-day
 323 accumulated evaporation (the fourth column) in different periods, and the first row (a,
 324 b, c, and d), the second row (e, f, g, and h), the third row (i, j, k, and l), and the fourth
 325 row (m, n, o, and p) represent the rainless period, spring flood period, major flood
 326 period, and summer drought period, respectively.

327 The $\delta^2\text{H}_R$ exhibits a consistent relationship with the corresponding 5-day average
 328 air temperature and accumulated evaporation within each respective runoff period.

329 However, positive or negative correlations may be observed in these relationships
330 across the four runoff periods. Specifically, in the spring flood period and summer
331 drought period, the $\delta^2\text{H}_R$ demonstrates either a highly significant ($p < 0.001$) or
332 non-significant ($0.1 > p > 0.05$ or $p > 0.1$) positive correlation with the corresponding
333 5-day average air temperature and accumulated evaporation (Fig. 4g-h and 4o-p).
334 Conversely, in the rainless period and major flood period, a highly significant ($p <$
335 0.001 or $p < 0.01$) negative correlation is observed (Fig. 4c-d and 4k-i). The negative
336 relationship between the $\delta^2\text{H}_R$ and the corresponding 5-day average air temperature or
337 accumulated evaporation may seem counterintuitive, as river water isotopes typically
338 become enriched with increasing air temperature and progressing evaporation (Gibson
339 et al., 2016; Jiang et al., 2021). This discrepancy can be explained by considering the
340 seasonality of the relationship between precipitation isotopes and air temperature in
341 different runoff periods (Fig. S1; right panel). For instance, the 5-day
342 volume-weighted $\delta^2\text{H}_P$ gradually decreases as the corresponding average air
343 temperature increases in the major flood period, while increasing as the corresponding
344 average air temperature decreases in the rainless period (Fig. 2 and 3). This would
345 lead to the negative relationship between the 5-day volume-weighted $\delta^2\text{H}_P$ and the
346 corresponding average air temperature in the rainless period and major flood period
347 (Fig. S1b and S1f), subsequently resulting in the negative relationship between the
348 $\delta^2\text{H}_R$ and the corresponding 5-day average air temperature in these two periods (Fig.
349 4c-d and 4k-i). Moreover, as there is strong consistency between evaporation and air
350 temperature (Allen et al., 2005), this alignment causes evaporation to also exhibit a
351 negative correlation with $\delta^2\text{H}_R$ in these two periods (Fig. 4). Therefore, in the major
352 flood period and rainless period, the influences of air temperature and evaporation on
353 river water isotopes are somewhat masked by the seasonality of precipitation isotopes.

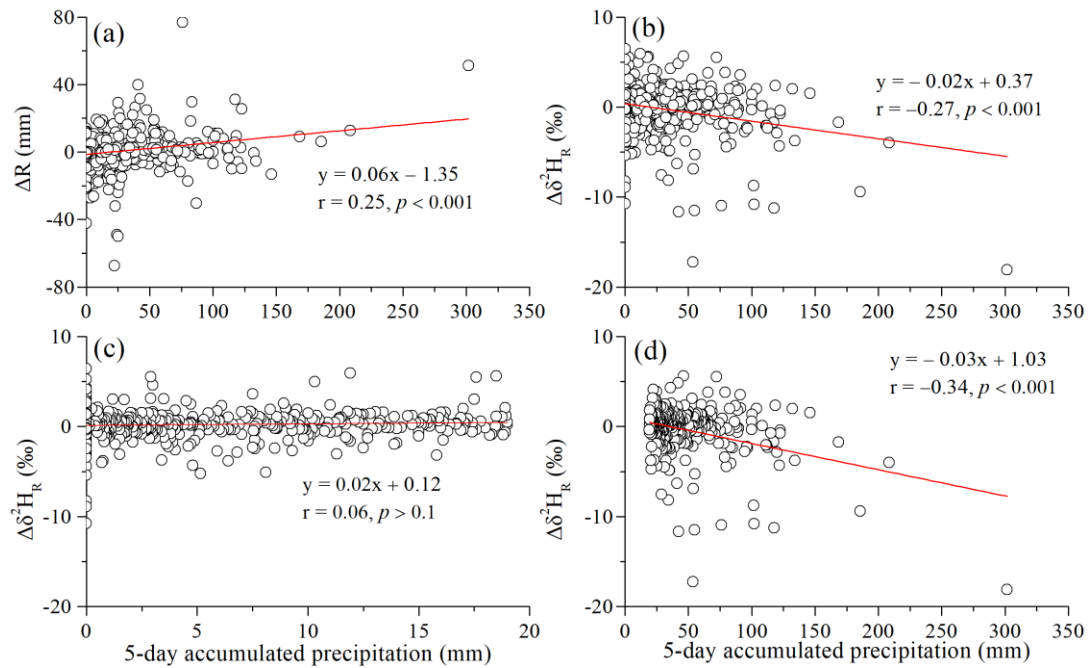
354 In the spring flood period and summer drought period, the river water isotopes
355 exhibited an enrichment trend with the increasing of the corresponding average air
356 temperature and accumulated evaporation (Fig. 4g-h and 4o-p). However, these
357 relationships may be somewhat misleading due to the positive correlation observed
358 between the 5-day volume-weighted $\delta^2\text{H}_P$ and the corresponding average air
359 temperature in the spring flood period ($p < 0.05$) and summer drought period ($p > 0.1$)
360 (Fig. S1d and S1h). This suggests that the positive correlation between river water
361 isotopes and air temperature or evaporation may also be influenced by the seasonality
362 of precipitation isotopes. Moreover, in the spring flood period, the increases in
363 precipitation amount and runoff discharge lead to more isotope-enriched river water,
364 as indicated in Fig. 4e and 4f. This phenomenon can be attributed to the most enriched
365 precipitation isotopes occurring in the spring flood period (Fig. 2c and 3b), as the
366 precipitation amount and runoff discharge gradually increase in this period (Fig. 2a), it
367 contributes to the positive relationship observed between the $\delta^2\text{H}_R$ and the
368 corresponding accumulated precipitation or average runoff discharge. Consequently,
369 based on the findings of this section, when interpreting the relationships between the
370 river water isotopes and hydrometeorological factors, it is important to consider the
371 uncertainty arising from the seasonality of precipitation isotopes.

372 **4.3 Relationship between the changes in river water isotopes and the** 373 **precipitation and evaporation**

374 As shown in Fig. 4, the relationship between the $\delta^2\text{H}_R$ and various factors may
375 not be significant or may contradict common sense—that is, precipitation input and
376 evaporation are likely the major driving factors that change the isotopic compositions
377 of river water. For instance, the river water isotopes tend to be more depleted and the
378 slope of RWL tends to be high in heavy precipitation events, while the river water

379 generally exhibits gradually enriched isotopes and lower evaporation line slope on
380 rainless days with high air temperature and evaporation (Gibson et al., 2016; Yang et
381 al., 2020; Jiang et al., 2021). Therefore, under the river water sample collection at a
382 5-day interval, it is essential to analyze the influences of the individual
383 hydrometeorological factors on the changes in the $\delta^2\text{H}_R$ between two contiguous
384 samplings ($\Delta\delta^2\text{H}_R$), which was calculated by the $\delta^2\text{H}_R$ differences between the $\delta^2\text{H}_R$ of
385 the following and preceding samplings (i.e. $\Delta\delta^2\text{H}_R = \delta^2\text{H}_R(t) - \delta^2\text{H}_R(t-1)$).

386 The 5-day runoff depth changes (i.e. $\Delta R = R(t) - R(t-1)$) and $\Delta\delta^2\text{H}_R$ exhibited
387 significant increases and decreases, respectively ($p < 0.001$), in response to the 5-day
388 accumulated precipitation (Fig. 5a and 5b). These findings indicate that precipitation
389 input is the primary factor influencing the variations in runoff discharge and river
390 water isotopes. Furthermore, based on the intersections between the linear fitting line
391 and the x-axis, the thresholds for precipitation amounts influencing the $\Delta\delta^2\text{H}_R$ and ΔR
392 at 5-day interval were determined to be 19.0 mm and 19.4 mm, respectively. This
393 suggests that heavier precipitation events are more likely to alter the river water
394 isotopes. The weak correlation ($p > 0.1$) between the $\Delta\delta^2\text{H}_R$ and corresponding 5-day
395 accumulated precipitation below the threshold value of 19.0 mm supports this
396 observation (Fig. 5c). Conversely when the 5-day accumulated precipitation exceeded
397 19.0 mm, a significant ($p < 0.001$) negative correlation was observed between the
398 $\Delta\delta^2\text{H}_R$ and the corresponding 5-day accumulated precipitation (Fig. 5d). In other
399 words, greater 5-day accumulated precipitation led to more negative $\delta^2\text{H}$ values in the
400 subsequent river water sample, with a correlation coefficient of -0.34 and $p < 0.001$.
401 Therefore, it can be concluded that the variation in river water isotopes reflects the
402 isotopic signal of the input precipitation, and the isotopic composition of river water
403 exhibits a significant “amount effect” by the precipitation input.



404

405 Figure 5. Relationship between the 5-day accumulated precipitation and the changes

406 in 5-day runoff discharge (ΔR) (a) and river water δ^2H ($\Delta\delta^2H_R$) (b), and the

407 relationship between the $\Delta\delta^2H_R$ and the corresponding 5-day accumulated

408 precipitation < 19.0 mm and > 19.0 mm were shown in subplot (c) and (d),

409 respectively.

410 Because of the confluence processes of the river water from upstream to

411 downstream and the mixing processes between the new and old waters in the

412 subsurface, river water may consist of a certain proportion of old water with a

413 relatively long residence time (Xiao et al., 2022a; 2023), thus we analysis the

414 relationship between the river water isotopes and the hydrometeorological factors at a

415 longer time interval. The relationships between the $\Delta\delta^2H_R$ and corresponding

416 accumulated evaporation at various time intervals (5-, 10-, 15-, 20-, 25-, and 30-day)

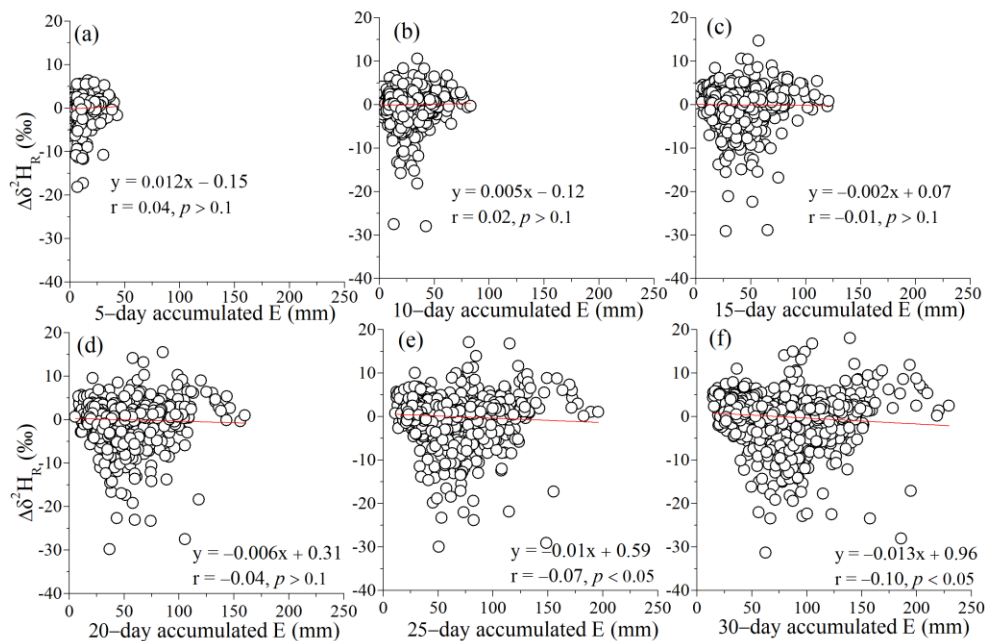
417 were shown in Fig. 6. As there is a strong consistency between evaporation and air

418 temperature (Allen et al., 2005), the relationship between the $\Delta\delta^2H_R$ and air

419 temperature was not analyzed in this paper. The results revealed a weak and

420 statistically non-significant correlation ($p > 0.1$) between the $\Delta\delta^2H_R$ and

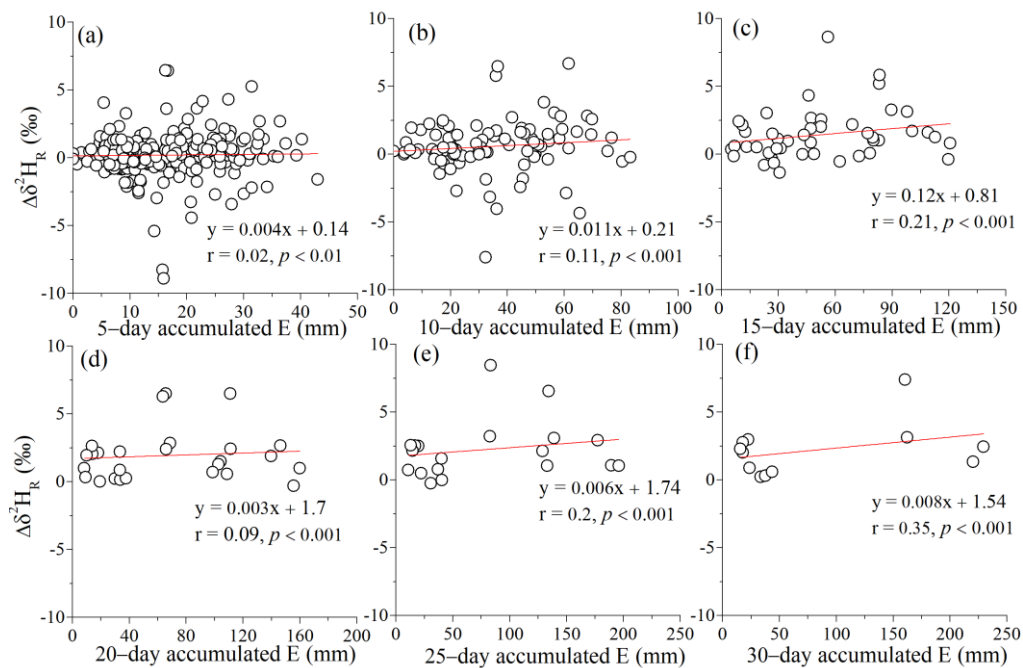
421 corresponding accumulated evaporation at the 5-, 10-, 15-, and 20-day intervals (Fig.
 422 6a-d). However, a significant ($p < 0.05$) negative correlation with relatively low
 423 correlation coefficients was observed at the 25- and 30-day intervals (Fig. 6e and 6f).
 424 The negative relationship between the $\Delta\delta^2H_R$ and the corresponding accumulated
 425 evaporation (Fig. 6c-f) also contradicts the common sense that the river water
 426 generally becomes more enriched under the influences of evaporation. This may be
 427 due to the negative relationship between the δ^2H_P/δ^2H_R and the corresponding average
 428 air temperature/accumulated evaporation in the rainless period and major flood period
 429 (Fig. 2 and 3) as discussed earlier, besides, the effect of dilution precipitation input on
 430 river water isotopes (Fig. 5 and S1) and the relatively low air temperature and high
 431 relative humidity in the heavy precipitation events may be greater than the enrichment
 432 effect of evaporation (e.g., similar as the effect demonstrated in Xiao et al., 2022b).



433
 434 Figure 6. Relationship between the changes in river water δ^2H ($\Delta\delta^2H_R$) and the
 435 corresponding accumulated evaporation (E) at 5-day (a), 10-day (b), 15-day (c),
 436 20-day (d), 25-day (e), and 30-day (f) time intervals.

437 To highlight the influences of evaporation on the river water isotopes and

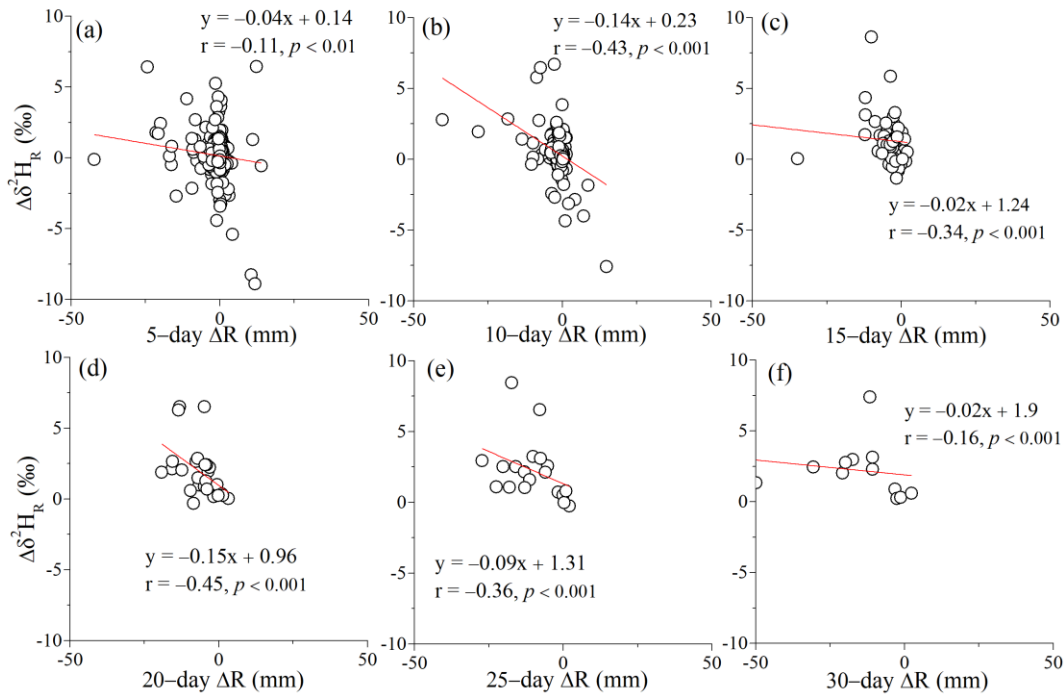
438 eliminate the influence of precipitation input, we analyzed the relationship between
 439 the $\Delta\delta^2H_R$ and the corresponding accumulated evaporation at different intervals (5-,
 440 10-, 15-, 20-, 25-, and 30-day) without precipitation input (Fig. 7). The findings
 441 revealed a significant ($p < 0.01$ or $p < 0.001$) positive correlation between these
 442 variables at different time intervals. In other words, as the accumulated evaporation
 443 increased, the $\Delta\delta^2H_R$ also increased, with the correlation coefficient generally
 444 increasing with longer rainless intervals. Notably, the influence of greater evaporation
 445 on the $\Delta\delta^2H_R$ was particularly pronounced at the 30-day interval, exhibiting a high
 446 correlation coefficient of 0.35 and a p value less than 0.001, while these intervals
 447 occurred exclusively in 2013 and 2022, which were characterized as very dry years
 448 with high evaporation and multiple 30-day intervals devoid of precipitation (Fig. 2
 449 and S3).



450
 451 Figure 7. Relationship between the changes in river water δ^2H ($\Delta\delta^2H_R$) and the
 452 corresponding accumulated evaporation (E) at 5- (a), 10- (b), 15- (c), 20- (d), 25- (e),
 453 and 30- (f) rainless time intervals.

454 The decrease in runoff discharge or water level in the basin can be attributed to

455 evaporation within the basin, as evaporation increases the outflow component in the
456 river water balance, leading to a reduction in the amount of water flowing out of the
457 basin. Additionally, as runoff discharge can increase due to precipitation input, we
458 examined the relationship between the $\Delta\delta^2\text{H}_\text{R}$ and the corresponding changes in the
459 runoff (ΔR) at different intervals (5-, 10-, 15-, 20-, 25-, and 30-day) without
460 precipitation input (Fig. 8). The results indicated a negative correlation between the
461 $\Delta\delta^2\text{H}_\text{R}$ and the corresponding ΔR at the 10-, 15-, 20-, and 25-day intervals,
462 demonstrating relatively high correlation coefficients around -0.4 and p values less
463 than 0.001 . Considering the higher correlation coefficients observed between the
464 $\Delta\delta^2\text{H}_\text{R}$ and the corresponding ΔR (Fig. 8) compared to those between the $\Delta\delta^2\text{H}_\text{R}$ and
465 the corresponding accumulated evaporation (Fig. 7), it can be inferred that the ΔR
466 serves as a suitable proxy to represent the effects of evaporation on river water
467 isotopes. However, the correlation between the $\Delta\delta^2\text{H}_\text{R}$ and the corresponding ΔR was
468 relatively weak at the 5-day intervals, with correlation coefficients of -0.11 (Fig. 8a),
469 thus could be attributed to the short time interval and the limited impact of
470 accumulated evaporation.



471

472 Figure 8. Relationship between the changes in river water $\delta^2\text{H}$ ($\Delta\delta^2\text{H}_R$) and runoff

473 depth (ΔR) at 5- (a), 10- (b), 15- (c), 20- (d), 25- (e), and 30- (f) rainless time

474 intervals.

475 **4.4 Influences of extreme drought and precipitation events on the**

476 **river water isotopes**

477 Analysis of the annual accumulated evaporation, average air temperature,

478 accumulated precipitation, and average runoff discharge in the major flood period and

479 summer drought period reveals that 2013 and 2022 experienced severe summer

480 drought conditions (Fig. S3). These periods were characterized by exceptionally high

481 temperatures and evaporation and low precipitation levels compared to the 13-year

482 observations, particularly in 2022. The summer drought period of 2022 recorded only

483 16.3 mm of precipitation, the lowest among the 13-year observations and significantly

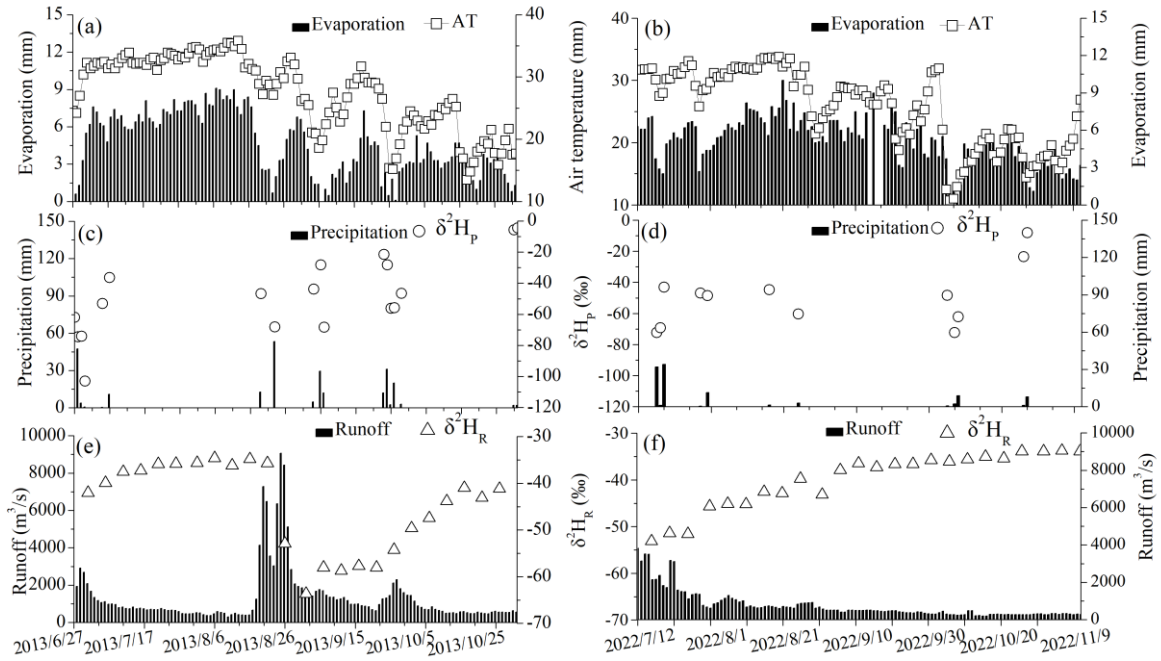
484 lower than the highest precipitation recorded in the summer drought period of 2010

485 (i.e. 300.5 mm). Accumulated evaporation and average air temperature in the summer

486 drought period of 2022 reached 385.1 mm and 28.8 °C, second only to the 393.7 mm

487 and 29.8 °C recorded in the summer drought period of 2013 (Fig. 3). Furthermore, the
488 extreme drought events in 2013 and 2022 have been extensively reported, indicating
489 widespread meteorological, hydrological, and soil droughts that pose a significant
490 threat to water resources for domestic, agricultural, ecological, and human needs (Ma
491 et al., 2022; Bonaldo et al., 2023). Therefore, this section primarily focuses on these
492 two extreme drought processes in 2013 and 2022.

493 As depicted in Fig. 9, the period from late June to mid-August 2013 witnessed
494 rare precipitation, high evaporation rates, and elevated air temperatures. Consequently,
495 the runoff discharge gradually decreased from 2699 m³/s on June 30 to 415 m³/s on
496 August 16. Simultaneously, the $\delta^2\text{H}_\text{R}$ progressively increased from -42.0% to -34.8%
497 (Fig. 9e). Similarly, from mid-July to early November 2022, only 72.6 mm of
498 precipitation was recorded, resulting in a gradual decline in runoff discharge until
499 early September. In this process, the $\delta^2\text{H}_\text{R}$ increased from -53.1% on July 16 to
500 -37.9% on September 6 (Fig. 9f). Subsequently, the Xiangjiang River maintained low
501 runoff discharge and raised $\delta^2\text{H}_\text{R}$ levels until the end of December, and the $\delta^2\text{H}_\text{R}$
502 increased by up to 20.2‰ from -53.1% on July 16 to -32.9‰ on November 26, 2022
503 (Fig. 9f). These findings align with the results obtained in the previous section,
504 indicating that decreases in runoff discharge and higher evaporation rates in long
505 rainless days contribute to the gradual enrichment of river water isotopes. However, it
506 is noteworthy that the $\delta^2\text{H}_\text{R}$ range (-63.7‰ to -21.7‰) mentioned earlier includes the
507 most positive $\delta^2\text{H}_\text{R}$ values influenced by the extreme drought events in 2013 and 2022
508 (Fig. 2d), while the most isotope-enriched river water occurred on May 21, 2014 (Fig.
509 2d) and most isotope-enriched precipitation occurred in the spring flood period (Fig.
510 3b), this indicates that the input of relatively enriched spring precipitation isotopes
511 plays a crucial role in controlling the isotopic enrichment of river water.



512

513

Figure 9. Temporal variations of evaporation and air temperature (a, b), daily

514

precipitation amount and precipitation δ^2H (δ^2H_p) (c, d), and runoff discharge and

515

river water δ^2H (δ^2H_R) (e, f) in the extreme drought processes in 2013 (left panel) and

516

2017 (right panel).

517

By examining the 13-year observations and ranking the 5-day accumulated

518

precipitation, we found that the maximum accumulated precipitation, totaling 301.6

519

mm, occurred from June 27 to July 1, 2017 (Fig. 2). Notably, on June 30 and July 1,

520

2017, daily precipitation reached 146.4 mm and 130.3 mm, respectively. Additionally,

521

between June 21 and June 26, 2017, the precipitation amount reached 185.5 mm.

522

Another significant precipitation event took place in June 2011, when the total

523

precipitation for the month reached 340.3 mm, with a single-day rainfall of 110.4 mm

524

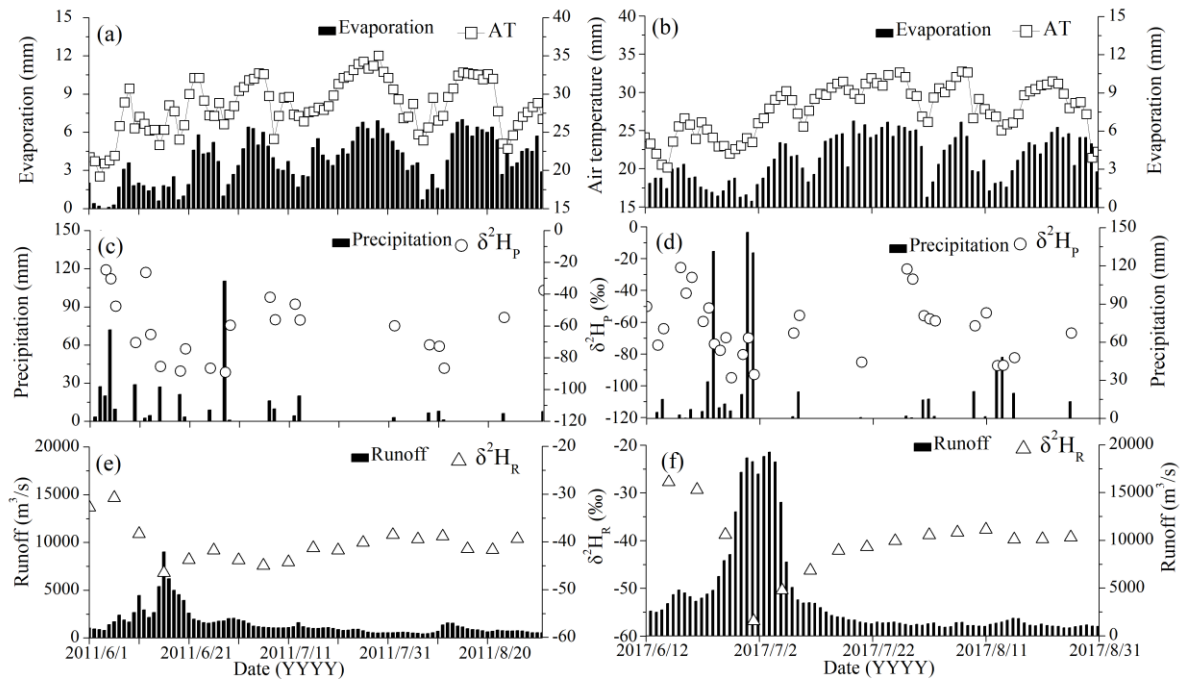
on June 28. To analyze the impact of extreme precipitation on river water isotopes in

525

the major flood period, the temperature, evaporation, precipitation, runoff discharge,

526

δ^2H_p , and δ^2H_R in these two extreme precipitation processes are presented in Fig. 10.



527

528 Figure 10. Temporal variations of the evaporation and air temperature (a, b),
 529 precipitation amount and precipitation $\delta^2\text{H}$ (c, d), and runoff discharge and river water
 530 $\delta^2\text{H}$ (e, f) in the extreme precipitation processes and the following summer drought
 531 period in 2011 (left panel) and 2017 (right panel).

532 In the heavy precipitation period from June 5 to June 16, 2011, the runoff
 533 discharge increased from 1410 m^3/s to 9010 m^3/s , while the $\delta^2\text{H}_R$ decreased from
 534 -30.8‰ to -46.5‰ (Fig. 10e). Similarly, from June 21 to July 1, 2017, the runoff
 535 discharge and river water isotopes exhibited significant fluctuations and depletion
 536 under the influence of precipitation input (Fig. 10f). For instance, the runoff discharge
 537 increased from 3961 m^3/s to 18237 m^3/s , while the $\delta^2\text{H}_R$ decreased from -29.3‰ to
 538 -56.8‰ , which represents the third lowest $\delta^2\text{H}_R$ value among the 13-year
 539 observations. In both extreme precipitation processes, the precipitation isotopes were
 540 relatively depleted (Fig. 10c and 10d). Specifically, the volume-weighted $\delta^2\text{H}_P$ was
 541 -50.9‰ from June 5 to June 16, 2011, and the value was -76.7‰ from June 21 to
 542 July 1, 2017. This indicates that the input of extreme precipitation leads to rapid
 543 decreases in $\delta^2\text{H}_R$. For instance, in the extreme precipitation process of June 2011, the

544 $\delta^2\text{H}_R$ was reduced by -15.7‰ under a precipitation input of 144.7 mm from June 5 to
545 June 16, while the $\delta^2\text{H}_R$ decreased by -27.5‰ with a precipitation input of 487.1 mm
546 in the extreme precipitation process from June 21 to July 1, 2017. Subsequently, in the
547 summer drought periods of 2011 and 2017, the river water isotope gradually enriched
548 to approximately -38‰ (Fig. 10e and 10f).

549 River water isotopes serve as a valuable record not only for detecting the isotopic
550 depletion signal of extreme precipitation input in the major flood period (Fig. 10) but
551 also for capturing the influence of moderate precipitation in the summer drought
552 period. In the latter case, the river water isotopes gradually become enriched with the
553 decrease of the runoff discharge in prolonged periods of drought. When the basin is
554 relatively dry—that is, the reserves of soil water, groundwater, and river water are
555 limited, the river water may be influenced by a medium precipitation amount,
556 resulting in a highly depleted river water isotope signal observed in this extended river
557 water sample series. For instance, following a precipitation input of 53.5 mm with a
558 $\delta^2\text{H}_P$ of -68.1‰ on August 23, 2013 (Fig. 9c), the river water isotopes exhibited a
559 significant depletion (Fig. 9e). Notably, the $\delta^2\text{H}_R$ rapidly declined from -35.7‰ on
560 August 21 to -63.7‰ on September 1, representing the most negative $\delta^2\text{H}_R$ value
561 observed over the 13-year observations. This $\delta^2\text{H}_R$ signal differs significantly from
562 rapid decreases in $\delta^2\text{H}_R$ caused by extreme precipitation input in the river water (Fig.
563 10), highlighting the importance of careful consideration when reconstructing
564 precipitation based on isotopic signals derived from river water.

565 **5. Discussion**

566 **5.1 Factors that influence the seasonality in river water isotopes**

567 By examining the relationship between the $\Delta\delta^2\text{H}_R$ and the corresponding
568 accumulated evaporation, it becomes evident that a stronger correlation between the

569 two variables emerges at time intervals exceeding 10 days (Fig. 6). This suggests that
570 the influence of evaporation on river water isotopes manifests over relatively long
571 time intervals, spanning from tens of days to even several months, particularly in long
572 dry periods without precipitation input (Fig. 9). The influences of evaporation on river
573 water isotopes occurs gradually, making it challenging to capture using short-term
574 analyses. Conversely, as indicated by Xiao et al. (2022a; 2023), the relatively weak
575 influence of evaporation on river water isotopes observed at short intervals (Fig. 6 and
576 7) can be attributed to the significant influx of precipitation input (i.e. new water)
577 rapidly flowing into the river network, which experiences limited evaporation effects
578 in the relatively short residence time. Furthermore, the variation in runoff discharge
579 exhibits a notable relationship with the $\Delta\delta^2H_R$ (Fig. 8), however, it is important to note
580 that the decline in runoff discharge may not be solely due to evaporation but could
581 also be influenced by water transport from the Xiangjiang River to the Dongting Lake
582 due to rapid downstream drainage (Zhan et al., 2015), this introduces uncertainties in
583 the analysis based on the changes of runoff discharge and river water isotopes
584 between different time intervals.

585 The independent variable including volume-weighted precipitation isotopes
586 (δ^2H_P), accumulated precipitation (P), accumulated evaporation (E), changes in runoff
587 depth (ΔR), average air temperature (T_{ave}), maximum air temperature (T_{max}), and
588 minimum air temperature (T_{ave}) were used to build the prediction model of the
589 dependent variable (i.e., the river water isotopes). According to the correlations
590 between the river water isotopes and the hydrometeorological factors (Fig. 4-8), the
591 changes in the δ^2H_R ($\Delta\delta^2H_R$) and a 15-day time interval were used as the dependent
592 variable and the time step of all the variables in the MLRs, respectively. As indicated
593 by the regression equations in different runoff periods (Eq. 2-5), the river water

594 isotopes showed strong seasonality and were controlled by different factors. For
 595 instance, in the major flood period and summer drought period, the $\delta^2\text{H}_\text{R}$ usually
 596 reflected heavy precipitation inputs with depleted isotopes, as supported by the
 597 negative correlation between the $\Delta\delta^2\text{H}_\text{R}$ and ΔR or accumulated precipitation (Eq. 2
 598 and 3), indicating the “amount effect” by the precipitation input. The “amount effect”
 599 of water stable isotopes was widely observed around the world, especially in the
 600 regions with flash input of depleted precipitation (e.g., Dansgaard, 1964; Zhou et al.,
 601 2019). Specifically, the precipitation isotopes were relatively depleted in these two
 602 periods (Fig. 3b), while the river water isotopes captured the precipitation input signal
 603 particularly when the accumulated precipitation exceeded the threshold precipitation
 604 amount (Fig. 5). Additionally, the extreme precipitation events mainly occurred in the
 605 major flood period, resulting in relatively isotope-depleted precipitation that was
 606 reflected as negative records in the $\delta^2\text{H}_\text{R}$ (Fig. 2, Fig. 10, Eq. 2).

$$607 \quad \delta^2\text{H}_\text{R} \text{ in MF} = (0.098 \pm 0.012)\delta^2\text{H}_\text{p} + (0.098 \pm 0.022)\text{E} - (0.027 \pm 0.007)\Delta\text{R} \\ - (3.01 \pm 0.861), r = 0.56, p < 0.001, n = 226 \quad (2)$$

$$608 \quad \delta^2\text{H}_\text{R} \text{ in SD} = -(0.064 \pm 0.01)\Delta\text{R} - (0.02 \pm 0.008)\text{P} \\ + (0.497 \pm 0.479), r = 0.51, p < 0.001, n = 161 \quad (3)$$

$$609 \quad \delta^2\text{H}_\text{R} \text{ in RL} = -(0.041 \pm 0.008)\Delta\text{R} + (0.01 \pm 0.004)\delta^2\text{H}_\text{p} \\ + (0.957 \pm 0.152), r = 0.29, p < 0.001, n = 384 \quad (4)$$

$$610 \quad \delta^2\text{H}_\text{R} \text{ in SF} = (0.055 \pm 0.013)\delta^2\text{H}_\text{p} + (0.013 \pm 0.003)\text{P} - (0.092 \pm 0.031)\text{T}_{\text{max}} \\ + (2.773 \pm 0.702), r = 0.43, p < 0.001, n = 155 \quad (5)$$

611 In the rainless period, the $\delta^2\text{H}_\text{R}$ values were more positive compared to the
 612 summer drought period (Fig. 3b), possibly influenced by the input of more enriched
 613 precipitation and evaporation enrichment along with the decreases of ΔR (Eq. 4).
 614 Besides, the $\delta^2\text{H}_\text{R}$ reached the highest positive values in the spring flood period,
 615 influenced by the precipitation input with relatively depleted isotopes (Fig. 2, Fig 3),

616 while “inverse amount effect” and “inverse temperature effect” were found in this
617 period, as indicated by the positive correlation between the $\Delta\delta^2\text{H}_R$ and accumulated
618 precipitation and the negative correlation between the $\Delta\delta^2\text{H}_R$ and air temperature
619 (T_{max}) (Eq. 5), and the reasons can be attributed to the seasonality of precipitation
620 isotopes and air temperature as discussed in section 4.3. Overall, the river water
621 isotopes in the Xiangjiang River basin are controlled by various complex factors in
622 different runoff periods, while such findings in the controlling factors that influence
623 river water isotopes may be beneficial in paleoclimate reconstruction and
624 establishment of isotope hydrologic models.

625 **5.2 Environmental significance implied by the seasonality of river** 626 **water isotopes**

627 The Xiangjiang River, serving as a significant inflow water source, exerts an
628 influence on the hydrologic and isotope mass balance of Dongting Lake, the
629 second-largest freshwater lake in China (Zhan et al., 2015; Zhou et al., 2019). The
630 isotopic composition of lake water primarily reflects the input waters, including lake
631 surface precipitation and inflowing river water (Steinman and Abbott, 2013; Gibson et
632 al., 2016; Xiao et al., 2022b), while the isotopic information in lake water can also
633 influence the stable isotopic signatures preserved in lake sediment. Consequently,
634 proxy indicators recorded in lake sediments can be utilized for paleoclimate
635 reconstruction, benefiting from the relationships between the input water isotopes and
636 the local environments.

637 Through the analysis of river water isotopes and various hydrometeorological
638 factors on a seasonal scale, it becomes evident that the $\Delta\delta^2\text{H}_R$ can reflect the
639 corresponding accumulated evaporation and precipitation input (Fig. 5, 6, and 7) and

640 the decline in runoff discharge (Fig. 8) at the observed time intervals. Moreover, river
641 water isotopes entering the lakes can record signals of extreme precipitation (Fig. 10)
642 or exhibit gradual isotopic enrichment under the influence of evaporation in relatively
643 dry periods spanning tens of days or even several months without precipitation (Fig.
644 9). Besides, the isotopic characteristics of precipitation are governed by large-scale
645 factors such as moisture sources, upstream effects, and circulation patterns, and are
646 less influenced by local meteorological factors (Aggarwal et al., 2016; Zhou et al.,
647 2019), thus the river water isotopes are better suited to reflect local environments.
648 Consequently, in comparison to the isotopic characteristics of precipitation, the river
649 water isotopes may provide valuable insights into the relationship between the proxy
650 indicators and the local environments.

651 In previous studies, due to limited data availability, the inflow water isotopes of
652 the lake were often represented by the volume-weighted precipitation isotopes in
653 hydrologic and isotope mass-balance models (e.g., Steinman and Abbott, 2013;
654 Skrzypek et al., 2015; Jones et al., 2016). However, based on the 13-year observations
655 conducted in this study, the annual volume-weighted $\delta^2\text{H}_R$ and $\delta^2\text{H}_P$ were found to
656 closely match only in the period of 2012-2015, with differences within 2‰ (Table 2).
657 In other years, the annual volume-weighted $\delta^2\text{H}_P$ was either more negative or more
658 positive compared to the annual volume-weighted $\delta^2\text{H}_R$. These differences in the
659 annual $\delta^2\text{H}_R$ and $\delta^2\text{H}_P$ were mainly influenced by the seasonality of $\delta^2\text{H}_P$ and
660 precipitation amount. For instance, significant variations were observed between the
661 volume-weighted $\delta^2\text{H}_P$ and $\delta^2\text{H}_R$ in the different runoff periods (Table 2). Therefore,
662 representing the inflow water of the lake solely by the annual volume-weighted
663 precipitation isotopes can only serve as a rough estimation. To accurately depict the
664 detailed variations in the lake hydrologic and isotope mass balance, more

665 comprehensive observations of the inflowing river water are required.

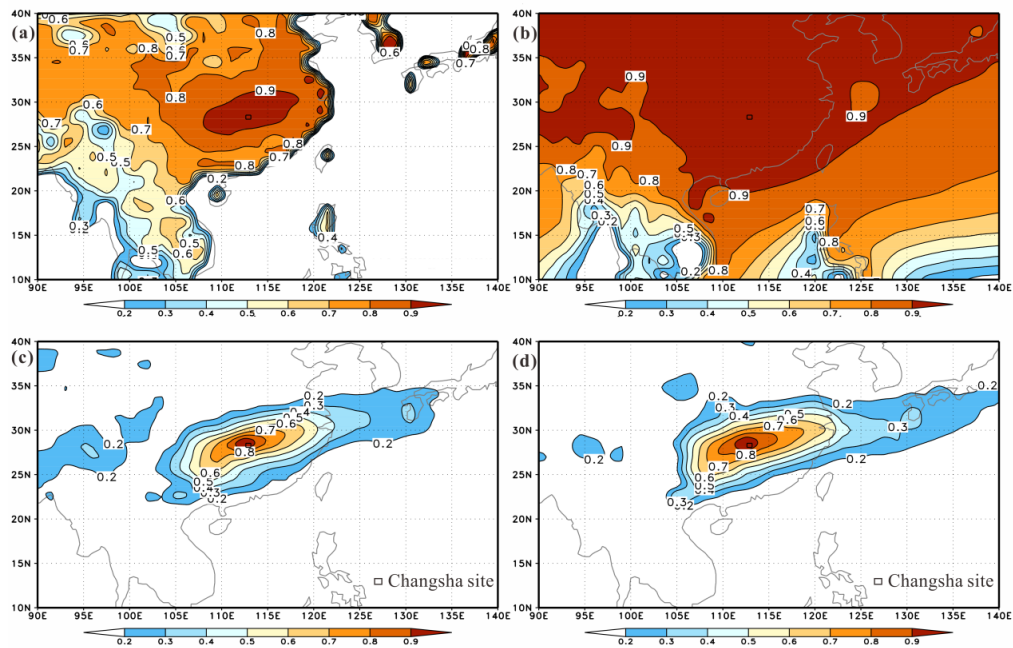
666 Table 2. Annual volume-weighted precipitation $\delta^2\text{H}$ and river water $\delta^2\text{H}$ ($\delta^2\text{H}_\text{R}$
667 and $\delta^2\text{H}_\text{P}$) and volume-weighted average values in different runoff periods. The letters
668 (RL, SF, MF, and SD) represent the rainless period, spring flood period, major flood
669 period, and summer drought period, respectively.

Year	Annual $\delta^2\text{H}_\text{R}$	Annual $\delta^2\text{H}_\text{P}$	$\delta^2\text{H}_\text{R}$ in RL	$\delta^2\text{H}_\text{P}$ in RL	$\delta^2\text{H}_\text{R}$ in SF	$\delta^2\text{H}_\text{P}$ in SF	$\delta^2\text{H}_\text{R}$ in MF	$\delta^2\text{H}_\text{P}$ in MF	$\delta^2\text{H}_\text{R}$ in SD	$\delta^2\text{H}_\text{P}$ in SD
2010	-34.6	-48.0	-38.1	-54.6	-26.7	-16.8	-36.0	-47.8	-40.1	-73.6
2011	-36.9	-45.3	-37.4	-52.0	-30.3	-11.4	-39.0	-54.3	-38.9	-49.3
2012	-36.3	-38.2	-36.9	-29.8	-31.1	-15.4	-37.9	-50.9	-45.9	-47.0
2013	-33.9	-33.3	-35.6	-72.1	-27.1	-3.7	-30.2	-28.3	-48.0	-47.7
2014	-29.0	-27.7	-33.2	-27.3	-26.3	-10.8	-27.8	-34.5	-36.0	-57.1
2015	-34.4	-36.1	-38.4	-43.9	-27.3	-10.6	-30.1	-34.4	-40.6	-64.0
2016	-31.4	-40.0	-35.5	-31.6	-27.8	-16.2	-30.2	-50.3	-36.2	-67.7
2017	-36.4	-48.2	-35.0	-26.6	-27.4	-14.5	-41.2	-59.3	-39.4	-75.4
2018	-34.7	-39.1	-35.8	-30.0	-30.6	-8.1	-33.2	-49.5	-39.5	-67.6
2019	-31.8	-24.0	-30.8	-25.3	-26.4	-2.5	-34.2	-31.2	-36.4	-28.7
2020	-28.5	-36.9	-32.2	-31.3	-24.2	-9.2	-28.4	-43.2	-28.0	-54.6
2021	-30.1	-32.4	-36.3	-31.1	-28.3	-12.1	-28.2	-32.4	-32.6	-66.5
2022	-36.1	-39.2	-34.2	-47.8	-32.1	-18.1	-37.5	-46.6	-42.8	-50.2

670 Nevertheless, according to the analysis on an annual scale based on the 13-year
671 observations, the volume-weighted $\delta^2\text{H}_\text{R}$ values in the different runoff periods
672 exhibited non-significant correlations ($0.1 > p > 0.05$ or $p > 0.1$) with the
673 corresponding total precipitation, average runoff discharge, average air temperature,
674 and total evaporation (Fig. S4). Although this study encompasses 13-year
675 observations with a sampling interval of five days, there is a need for longer and
676 systematic observations of various water types and hydrometeorological factors,
677 spanning decadal or longer time scales, to better elucidate the relationships between
678 river water isotopes and local environments on the annual scale.

679 **5.3 The representation of the Observation at the Changsha site in the**
680 **Xiangjiang River basin**

681 The increases in runoff discharge and water level in the Changsha section of the
682 Xiangjiang River are primarily attributed to the precipitation recharge in the middle
683 and upper reaches, while the influences of evaporation on river water isotopes mainly
684 occur within the basin. It should be noted that the sampling and observation sites for
685 precipitation, air temperature, and evaporation in this study, located at Hunan Normal
686 University and the National Meteorological Reference Station in Changsha,
687 respectively, only represent the local conditions in Changsha. Therefore, the extent of
688 their influence on the runoff discharge and water stable isotopes of the entire
689 Xiangjiang River may be limited. To assess whether the sampling and observations in
690 Changsha can adequately represent the Xiangjiang River basin, the spatial correlation
691 analysis based on the iAWBM was conducted and the results of air temperature (Fig.
692 11a), evaporation (Fig. 11b), precipitation amount (Fig. 11c), and precipitation
693 isotopes (Fig. 11d) were shown respectively.



694
695 Figure 11. Spatial correlation analysis of the air temperature (a), evaporation (b),
696 precipitation amount (c), and precipitation isotope (d) between the Changsha (CS) site
697 and the surrounding regions at 5-day interval, this analysis employed the simulated

698 precipitation isotope data generated by the isotopic Atmospheric Water Balance
699 Model (iAWBM) (Zhang et al., 2015) and the air temperature, evaporation, and
700 precipitation amount data from the ERA5 reanalysis dataset.

701 The results of spatial correlation analysis revealed a high correlation between the
702 reanalysis data of air temperature and evaporation at the Changsha site and those in
703 the surrounding regions, with correlation coefficients above 0.8 and $p < 0.001$ for the
704 grid points in the Xiangjiang River basin (Fig. 11a and 11b). Furthermore, while the
705 relationship between the reanalysis data of precipitation amount and simulated
706 precipitation isotopes at the Changsha site and in the surrounding regions is not as
707 strong as that for air temperature and evaporation, the correlation is still high (Fig. 11c
708 and 11d). For instance, the correlation coefficients between the Changsha site and the
709 grid points in the Xiangjiang River basin exceed 0.7 with $p < 0.001$ for both the
710 reanalysis data of precipitation amount and simulated precipitation isotopes (Fig. 11c
711 and 11d).

712 Overall, the high correlation coefficients for these factors support the time
713 consistency between the Changsha site and the surrounding regions, while the high
714 spatial consistency is characterized by the large area of the high correlation
715 coefficients, which covers the whole Xiangjiang River basin. These may be related to
716 the fact that the Xiangjiang River Basin as a whole is located in the subtropical zone
717 of southern China, which makes the meteorological elements (precipitation,
718 evaporation, temperature) of the basin have a certain consistency. Moreover, the
719 precipitation isotope of the basin also has a high correlation, which can be attributed
720 to the uniform water vapor source, precipitation form, and atmospheric circulation
721 within the Xiangjiang River basin (Zhou et al., 2019; Liu et al., 2023). These spatial
722 correlation analyses provide support for the study basis of using the observations at

723 the Changsha site as representative of the Xiangjiang River basin.

724 **6. Conclusions**

725 The main findings of this study are as follows: (1) Both the $\delta^2\text{H}_\text{P}$ and $\delta^2\text{H}_\text{R}$
726 displayed significant seasonal variation throughout the year. The temporal pattern of
727 the $\delta^2\text{H}_\text{R}$ was similar but attenuated compared to the $\delta^2\text{H}_\text{P}$, indicating the influences of
728 direct precipitation input, evaporation, and mixing with older waters. (2) The $\delta^2\text{H}_\text{R}$
729 showed weak correlations with the corresponding hydrometeorological factors, which
730 can be attributed to the mixing between the new input precipitation and the old waters
731 within the basin and the seasonality of the precipitation isotopes and air temperature.
732 (3) The ΔR and $\Delta\delta^2\text{H}_\text{R}$ exhibited significant responses to the corresponding
733 accumulated precipitation, with heavier precipitation events more likely to alter runoff
734 discharge and river water isotopes. However, the input of moderate precipitation leads
735 to the most negative $\delta^2\text{H}_\text{R}$ in the summer drought period, when wetness conditions are
736 limited. (4) The $\Delta\delta^2\text{H}_\text{R}$ showed a notably positive correlation with the corresponding
737 accumulated evaporation and average ΔR , particularly at longer time intervals without
738 precipitation input, but the spring flood period shows the most positive $\delta^2\text{H}_\text{R}$ due to
739 the input of enriched precipitation isotopes. (5) In the major flood period, the $\delta^2\text{H}_\text{R}$
740 may rapidly decrease with a maximum range of -27.5‰ due to the input of extreme
741 precipitation with relatively depleted isotopes, while the river water isotopes gradually
742 enriched in the subsequent summer drought period. In the summer drought periods of
743 2013 and 2022, the runoff discharge and $\delta^2\text{H}_\text{R}$ showed gradual decrease and increase,
744 respectively, with the $\delta^2\text{H}_\text{R}$ potentially increasing by up to 20.2‰ influenced by the
745 extreme drought.

746 The main contributions and scientific values of these findings can be concluded
747 as follows: (1) Better than $\delta^2\text{H}_\text{R}$, the $\Delta\delta^2\text{H}_\text{R}$ can be served as a proxy that was

748 influenced by the local environment; (2) Caution is advised when interpreting extreme
749 isotopic signals in river water due to complex influences of hydrometeorological
750 factors; (3) River water isotopes were controlled by various complex factors, which
751 may show “amount effect” and “inverse amount effect” in different runoff periods; (4)
752 The spatial correlation analysis based on the iAWBM confirms the representation of
753 site observations in representative for the Xiangjiang River basin. These implications
754 may be valuable for water stable isotopes applied in the future paleoclimate
755 reconstruction and establishment of the isotope hydrologic models. To enhance the
756 reliability of the observations and ensure their representativeness for the entire
757 Xiangjiang River basin, further spatial measurements of hydrometeorological factors
758 and sampling of precipitation samples are needed within the basin itself. Furthermore,
759 the more extensive sampling of river water (e.g., daily sampling) should be conducted
760 in future fieldwork, for the aim of a more detailed depiction and interpretation of the
761 seasonal variation and influence factors of river water isotopes.

762 **Code/Data availability**

763 The data and code that support the findings of this study are available from the
764 corresponding author upon reasonable request

765 **Author contribution**

766 Xiong Xiao: Data curation, Methodology, Software, Writing – original draft, &
767 editing. Xiping Zhang: Methodology, Writing – original draft, & editing. Zhuoyong
768 Xiao: Data curation. Zhiguo Rao, Xinguang He, and Cicheng Zhang: Methodology.

769 **Competing interests**

770 The authors declare that they have no known competing financial interests or personal
771 relationships that could have appeared to influence the work reported in this paper.

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