Background:
Over the past three decades, stable hydrogen (H) and oxygen (O) isotopic compositions in river water have provided deep insights into various hydrological processes and river water cycling at different spatial and temporal scales [1–5]. In general, these studies were mostly conducted in small and well-instrumented catchments with drainage areas ranged from 0.01 to 100 km² and located typically in headwater regions, yet little attention is paid to the larger (100 to > 1000 km² in catchment area), and the poorer instrumented basins [2, 6]. Isotopic responses are often intricate in large river systems, which often reflect an integrated influence of hydrological processes from meteoric precipitation to various discharges, including those from the groundwater, melting glaciers,
dams, lakes, karst terrain, evaporation, snowmelt events, and tributary mixing [7, 8]. The use of isotopic tracer has been greatly limited in the river due to the lack of long-term isotopic data [9]. For instance, though a conceptual framework has been established in estimating global isotope balance, the isotope mass balance on modern continents has remained poorly understood, primarily due to the lack of long-term systematic observations on riverine fluxes to the oceans [4]. Moreover, the reconstructions of continental palaeoclim ate and palaeohydrology based on stable isotopic signals preserved in various archives may be hampered by poor recognition of the modern isotopic patterns and the hydrologic cycle. Therefore, it is crucial to commence with a long-term stable isotope monitoring for the collection of baseline isotopic data. Moreover, the long-term stable isotopic observations in the extensive river system can improve our understanding on the sustainable management of water supply, flood–drought cycles, ecosystem, and human health in the catchments [2].

In the year 2002, the International Atomic Energy Agency (IAEA) launched a coordinated research project entitled “Isotope tracing of hydrological processes in large river basins”, aimed to develop and examine quantitative isotopic analysis methods for water balance and related hydrological processes [10]. In 2007, another research program, “Global Network of Isotopes in Rivers (GNIR)”, also led by IAEA, compiled isotopes data from global rivers to complement with the IAEA/World Meteorological Organization (WMO)’s database of the “global network of isotopes in precipitation” (GNIP). The GNIR encourages systematic collections of global river water isotopic data to provide a better understanding of the resilience of major global river systems to environmental and human perturbations (http://www-naweb.iaea.org/napc/ilh/ihs_resources_gnir.html).

The Changjiang River originates from the Tibetan Plateau and enters the East China Sea near the city of Shanghai, with a watershed of about $1.8 \times 10^6 \text{ km}^2$ (Fig. 1). Changjiang tributary is extensively developed in its large drainage basin, which fosters 49 tributaries with each catchment area covers over 10,000 km$^2$. Traditionally, the upper reaches of the Changjiang River refers to the section from Yibin to Yichang; the middle refers to the section from Yichang to Hukou, where Poyang Lake meets the river; whereas the lower reaches extended from Hukou to the river mouth. Many of the large tributaries of the Changjiang River are located in the upstream of the Three Gorges.

The Changjiang (Yangtze) River is the longest (about 6397 km) river in Asia and the third-longest in the world, and it plays a vital role in the socio-economic development of China. Over the past five decades, water consumption has increased dramatically due to the domestic, industrial, and agricultural developments in the Changjiang catchment. Anthropogenic perturbation mainly constituted of deforestation, dam/reservoirs construction, and sand/stone excavation. Today, the Changjiang River is subjected to increasing environmental problems such as floods and droughts, e.g., 1320 people died in the disastrous floods in 1998 with a direct economic loss exceeding 166 billion CNY [11]. Furthermore, water quality and its ecosystem [12, 13], water and soil loss [14], erosion of river channel, and delta [15–17] within the
Changjiang catchment are all of prodigious concerns to the government, public, as well as the scientists. A systematic investigation of H and O isotopes in the Changjiang river water was initiated in 2002 by a program namely “The isotopic tracing of hydrology processes in the Yangtze River basin”, which was a joint-research with “Designing criteria for a network to monitor isotope composition of runoff in large rivers” by IAEA [10]. This investigation provides the first systematic analysis of stable H and O isotopes in the Changjiang River, which then inspired a series of investigations focused on spatial and temporal variations of stable isotopes [18–23]. These studies suggest that the δD and δ18O of the Changjiang river water increase gradually from the upstream to estuary due to reducing runoff influences from the alpine catchments [19], “continental effect” [24] of the local precipitation [10], and increasing water contributions from tributary rivers and lakes in the middle and lower reaches [19, 25, 26]. Notwithstanding, these studies mainly focus on the spatial distribution of H and O isotopes along the Changjiang River, while few explicit analyses concerning the seasonal isotopic variations were conducted [27].

In this study, we present a 2-year H and O isotopes time series in the lower Changjiang mainstream to develop an application of isotopic tracers for surface water cycle in a large river basin subject to the sophisticated natural setting facing increasing human activities. The primary purpose of this study is to: (1) identify the seasonal variations of H and O isotopes in the Changjiang river water and its associated controlling mechanisms; (2) to elucidate how natural climate change and human activities (dam construction and artificial regulations) affect the water cycle in the Changjiang River.

**Methods**

A total of 75 river water samples were collected from the lower Changjiang mainstream close to Nantong (31.96° N, 120.83° E; Fig. 1) from November 12, 2012, to December 13, 2014, with the sampling interval ranged from 1 to 2 weeks. 6 other supplementary water samples were taken from Dongting Lake (4 samples) and Poyang Lake (2 samples) between 2012 and 2013 (Additional file 1: Table S1). The lake water was collected close to the confluence where lake water first joins the Changjiang mainstream. All of the water samples were collected at the depth of about 50 cm below the water surface and sealed in the plastic bottles immediately after collection. The samples were analyzed for stable hydrogen and oxygen isotopes using the Isotopic Water Analyzer (IWA-45EP, Los Gatos Research, USA) in the State Key Laboratory of Marine Geology at Tongji University, Shanghai. The results are presented in relative abundance (δD and δ18O, respectively) of D and 18O isotopes, given in per mil (‰) with reference to the international standard VSMOW (Vienna Standard Mean Ocean Water). The precisions of δD and δ18O measurements are higher than ±0.5‰ and ±0.1‰, respectively.

Existing δD and δ18O data available in the river water from Chongqing, Datong, and in the lake water from Dongting and Poyang are used as references in the study. This study referred to the δ18O values of the monthly precipitation in the selective sites over the Changjiang catchment (Fig. 2), and the precipitation data derived mainly from the GNIP (IAEA) isotopic database. Detailed information on the samples and reference data can be found in Table 1 and Additional file 1: Table S1.

**Results**

**Seasonal variations of river water δD and δ18O in the Changjiang mainstream**

The δD and δ18O in the Changjiang river water in Nan- tong are given in Additional file 1: Table S1. The δD ranges from −73.3‰ to −38.3‰, with a mean value of −56.4‰, while δ18O varies from −106‰ to −6.4‰ with an average of −8.5‰. A plot of δD versus δ18O (Fig. 3) reveals that the Changjiang River samples (excluding the lake samples) show a strong positive linear relationship: δD = 8.5 × δ18O + 15.5 (R² = 0.98). Both δD and δ18O in the lower Changjiang mainstream in Nantong and Datong are higher than those in the upper mainstream in Chongqing. As δD is highly correlated with δ18O in the Changjiang river water, only δ18O will be discussed in the following discussion.

The δ18O time-series data in the Changjiang river water are presented in Fig. 4a, showing an evident seasonal variation between dry and flood seasons. During our sampling period, the δ18O is in overall enriched in the dry season (November to April), but depleted during the flood season (May to October). The seasonal δ18O variability in Nantong is very similar to that of Datong (Fig. 4a), which is as well located in the lower Changjiang reaches but upstream of Nantong. The seasonal variation of δ18O in Poyang Lake is always higher, but relatively stable than that of Nantong within the year, while the seasonal δ18O variability in Chongqing, which is located in the upper Changjiang reaches, is much variable and in overall lower except in May and June. The δ18O in Nantong and Datong fell within the ranges between Chongqing and the Poyang Lake. Note that some discrete data (scattered points in Fig. 4a) from the Dongting Lake, Poyang Lake, and Chongqing station (this study and reference data) are also compared to assess for the representative time-series samples.
The topography in the Changjiang River catchment is sewn by three China continent terraces, spanning from the western highlands to the eastern low-relief delta plain. The river basin subjects to two different monsoon climate regimes, the East Asian Monsoon system in the middle/lower valleys and the Indian Monsoon zone in the uppermost basin and source area [28]. As a result, the precipitation amount and its $\delta^{18}O$ value vary in space and times within the Changjiang catchment.

In this regard, a basin-scale seasonal variation in precipitation $\delta^{18}O$ is a prerequisite for a comprehensive $\delta^{18}O$ comparison between the precipitation and river water. To evaluate for the total precipitation in Changjiang catchment, the catchment is divided into 12 sub-basins based on unique characteristics possessed by its tributaries, alphabetically named from Zone A1 to Zone K from the upper river basin to the river mouth (Fig. 5). A total of 12 GNIP stations with multi-year records of precipitation $\delta^{18}O$ were selected to quantify the precipitation of each sub-basin. Meanwhile, long-term precipitation data and sub-basin coverage areas are used to calculate the precipitation amount for each sub-basin. On this basis, the sub-basin weighted $\delta^{18}O$ in precipitation covering the Changjiang river basin in each month can be estimated by Eq. (1):

\[
\delta^{18}O = \frac{\sum (\delta^{18}O_i \times P_i \times A_i)}{\sum (P_i \times A_i)}.
\]
Table 1 Average δ¹⁸O (standard deviations in brackets) in precipitation for each Changjiang sub-basin

| Month | LS* (A₁) | KM (A₂) | CD (B) | CQ (C, D) | ZY (E) | CS (H) | WH (G, F) | YT (I) | NJ (J) | CU (K) |
|-------|----------|---------|--------|-----------|--------|--------|-----------|--------|--------|--------|
| Jan   | 10.45    | −3.01 (±1.50) | −c | −3.72 (±2.19) | −5.34 (±2.40) | −5.91 (±1.95) | −4.26 | −7.89 (±0.76) | −5.04 |
| Feb   | −16.83 (±5.25) | −8.17 (±3.18) | −1.34 (±5.01) | −3.25 (±1.22) | −3.33 (±0.36) | −5.19 (±2.41) | −4.00 | −6.75 (±3.12) | −3.01 |
| Mar   | −3.88 (±3.77) | −12.37 (±2.22) | −2.14 (±1.88) | −4.08 (±3.85) | −2.22 (±1.54) | −2.16 (±1.68) | −3.50 | −2.91 (±1.61) | −4.55 |
| Apr   | −6.51 (±7.80) | −13.10 (±2.62) | −2.02 (±1.22) | −4.67 (±2.39) | −3.04 (±2.94) | −3.01 (±1.38) | −4.38 | −4.49 (±1.59) | −5.84 |
| May   | −9.19 (±5.08) | −10.75 (±1.69) | −5.08 (±1.73) | −9.16 | −7.91 (±2.32) | −7.53 (±1.54) | −7.14 (±2.76) | −6.67 | −9.55 (±1.20) | −8.89 |
| Jun   | −13.96 (±4.48) | −10.49 (±2.70) | −7.75 (±1.00) | −11.06 | −10.99 (±2.92) | −9.11 (±1.53) | −9.63 (±0.38) | −10.85 | −9.88 (±1.28) | −8.71 |
| Jul   | −21.55 (±3.22) | −8.58 (±2.74) | −9.46 (±2.05) | −11.93 | −10.20 (±3.02) | −7.67 (±2.97) | −7.35 (±1.30) | −8.70 | −9.13 (±1.21) | −7.51 |
| Aug   | −15.87 (±4.73) | −5.15 (±2.06) | −7.33 (±1.77) | −12.82 | −10.92 (±2.74) | −9.74 (±2.78) | −7.30 (±3.51) | −8.95 | −7.99 (±1.18) | −7.78 |
| Sep   | −22.37 (±4.40) | −4.32 (±3.22) | −9.08 | −11.89 | −8.53 (±3.06) | −6.02 (±2.35) | −6.86 (±2.55) | −6.41 | −6.66 (±1.91) | −5.31 |
| Oct   | −3.15 (±3.02) | −4.52 (±2.28) | −6.97 (±2.48) | −4.68 (±1.99) | −7.24 (±1.32) | −6.92 | −7.18 (±3.17) | −6.25 |
| Nov   | −14.52 | −3.51 (±2.76) | 7.20 | −3.85 (±1.12) | −4.12 (±2.68) | −5.07 (±0.78) | −4.38 | −8.06 (±1.81) | −5.87 |

Data for YT and CU station are referred from Liu et al. [40] while the rest is from GNIP (http://www-naweb.iaea.org/napc/IH/IHS_resour ses_isohis.html)

a Abbreviations for isotopic observation stations in the Changjiang catchment: LS Lhasa, KM Kunming, CD Chengdu, CQ Chongqing, ZY Zunyi, CS Changsha, WH Wuhan, NJ Nanjing, YT Yingtan, CU Changshu

b The 12 sub-basins of the Changjiang catchment are indicated by capital letters from A₁ to K in Fig. 5

c No data available
although with considerable variability.

result of the "catchment effect" [29]. In Fig. 3, the regression line of δD and δ18O for the Changjiang river water is calculated based on the samples obtained from Nantong, Datong, and Chongqing sites.

where δ18Oj stands for monthly δ18O in station i, Pj, and Ai represent the precipitation amount and drainage basin area for the corresponding sub-basin. The details of each station and sub-basin are listed in Tables 1 and 2.

The monthly sub-basin-weighted precipitation δ18O data are displayed in Fig. 4a. The precipitation δ18O in the Changjiang catchment is overall higher (~ −4‰) from January to May, albeit with a decreasing trend, and remains lower from June to October (~ −10‰), finally increases to a high level again in November and December. In other words, the precipitation δ18O is higher in the dry season (winter), but lower in flood season (summer). The precipitation δ18O has a similar overall trend with the river water δ18O in the time-series monitoring, albeit with considerable variability.

Discussion

Distribution of δD and δ18O in the Changjiang river water

The water on the land surface is predominantly replenished by precipitation during the global water cycle. As a result, δD and δ18O in the river water are determined by the isotopic composition of precipitation and thus may serve as a good proxy for precipitation isotopic composition [1]. However, in some cases, the δD and δ18O in river water are different from the local precipitation due to evaporation, transpiration from different altitudes [4]. In particular, for the large rivers, the δD and δ18O of river water may vary significantly from the precipitation as a result of the "catchment effect" [29]. In Fig. 3, the regression line of δD and δ18O for the Changjiang river water is δD = 8.5 × δ18O + 15.5 (R² = 0.98), displays a more pronounced slope and higher intercept than GMWL [30]. However, the correlation of river water δD and δ18O in accordance with local meteoric water line (LMWL) observed in specific cities in the Changjiang catchment, e.g., δD = 7.34 × δ18O + 2.56‰ (R² = 0.98; Kunming site), δD = 8.47 × δ18O + 15.46‰ (R² = 0.99; Changsha site) and δD = 8.43 × δ18O + 17.46‰ (R² = 0.98; Nanjing site), which are calculated based on archived precipitation data retrieved from GNIP [31].

Compared to the riverine samples, the lake samples show the highest δD and δ18O values and significant variations, which suggest that the lake water in the Changjiang catchment suffers from more significant evaporative fractionation than river water. The river water samples from Chongqing in the upstream are more depleted in both δD and δ18O than those from the lakes in the middle reaches and from Nantong and Datong downstream. δ18O depletion in the Changjiang river water with increasing elevation is probably due to the "continent effect/elevation effect", which has been thoroughly investigated by [10, 19].

These substantial differences in isotopic ratios between Changjiang sub-basins are primarily fashioned by different isotopic compositions in the local precipitation, and partly by the combined effects of evaporation, groundwater replenishment, and perhaps snow melting in the mountain area in each specific sub-basin [10, 19, 25].

The seasonal variations of δ18O in Nantong river water from lower Changjiang reaches show a similar time series with other large rivers in the world, e.g., the Amazon [32], Danube [33], Mekong [34]. The seasonal variations of water isotopes for large rivers are believed to be dominated by the water isotopic composition of precipitation [9, 35]. Except the precipitation, snowmelt water can also have significant impact on large river water isotopic composition. For example, runoff with snowmelt water having a low δ18O causes clear seasonality with low δ18O in Lena river water isotope time series, while contribution of summer precipitation to Lena river water is not significant [36]. The overall seasonal variations of water isotopes for large rivers are complex and can be influenced by many factors like precipitation, snowmelt, groundwater and so on.

Seasonal variation of δ18O for the precipitation in a basin-scale

A deep insight into the spatial distribution of precipitation isotopes will improve our understanding of large-scale catchment water cycling dynamics. In the 1980s and 1990s, GNIP has been systematically monitored over the precipitation δD and δ18O in the Changjiang basin.
Fig. 4  a Time series of $\delta^{18}O$ in the Changjiang river water in Nantong and precipitation over the Changjiang catchment. The $2\sigma$ errors for precipitation are calculated with Eq. (1) based on the deviation for monthly precipitation for each sub-basin (see Table 1). See the text for a detailed calculation of precipitation isotopic composition. Time series of $\delta^{18}O$ in Changjiang River in Chongqing and Datong, Dongting Lake and Poyang Lake are likewise compared. The sampling time for each time series is shown in bracket (YY/MM ~ YY/MM). b Daily river discharge data of the Changjiang River at different gauge stations from October 2012 to December 2014. All discharge data refer to http://yu-zhu.vicp.net/. c Correlation between $\delta^{18}O$ time series (17 days shift forward) in the Changjiang river water in Nantong and the defined lake contribution in terms of water discharge ratio. The water level at the Three Gorges Reservoir is retrieved from the Wanxian Station (http://yu-zhu.vicp.net/)
catchment. Among the 37 GNIP stations in China, 8 stations were set up within the Changjiang catchment to collect the primary isotopic data of precipitation across the basin. In most of the mid- and high-latitude land areas, the precipitation δ18O is enriched in summer and depleted in winter because both the δD and δ18O are positively correlated with temperature [37]. However, this seasonal isotopic trend was reversed in the coastal region of East China, e.g., the Changjiang catchment (Fig. 4a), where δD and δ18O values are higher in winter than in the summer [28, 38]. During the past decades, many investigators have attempted to explain the isotopic characteristics of precipitation observed in East China, and most agree that the

Fig. 5 A two-end-member model shows the water mixing in the Changjiang mainstream. Source 1 indicates the contribution from catchment upstream, Yichang and Source 2 indicates the contribution of Dongting and Poyang Lakes in the middle valley. The sub-basins were defined based on different tributary systems and are labeled with a capital letter from A to K. Note that the Jinshajiang sub-basin is further divided into two parts (the region upstream Shigu (A1) and downstream Shigu (A2), due to two distinct topography and climate regimes span across the Jinshajiang catchment. The stations for isotopic sampling and meteorological data are likewise indicated in this figure. Refer to Tables 1 and 2 for details of the abbreviations for each station.

Table 2 Basin area and precipitation amount for each Changjiang sub-basin

|       | Area for each sub-basin (x 10^4 km²) | Precipitation (mm) for selective meteorological stations in each sub-basin |
|-------|-------------------------------------|--------------------------------------------------------------------------|
|       |                                    | Jan  | Feb  | Mar  | Apr  | May  | Jun  | Jul  | Aug  | Sep  | Oct  | Nov  | Dec  |
| YS     | 21.42                              | 4.0  | 4.5  | 8.6  | 14.5 | 54.6 | 99.5 | 102.0| 87.2 | 74.7 | 28.8 | 2.9  | 1.7  |
| A1     | 28.05                              | 13.5 | 12.3 | 16.5 | 22.8 | 89.8 | 175.4| 204.6| 196.0| 117.2| 83.4 | 35.9 | 13.1 |
| CD     | 16.34                              | 9.1  | 8.3  | 25.0 | 35.5 | 104.9| 111.7| 224.6| 170.3| 119.3| 47.0 | 15.3 | 6.2  |
| CQ (C, D) | 26.52                              | 19.3 | 21.1 | 42.6 | 92.9 | 152.2| 180.0| 160.0| 133.5| 123.4| 92.1 | 48.1 | 24.3 |
| ZY (E) | 7.59                                | 23.4 | 21.9 | 38.4 | 85.5 | 147.0| 195.9| 149.9| 126.4| 93.3 | 102.1| 48.1 | 24.0 |
| CS (H) | 25.24                              | 75.6 | 91.5 | 142.4| 182.9| 200.1| 224.8| 151.7| 108.5| 82.1 | 66.5 | 48.1 | 49.1 |
| WH (G, F) | 25.47                              | 40.4 | 62.6 | 97.2 | 137.5| 169.0| 216.4| 191.6| 120.1| 83.3 | 71.1 | 53.2 | 28.8 |
| NC (I) | 15.64                              | 67.0 | 99.9 | 172.1| 216.7| 256.0| 292.0| 128.6| 112.5| 70.9 | 54.4 | 65.4 | 46.5 |
| NJ (J) | 10.53                              | 368  | 52.7 | 175.7| 829  | 924  | 292.0| 197.2 | 112.5| 81.4 | 51.1 | 49.9 | 28.9 |
| SH (K) | 3.21                                | 66.2 | 63.2 | 175.7| 685  | 82.6 | 175.7| 134.6| 202.2| 79.5 | 61.3 | 51.0 | 43.4 |

YS Yushu, KM Kunming, CD Chengdu, CQ Chongqing, ZY Zunyi, CS Changsha, WH Wuhan, NC Nanchang, NJ Nanjing, SH Shanghai

a Data on the precipitation amount for each meteorological station in the Changjiang catchment are retrieved from the Chinese Meteorological Data Share Service System (http://cdc.cma.gov.cn/home.do)

b The 12 sub-basins of the Changjiang catchment are indicated by capital letters from A to K (see Fig. 5)
isotopic characteristics of precipitation are strongly regulated by the distinct monsoon system and topography in East Asia [28, 38–42].

The Changjiang River basin is located primarily in the subtropical and temperate climate zone, and most parts of the basin prevailed by the subtropical monsoon climate. Two types of monsoon current flow through the basin in a year, the Siberian northwest winter monsoon and the Asian southeast summer monsoon (or Indian southwest summer monsoon in the upper Changjiang reaches) [28]. Changjiang River discharge sourced primarily from precipitation. The mean annual precipitation was 1057 mm, made up of an approximate total discharge of $1912 \times 10^9$ m³/year. In general, the summer monsoon initiated in April and impacts the Changjiang basin then retreats in October, which determines the timing of the rainy season from May to October, and most precipitation concentrates from July to August [43]. However, the spatial and temporal variations of precipitation in the Changjiang catchment are rather intricate and highly associated with the prevailing monsoon system and diverse topography. As a whole, about 70–90% of the total annual precipitation occurred from May to September, with significant temporal variations, but no apparent long-term trend observed over the last five decades (Fig. 2a). On the other hand, the spatial distribution of rainfall is particularly irregular [44]. Overall, the rainfall in general decreases from the southeast (lower reaches) to the northwest (upper reaches) of the basin because of the migration of monsoon-induced rain front from the southeast to the northwest of the coastal region in China [43].

Previous studies on precipitation water isotopes in the Changjiang catchment were based primarily on the data from the individual meteorological station, while the basin-scale isotopic characteristics have been scarcely investigated. As the spatial distribution of the rainfall is exceptionally irregular in the Changjiang basin, the rainfall amount and its H and O isotopic composition can vary by region, especially between the upper and lower reaches [28, 38, 40]. The Changjiang river water, in particular from the lower reaches, integrates the water from the entire basin. Therefore, a more comprehensive comparison of δD and δ18O between river water and basin-scale precipitation is critical to understand the influence of precipitation on river water. In this regard, our study provides the first practical synthesis of basin-scale precipitation δ18O. As shown in Fig. 4a, the basin-scale δ18O in the precipitation is nearly the same in each site, but slightly varies due to variable climate and topography in the catchment. Our calculation indicates that the precipitation δ18O is high (~–4‰) from January to May, but decreases rapidly in June and remains in a lower value (~–10‰) until October. The δ18O then rises back to a higher value (~–4‰) and maintains till the next year. Although our calculation may somewhat underestimate the complex precipitation processes in each sub-basin (Fig. 5 and Eq. (1)), dividing the basin into different sub-catchments based on its key tributaries does allow for a first-order estimation of δ18O in a basin-scale, made a significant difference compared to the previous attempts.

In comparison, the 2-year time series Changjiang river water δ18O in Nantong reveals similar seasonal variations with the precipitation, yielded high δ18O in winter and low δ18O in summer (Fig. 4a), suggests a potential correlation between river water and precipitation. The river water δ18O variation in Datong also displays a similar trend as that observed in Nantong, while the δ18O variation in Chongqing is different from those in Nantong and Datong. The river water δ18O in Chongqing is exceptionally high in May and June 2004. The reason behind the phenomenon remains unclear, but may be attributed to some specific climate or local events. Regardless of the several abnormal values observed in May and June, the river δ18O in Chongqing exhibits similar seasonal variations with those in Nantong and Datong, though the variation between winter and summer is not as notable as the latter two sites.

In contrast, the seasonal variations of δ18O in Poyang Lake are remarkably different from the other sites, showing a V-pattern with the lowest δ18O observed in June and July in the first monitoring year (Fig. 4a). This feature to some extent may be determined by evaporation depending on the local temperature and humidity. Apart from the trends, there are differences observed in absolute δ18O values between the precipitation and Changjiang river water. For instance, both the absolute values and the δ18O range in the Changjiang river water are smaller than that of the precipitation. This is probably due to the derivation of river water, primarily from precipitation upstream of the sampling location (i.e., at higher elevations), though the upstream δ18O values are often lower than local precipitation δ18O, particularly in catchments with high elevation gradients [29]. Different isotopic ranges between river water and precipitation could be resulted from the catchment which receiving water tracer (e.g., δ18O) inputs that were transported across diverse flow paths through the unsaturated and saturated zones as tracers migrate through the sub-surface toward the stream network [45], thus the amplitudes of δ18O can be significantly dampened in river water relative to those of precipitation.

Despite the discussion above, the seasonal variations of δ18O in the Changjiang river water are generally consistent with the basin-scale pattern of precipitation δ18O. Combined with the findings in this research, it is believed
that the long-term δ18O time series in the Changjiang river water is mainly dominated by local precipitation. Nevertheless, it is worth mentioning that the isotopic signature of a river, especially for the enormous river, is multifaceted, and can be altered by many hydrological processes, such as evaporation in the lakes and river surface [46], transpiration of vegetation [47, 48], and recharge from groundwater [49]. These hydrological processes, however, are beyond the scope of this study that focuses on the temporal variation of stable isotopes rather than the constraint of absolute isotopic value in the given catchment.

Our calculation on δ18O in precipitation over the Changjiang catchment may yield significant uncertainty due to limited isotopic observation stations available (mostly from GNIP) and antiquity of dataset (mainly in the late 1980s and 1990s). Nevertheless, this work provides the first attempt to estimate the seasonal variability of precipitation δ18O of the basin-scale and offers a quantitative isotopic comparison between river water and precipitation. As shown in Fig. 2a, the monthly precipitation average from Nanjing (GNIP station) in the lower Changjiang River is generally constant albeit the large seasonal fluctuations from 1987 to 1993, while a longer basin-scale precipitation record (Fig. 2b) in the Changjiang River also reveals a similar trend since the 1950s [15]. At the same time, the nationwide precipitation amount in China increases only by 2% from 1960 to 2000 [50] that conforms with the findings in the Changjiang catchment. Similar to the precipitation pattern, the stable H and O isotopic compositions in precipitation (e.g., δ18O of precipitation in Nanjing, Fig. 2a) yielded significant seasonal variations but an overall constant annual average during the past several decades. Similar observations have also been recently reported [38] based on the dataset provided by the Chinese Network of Isotopes in Precipitation (CHNIP). In this case, our estimation of basin-scale δ18O in precipitation over the Changjiang catchment may serve as a long-term dataset, provides essential background for the future isotopic study in the Changjiang River.

**Water mixing determines the seasonal variation of δ18O in the lower Changjiang river water**

The seasonal variations of δD and δ18O in river water from large rivers made a useful proxy to investigate the catchment hydrology, impacts of climate change and human activities on river discharges, and can be used to structure and validate on newly proposed hydrological models [22, 51]. However, the reasonable interpretation of seasonal stable isotopes variation depends mostly on the understanding of the hydrological setting and meteorological conditions of the river. For instance, the low-resolution isotopic sampling or hydrological monitoring may hinder the discovery of subtle relations between river water isotopes and local hydrological settings.

For the Changjiang river system, major tributaries are primarily located in the upper reaches of the Three Gorges except for the Hanjiang River, while many lakes, including the two largest lakes, Dongting Lake and Poyang Lake, are located in the middle and lower reaches. The Changjiang water discharge into the East China Sea is hence largely determined by the upstream contribution (regulated by Yichang gauging station) and the discharges from the Dongting and Poyang lakes (Fig. 4b). The two most significant freshwater lakes, Poyang Lake and Dongting Lake, are located in the middle, and lower Changjiang reaches, with basin coverage up to 4125 km2 and 4040 km2, respectively. Both lakes receive river water from several tributaries as well as the Changjiang mainstream (Fig. 1), which exerts an essential role in buffering the flood from the Changjiang upstream during the flood season. Here, we employ a simple conceptual model to quantitatively estimate the relative water contributions from the upper reaches and from the lakes to the lower Changjiang mainstream.

The water discharges data from Dongting Lake, Poyang Lake, and Hanjiang River were obtained from the gauging stations in Chenglingji, Hukou, and Huangzhuang, respectively. The river water discharge in Nantong is derived from the Datong gauging station as there is no regular gauging station in Nantong, and no significant tributaries exist between these two sites. Locations of each gauge station are shown in Fig. 1. Daily river water discharge data (November 2012 to December 2014) for all these stations are sourced from Changjiang Wuhan Waterway Bureau (http://yu-zhu.vicp.net/) and plotted in Fig. 4b. Apparently, the Hanjiang River only accounts for a small proportion (less than 5%) of total discharge in Datong, which will not be considered in the following calculation.

The total water discharge from the Dongting Lake, Poyang Lake, and Yichang upstream is very similar to that of Datong (Fig. 4b), suggesting that these three end-members predominantly supply the water discharge to the lower Changjiang mainstream in Datong. As Dongting and Poyang lakes have very similar temporal variations in water discharges (Fig. 4b) and isotopic compositions (Fig. 3), their total water discharges to the Changjiang mainstream are categorized under the same unit, as lake contribution. The river water across Nantong, therefore, can be simplified to merely two main end-members, i.e., the source (1) from the Yichang upstream and (2) from the two lakes in the middle reaches (Fig. 6). In this case, the daily water contribution from the lakes to water discharge in Nantong can be simply calculated by Eq. (2):

\[ Q_{lake} = Q_{lake1} + Q_{lake2} \]
\[ Q_{lake1} = Q_{lake11} + Q_{lake12} \]
\[ Q_{lake2} = Q_{lake21} + Q_{lake22} \]
Lake contribution = \frac{\text{Dis}_L}{\text{Dis}_L + \text{Dis}_{YC}}, \quad (2)

where \text{Dis}_L and \text{Dis}_{YC} represent the water discharges from the lakes and the Yichang station, respectively. The calculated lake contribution to Changjiang discharge is presented in Fig. 4c. From the periods of November 2012 to June 2013 and March to July 2014, the Changjiang water discharge in Nantong is primarily sourced from the lakes. In other months during the monitoring period, the upper catchment upstream of Yichang has supplied much water to the lower Changjiang mainstream.

The injection of the lake water with higher \( \delta^{18}O \) due to evaporation [25], to the Changjiang mainstream, causes elevated \( \delta^{18}O \) in the Changjiang river water downstream of the lakes (Figs. 3 and 4a) [10, 19, 26]. From the periods of July 2013 to late February 2014, and from July to December 2014, the river water \( \delta^{18}O \) values in Nantong are relatively low, which corresponds to the reducing water contribution from the lakes. It is interesting to note that the \( \delta^{18}O \) in the lower Changjiang river water does not vary synchronously with the lakes’ water contribution, but with a time lag (Fig. 4b). A non-linear correlation analysis between the \( \delta^{18}O \) time series and daily lake contribution indicates that a forward shift of the \( \delta^{18}O \) curve by about 17 days yields the best correlation \( (R^2 = 0.69) \) between these two curves (Fig. 4c). This finding suggests that the seasonal variations of river water \( \delta^{18}O \) in Nantong are closely related to the river water mixing from the Changjiang upstream and the lakes (Dongting and Poyang Lakes). In addition, the 17-day time lag between river water isotopic signals and lake water contribution indicates that it takes about 2 weeks for the river water to travel from the middle reaches to the river mouth. Consequently, the \( \delta^{18}O \) signal in Nantong was 2 weeks lagged after the river water mixing in the middle reaches. It is notable that the actual water traveling time in Changjiang River may vary in different seasons and the 17-day water traveling time is only an average river water traveling time from the middle reaches to the river mouth.

In conclusion, the time-series investigation of river water isotopic signatures and water discharges at the four key hydrometric stations in the Changjiang River demonstrates that the river water \( \delta^{18}O \) variation in Nantong is in general defined by local precipitation, but more directly related to the river water mixing in middle-lower reaches. The water contributions from the upstream and tributary lakes thus determine the daily \( \delta^{18}O \) variation in the Changjiang river downstream.

Damming impacts on the water cycle and river water isotopes in the lower Changjiang mainstream

Nowadays, the water discharge in the Changjiang mainstream at Yichang station is controlled mainly by the anthropogenic regulation (impounding/releasing) of the Three Gorges Reservoir (TGR) since its first impoundment in 2003. The impact of TGR on the Changjiang water discharge is not confined to only annual scale [16, 52, 53], but also seasonal scale [21, 54]. The regulation of TGR impoundment determines the water discharge downstream in Yichang and consequently controlled the water mixing between the Changjiang mainstream and the lakes [26]. From August to December 2013, the TGR was impounded (indicated by the high water level in TGR) to lower the flood risk to the downstream region, which subsequently resulted in a higher contribution of the lake water to the lower mainstream. On the contrary, the TGR released the water from December 2013 to May 2014 for shipping and irrigation, which resulted in a higher upstream contribution relative to the lake contribution.

To better expose the damming effect on the water mixing and stable isotopes in the lower Changjiang river water, we examined the relationship between the water samples \( \delta^{18}O \) and the frequency (%) of its occurrence in the mid-lower Changjiang (Fig. 6). The data indicate that \( \delta^{18}O \) variability \( (\delta^{18}O \text{ range in X-axis}) \) in the upper mainstream (Chongqing) above the TGR is more substantial than that in the mid-lower Changjiang mainstream (Nantong and Datong) and Poyang Lake. The Nantong and Datong sites are located downstream of TGR. The river water sourced from the upper Changjiang basin retained in the vast reservoir is well-mixed during the TGR impoundment may result in a homogenized isotopic signal. Furthermore, there are two prominent \( \delta^{18}O \) peaks observed in the river water in Nantong and Chongqing.
in Fig. 6 that correspond to the two notable $\delta^{18}$O values measured during the summer and winter (Fig. 4a). However, these temporal features are less pronounced in the water samples from Datong and Poyang Lake; values generated were probably insignificant statistically due to fewer water samples available.

It is noteworthy that apart from the damming effect, other environmental factors such as evapotranspiration and the mixing of groundwater can also impact the $\delta^{18}$O in river water [47, 48]. These influences are, however, hard to be quantified thus clarified in this paper due to limited stable H and O isotopic data retrieved from the soil, vegetation, and underground water in the catchment. Further modeling work may help in making a quantitative assessment of the evapotranspiration contribution to the river water $\delta^{18}$O possible in the future.

Conclusions

In this contribution, we report a 2-year time series of $\delta^{18}$O in the Changjiang river water and discuss the natural and anthropogenic forcing on the $\delta^{18}$O variation. The sub-basin-weighed $\delta^{18}$O in precipitation over the Changjiang catchment is calculated by the long-term meteorological observation data and multi-year $\delta^{18}$O record from GNIP. The monsoon-induced precipitation in overall determines the temporal variations of $\delta^{18}$O in the lower Changjiang mainstream in Nantong, but more straightforwardly related to the mixing of different waters from the upper Changjiang mainstream above Yichang and the tributary lakes in the middle reach. A comparison of river water $\delta^{18}$O with discharge contribution from the lakes suggests that it takes about 2 weeks (~17 days) for the Changjiang river water to travel through the mid-lower reaches to the sea. The TGR has changed the temporal variability of river $\delta^{18}$O, through regulating the water releasing in the mid-lower reaches.

This research suggests that the temporal variations of water stable isotopes in larger rivers are driven by composite factors. Apart from the natural climatic constraints, the local hydrological conditions must be taken into account in such a study. Besides, the estimation of basin-scale $\delta^{18}$O in precipitation may be an essential complement for water cycle modeling in the Changjiang catchment, and also provides baseline data for other hydrological isotope studies.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s12302-020-00359-w.

Additional file 1. A summary of sample information and their $\delta D$ and $\delta^{18}$O.

Abbreviations

IAEA: International Atomic Energy Agency; GNIR: Global Network of Isotopes in Rivers (GNIR); TGR: Three Gorges Reservoir; GNIP: Global Network of isotopes in precipitation; LMWL: Local meteoric water line; CHNIP: Chinese Network of Isotopes in Precipitation.

Acknowledgements

We thank Shilun Yang and Zhijun Dai (both from East China Normal University) for providing the river discharge data of the Changjiang River. CL is grateful to Nicholas Ng Chia Wei for his help in improving the English language.

Authors’ contributions

CL, EL, CT, and SY were involved in the experiments and manuscript writing. CL, KD, and PQ were responsible for the sample acquisition. CL and SY designed the study SX and ZL contributed to comments on this manuscript. All authors read and approved the final manuscript.

Funding

This work was supported by the National Natural Science Foundation of China (Grant Nos: 41673035, 41730531 and 41671003) and National Programme on Global Change and Air–Sea Interaction (GASI-GEOGE-03).

Availability of data and materials

All data generated or analyzed during this study are included in this published article [and its additional information files].

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

Author details

1 State Key Laboratory of Marine Geology, Tongji University, Shanghai 200092, People’s Republic of China. 2 School of Geography, Nantong University, Nantong 226019, People’s Republic of China. 3 College of Hydraulic & Environmental Engineering, China Three Gorges University, Yichang 443002, People’s Republic of China.

Received: 5 December 2019 Accepted: 20 May 2020

Published online: 29 May 2020

References

1. Kendall C, Coplen TB (2001) Distribution of oxygen-18 and deuterium in river waters across the United States. Hydrol Process 15:1363–1393
2. Gibson JJ, Aggarwal P, Hogan J, Kendall C, Martinelli LA, Stichler W, Rank D, Goni I, Choudhry M, Gat J (2002) Isotope studies in large river basins: a new global research focus. EOS Trans Am Geophys Union 83:613–617
3. Gat JR (1996) Oxygen and hydrogen isotopes in the hydrologic cycle. Annu Rev Earth Planet Sci: 24:225–262
4. Gibson JJ, Fekete BM, Bowen GJ (2010) Stable isotopes in large scale hydrological applications. In: West JB, Bowen GJ, Dawson TE, Tu KP (eds) Isoscapes: understanding movement, pattern, and process on earth through isotope mapping. Springer, New York, pp 389–405
5. Good SP, Noone D, Kunta N, Benetti M, Bowen GJ (2015) D/H isotope ratios in the global hydrologic cycle. Geophys Res Lett 42:5042–5050
6. Vitvar T, Aggarwal PK, McDonnell JJ (2005) A review of isotope applications in catchment hydrology. In: Aggarwal P, Gat J, Froehlich KO (eds) Isotopes in the water cycle. Springer, Dordrecht, pp 151–169
7. Gibson JJ, Edwards T, Birks SJ, Amour NA, Buhay WM, McEachern P, Wolfe BB, Peters DL (2005) Progress in isotope tracer hydrology in Canada. Hydrolog Process 19:303–327
8. Darling WG, Bath AH, Gibson JJ, Rozanski K (2006) Isotopes in water. In: Leng MJ (ed) Isotopes in palaeoenvironmental research. Springer, Dordrecht, pp 1–66
30. Craig H (1961) Isotopic variations in meteoric waters. Science 133:702–703

31. Zhang X, Yao T (1998) Distributional features of δ18O in precipitation in China. J Chin Geogr 8:157–164

32. Tardy J, Bustillo V, Roquin C, Mortati J, Victoria R (2005) The Amazon. Biogeochemistry applied to river basin management: part 1. Hydro-climatology, hydrograph separation, mass transfer balances, stable isotopes, and modelling. Appl Geochem 20:1746–1829

33. Rank D, Papesch W, Heiss G, Tesch R (2012) Environmental Isotope Ratios of River Water in the Danube Basin. Monitoring Isotopes in Rivers: Creation of the Global Network of Isotopes in Rivers (GNIR). Results of a Coordinated Research Project 2002–2006, Vienna, p 211–219

34. Nguyen K, Huynh L, Le D, Nguyen V, Tran B (2012) Isotope Composition of Mekong River Flow Water in the South of Vietnam. Monitoring Isotopes in Rivers: Creation of the Global Network of Isotopes in Rivers (GNIR) 13–31

35. Jouzel J, Froehlich K, Schütterer U (1997) Deuterium and oxygen-18 in present-day precipitation: data and modelling. Hydro-Sol J 42:747–763

36. Sugimoto A, Maximo T (2012) Study on Hydrological Processes in Lena River Basin using Stable Isotope Ratios of River Water. Monitoring Isotopes in Rivers: Creation of the Global Network of Isotopes in Rivers (GNIR) 41–49

37. Dansgaard W (1964) Stable isotopes in precipitation. Tellus 16:436–468

38. Liu J, Song X, Yuan G, Sun X (2014) Stable isotope compositions of precipitation in eastern Monsoon China and the water vapor sources. Chin Sci Bull 55:200–211

39. Posmentier ES, Feng X, Zhao M (2004) Seasonal variations of precipitation δ18O in eastern Asia. J Geophys Res 109:D23106

40. Liu Z, Tian L, Chai X, Yao T (2008) A model-based determination of spatial variation of precipitation δ18O over China. Chin Geol 249:203–212

41. Ding Y, Chan JC (2005) The East Asian summer monsoon: an overview. Meteorol Atmos Phys 89:117–142

42. Qian W, Kang HS, Lee DK (2002) Distribution of seasonal rainfall in the East Asian monsoon region. Theor Appl Climatol 73:151–168

43. McGuire KJ, McDonnell JJ (2008) A review and evaluation of catchment transit time modeling. J Hydrology 330:543–563

44. Cockerton H, Street-Perrott F, Leng M, Barker P, Horstwood M, Pashley V (2013) Stable-isotope (H, O, and Si) evidence for seasonal variations in hydrology and Si cycling from modern waters in the Nile Basin: implications for interpreting the Quaternary record. Quat Sci Rev 66:4–21

45. Jaschek S, Sharp ZD, Gibson JJ, Birks SJ, Yi Y, Favett PJ (2013) Terrestrial water fluxes dominated by transpiration. Nature 496:457–450

46. Good SP, Noone D, Bowen G (2015) Hydrologic connectivity constrains partitioning of global terrestrial water fluxes. Science 349:175–177

47. Kanduč T, Grasa F, McIntosh J, Stibil V, Ulrich-Supovec M, Supovec L, Jamnikar S (2014) A geochemical and stable isotope investigation of groundwater/surface-water interactions in the Velenje Basin, Slovenia. Hydrogeol J 22:971–984

48. Liu B, Xu M, Henderson M, Qi Y (2005) Observed trends of precipitation amount, frequency, and intensity in China, 1960–2000. J Geophys Res 110:D08103

49. Ogrinc N, Kanduč T, Sticher W, Vreča P (2008) Spatial and seasonal variations in δ18O and δD values in the River Sava in Slovenia. J Hydrology 359:307–318

50. Dai Z, Du J, Li J, Li W, Chen J (2008) Runoff characteristics of the Changjiang (Yangtze) River basin, China, with special reference to the impacts on Three Gorges Dam. Geophys Res Lett 35:L07406

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.