Spatial variation of stable isotopic composition in surface waters of the Huai River basin, China and the regional hydrological implication

Liang Zhang, Ruiqiang Yuan, Xianfang Song and Jun Xia

ABSTRACT

Oxygen ($\delta^{18}O$) and hydrogen (δD) stable isotopes in the surface waters of the Huai River basin were analyzed in this study. Results indicated the northern waters had higher $\delta^{18}O$ and δD than the southern waters, the water $\delta^{18}O$ and δD increased along the water flow directions. These variations mostly resulted from the spatial differences of precipitation and evaporation. Comparing with published different continents' river water $\delta^{18}O$ data, this study suggests that evaporation effect is a more plausible interpretation than altitude effect as the cause of $\delta^{18}O$ increasing from upriver to downriver waters. This region's local surface water line (LSWL, $\delta D = 5.36\delta^{18}O - 18.39$; $r^2 = 0.84$) represents one of the first presented LSWLs in eastern China. The correlation between *d*-excess and $\delta^{18}O$ demonstrates this region is dominated by the Pacific oceanic moisture masses in summer. Comparing the various LSWLs from eastern China and eastern United States river waters, this study proposes a hypothesis that the water LSWLs slopes of lower latitude regions may be less than those of higher latitude regions within similar topographic areas. This hypothesis may be tested in other geographically comparable coupled areas in the world if corresponding large-scale data can be found.

Key words | evaporation, Huai River basin, local surface water line, surface water, $\delta^{18}O$ and δD

Liang Zhang (corresponding author)
Ruiqiang Yuan
Xianfang Song
Jun Xia
Institute of Geographic Sciences and Natural Resources Research,
Chinese Academy of Sciences,
Beijing 100101,
China
E-mail: *zhang.on.ca@gmail.com*

Liang Zhang
Department of Biological Sciences,
University of Windsor,
401 Sunset Avenue, Windsor, ON,
Canada,
N9B 3P4

Ruiqiang Yuan
College of Environmental & Resource Sciences,
Shanxi University,
Taiyuan, Shanxi 030006,
China

Jun Xia
School of Water Resources and Hydropower Engineering,
Wuhan University,
Wuhan, Hubei 430072,
China

INTRODUCTION

The analysis of oxygen ($\delta^{18}O$) and hydrogen (δD) stable isotopic composition of water may help improve our understanding of hydrological processes such as precipitation, groundwater recharge, basin water hydrology, and evolution of surface waters undergoing evaporation (Gammons *et al.* 2006; Ahmad *et al.* 2012; Katsuyama *et al.* 2015; Darling & Bowes 2016). This has become an effective method for investigating the hydrologic system on a range of spatial and temporal scales. Basin-wide river waters could provide more convincing information about regional precipitation than that of recent precipitation at a single location in certain areas (Kendall & Coplen 2001). A number of stable isotopic (oxygen and hydrogen) studies have been done in many large river water systems around the world (Simpson & Herczeg 1991; Kendall & Coplen 2001; Dalai *et al.* 2002; Gammons *et al.* 2006; Ahmad *et al.* 2012), and these studies demonstrated that $\delta^{18}O$ and δD were useful tracers for regional hydrological studies.

Previous studies have addressed the variation of $\delta^{18}O$ and δD in regional surface waters and have suggested they are affected by seasonal precipitation (Dutton *et al.* 2005; Ahmad *et al.* 2012; Katsuyama *et al.* 2015), irrigation or evaporation (Simpson & Herczeg 1991; Ahmad *et al.* 2012; Darling & Bowes 2016), and latitude or elevation (Dutton *et al.* 2005; Timsic & Patterson 2014; Katsuyama *et al.* 2015). However, large-scale (e.g., basin wide) surface water

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$\delta^{18}O$ and δD studies, such as US country-wide rivers (Kendall & Coplen 2001; Dutton *et al.* 2005), are still limited in the East Asian continent.

The Huai River basin is one of the five largest basins in China and is situated between the Yellow River and the Yangtze River, the two largest rivers in China. The whole Huai River basin (30°55′–36°36′N, and 111°55′–121°25′E) covers five provinces (Hubei, Henan, Anhui, Shandong, and Jiangsu) of China, and has a total drainage area of 270,000 km^2 (Figure 1). This basin is an important socio-economic region in China and has been examined in many studies (Wang & Ongley 2004; Ge *et al.* 2006; Tan *et al.* 2009; Li *et al.* 2010a). However, the water $\delta^{18}O$ and δD studies in this region are very limited and mostly focused on small areas or few sites. For example, Tan *et al.* (2009) reported $\delta^{18}O$ and δD data for a one-time precipitation event in October 2007 in Wudaogou (nearby to site 7 in this study) of this region, a hydrological experimental catchment (drainage area = 1.36 km^2). They indicated that the groundwater of that area mostly recharged from surface water infiltration and less so from deep groundwater. Li *et al.* (2010a) reported that $\delta^{18}O$ values in the main channel of the Huai River (site 2 in our study) were more enriched than that of groundwater from either side of the main channel in both the wet and dry seasons, and revealed that the Huai River main channel recharges its two sides groundwater.

In this study, we analyze the isotopic ($\delta^{18}O$ and δD) composition of large-scale surface water samples in the Huai River basin, which includes eight rivers, two large lakes, and one long artificial canal (East Line of the South-North Water Transfer Project (SNWTP)) in the Huai River basin, Eastern China. Our objectives are: (1) to identify the spatial water $\delta^{18}O$ and δD characteristics in this region; (2) to discuss the causes that lead to spatial variations in isotope values of this region and, if possible, to identify the most important factor contributing to these variations; (3) to incorporate findings from studies of $\delta^{18}O$ and δD values taken from the Yangtze River and Yellow River basin and to explore, at a

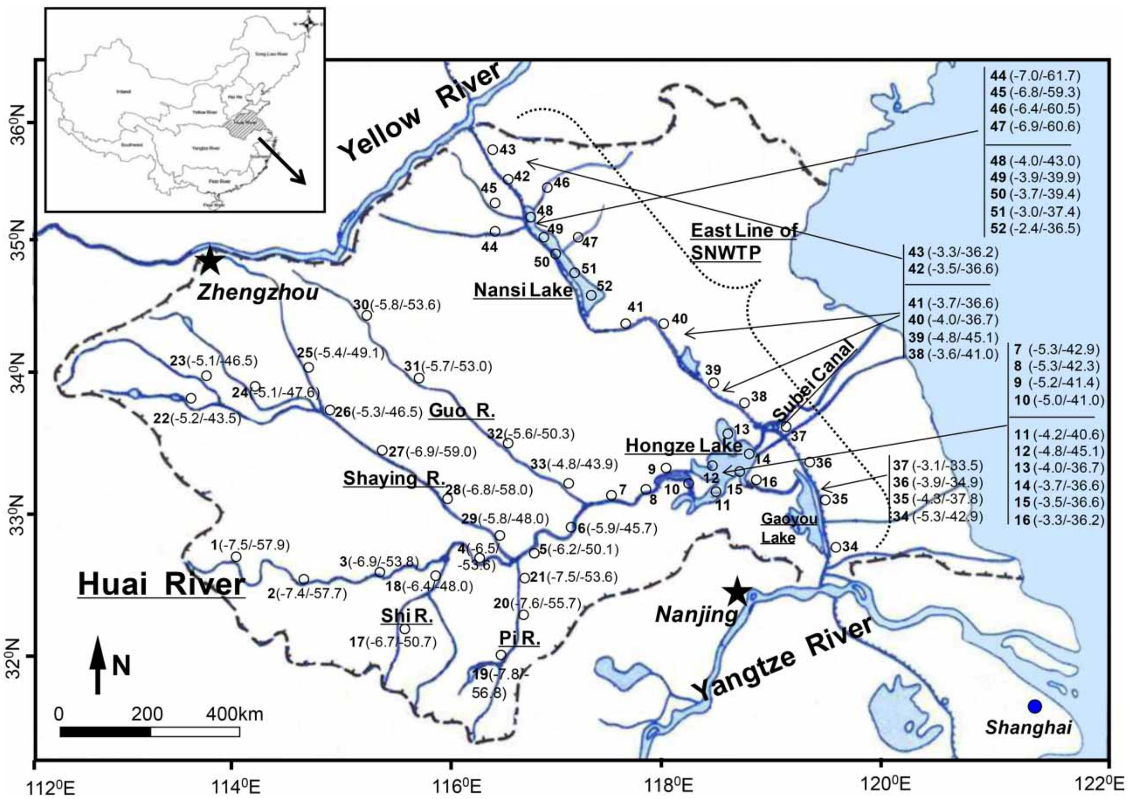


Figure 1 | Sampling sites and the water $\delta^{18}O$ and δD values at each site in the Huai River basin and the East Line of SNWTP. The upper-left plot shows the location of the Huai River basin in China. The black numbers in the figure present the site number, and the numbers inside the brackets present the $\delta^{18}O/\delta D$ values at each site.

large scale, surface water $\delta^{18}O$ and δD variations over these three river basins in China; (4) to compare local surface water lines (LSWLs) (using $\delta^{18}O$ and δD values) of the rivers in eastern China and the eastern United States, to explore at a larger scale (two continents) a view of surface water isotopes.

STUDY AREA AND METHODS

Study area

The terrain of the Huai River basin is generally mountainous to the west and increasingly flat to the east. The landforms of this region consist of 13% mountainous areas, 19% small hills, 52% plains, and 16% swales (lakes) (Ge *et al.* 2006). In this region, the Hongze Lake (area ~1,577 km^2), Nansi Lake (~1,097 km^2), and Gaoyou Lake (~675 km^2, no samples in this study) are three large open lakes in this region (Figure 1) and their water areas can be large in the rainy season and shrink in the dry season. The average water residence times of the three lakes are 35 days (Hongze Lake), 226 days (Nansi Lake), and 21 days (Gaoyou Lake), respectively. These can be shorter in the rainy season and longer in the dry season (Wang & Dou 1998). The annual mean discharge of water from the Huai River basin is 62 km^3 and is similar to the mean discharge of the Yellow River (66 km^3/per year). The mean annual precipitation and the evaporation of this region are 920 mm and 1,200 mm, respectively, and vary from site to site. Generally, the annual great precipitation and evaporation in this region happen between June and August (Figure 2).

The East Line of the SNWTP, which is a strategically significant project to supply water to north China, involves the Nansi Lake as its water channel and the waters in Nansi Lake are separated into several sections by sluices (Li *et al.* 2013). The East Line of the SNWTP (hereafter SNWTP) is constructed at the base of the Jing-Hang Grand Canal. There is about a 650 km part of the SNWTP inside the Huai River basin (from site 43 to site 34), but the SNWTP has no hydraulic connections with Hongze Lake and Gaoyou Lake. There is another man-made canal (Subei Canal) between the Hongze Lake and the Yellow Sea. The Subei Canal is mainly used to irrigate farms and the water is mostly pumped from Hongze Lake. The Subei Canal also discharges the flood waters from Hongze Lake to the Yellow Sea in heavily rainy days. There are several sluices built at the intersection of the SNWTP and the Subei Canal, but no merging of the waters between the SNWTP and the Subei Canal. In the 1970s, the southern section sluices were constructed to pump the Yangtze River water from site 34 to 37 (site 34 is 1 meter more elevated than site 37, Huai'an) for seasonal irrigation purposes. However, the northern section sluices (for the purposes of water transfer to north China) were not started until 2009 (Li *et al.* 2013). In our sampling period in 2008, the water flow directions in the SNWTP are 'North to South' in the northern section (from site 43 to site 38) and 'South to North' in the southern section (from site 37 to site 34).

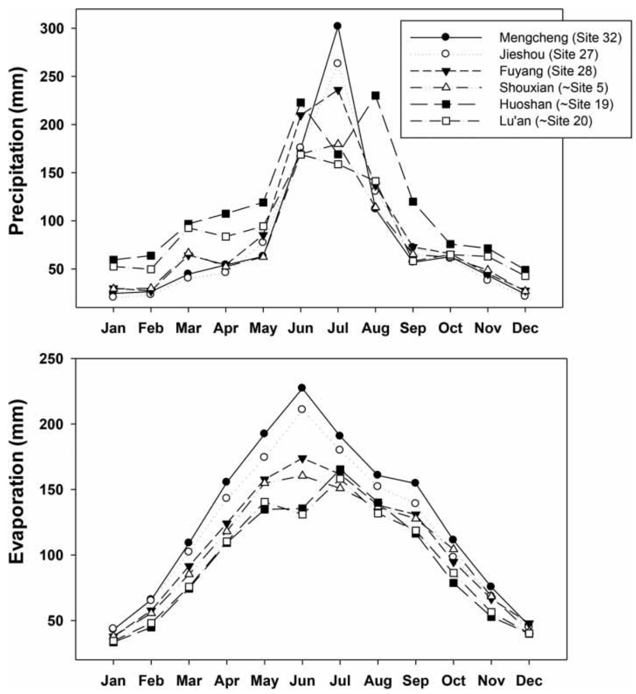


Figure 2 | Monthly evaporation and precipitation differences (ten-year average values for 1996–2005) between northern and southern areas in the Huai River basin (data was obtained from Anhui Province Meteorological Data Sharing Service Database, http://www.ahqh.org.cn). Site Shouxian is very close to site 5 on the Huai River main channel (see Table 1 and Figure 1); Huoshan and Lu'an are very close to site 19 and 20, respectively, on the Pi River.

Methods

Annual precipitation in the Huai River basin is distinct between the south and north areas, and precipitation is more abundant during the summer season. Because many dams and sluices have been constructed in this region, in the rainy season (June to September, Figure 2) most tributaries are in flowing condition, whereas during the other seasons some sections have little flowing water. Thus, we chose the rainy season for our sampling period in this region. Samples were collected from 52 sites of the Huai River basin in July 2008 (Figure 1 and Table 1). All sampling sites (except sites located on the two southern tributaries, Shi River and Pi River) are located on the plains or swales in this region, according to previous reports (Ge *et al.* 2006). In the Huai River basin, the river leakage recharges groundwater in the rainy season (June to September), whereas the groundwater may only charge the surface water in some mountainous areas (Hu *et al.* 2009). However, Hongze Lake discharges to ambient groundwater throughout the year due to lake water levels being higher than the surrounding land areas (Wang & Chen 1999). In this study, all the water sampling sites are situated in the plains or lakes, and the water quantities may cover more than 95% of the discharge in this region.

The weather conditions were noted every day during the sampling period. All water samples were collected before a precipitation event on the sampling date except for site 18 (Table 1 and Figure 1), where there was a rainfall event occurring at midnight before our sampling date, and the water samples at site 18 had been mixed by new rainfall and upriver waters. Water samples were collected from the top, middle, and bottom at each site, mixed together and filtered (0.45 μm GF/C Millipore nitrocellulose filter) in the

Table 1 | Sampling information, $\delta^{18}O$ and δD compositions, Cl and SO_4 concentrations of the surface waters in the Huai River basin

Water system	Type		Sampling site	Date	Precipitation (mm)	T (°C)	$\delta^{18}O$ (‰)	δD (‰)	*d* (‰)	Cl (mg/L)L)	SO_4 (mg/L)L)
Huai River main channel (HRMC)	Main Channel	1	Minggang	12-Jul	5.5	28.9	−7.5	−57.9	2.5	35.5	24.5
		2	Xixian	12-Jul	5.5	28.6	−7.4	−57.7	1.3	20.1	24.5
		3	Huaibin	12-Jul	5.5	28.7	−6.9	−53.8	1.7	10.7	19.6
		4	Nanzhao	13-Jul	0	28.2	−6.5	−53.6	−1.8	10.2	18.6
		5	Lutaizi	14-Jul	0	28.7	−6.2	−50.1	1.6	16.2	21.9
		6	Huainan	14-Jul	0	28.7	−5.9	−45.7	−0.6	15.1	20.3
		7	Bengbu	14-Jul	0	29.8	−5.3	−42.9	−0.4	28.0	35.9
		8	Linhuaiguan	17-Jul	2.3	29.6	−5.3	−42.3	−0.3	23.5	29.4
		9	Wuhe	17-Jul	2.3	29.6	−5.2	−41.4	−0.2	24.0	29.0
		10	Xuyu	18-Jul	39.5	30.6	−5.0	−41.0	−1.3	41.9	50.9
Hongze Lake (HZL)	Lake	11	Laozishan	18-Jul	0	31.3	−4.2	−40.6	−6.9	66.6	62.5
		12	Lihewa	17-Jul	0	29.2	−4.8	−45.1	−6.5	46.3	63.0
		13	Chenzihu	17-Jul	0	28.9	−4.0	−36.7	−4.6	45.4	48.4
		14	Erheza	17-Jul	0	29.3	−3.7	−36.6	−6.8	49.7	68.0
		15	Sanheza	18-Jul	0	29.6	−3.5	−36.6	−8.4	29.2	37.6
		16	Jinhu	18-Jul	0	31.5	−3.3	−36.2	−9.7	40.9	47.7
Shi River (SR)	South Trib	17	Yeji	12-Jul	0	29.8	−6.7	−50.7	2.8	6.7	14.6
		18	Shangshiqiao	12-Jul	0	30.3	−6.4	−48.0	2.8	7.8	17.5
Pi River (PR)	South Trib	19	Hengpaitou	12-Jul	0	26.7	−7.8	−56.8	5.5	5.0	14.9
		20	Matou	13-Jul	0	30.0	−7.6	−55.7	5.1	6.0	14.2
		21	Zhengyang	13-Jul	0	31.5	−7.5	−53.6	6.2	7.9	14.3
Shaying River (SYR)	North Trib	22	Pingdingshan	11-Jul	0	29.8	−5.2	−43.5	−1.9	19.2	55.9
		23	Luohe	11-Jul	0	29.9	−5.1	−46.5	−5.5	205.1	103.5
		24	Huahang	10-Jul	0	30.0	−5.1	−47.6	−6.6	72.3	93.3
		25	Huangqiao	11-Jul	0	29.8	−5.4	−49.1	−5.6	109.7	129.5
		26	Zhoukou	11-Jul	0	29.7	−5.3	−46.5	−4.2	266.8	124.9
		27	Jieshou	13-Jul	2.5	30.1	−6.9	−59.0	−4.0	131.5	110.3
		28	Fuyang	13-Jul	2.5	29.9	−6.8	−58.0	−3.8	126.8	128.6
		29	Yingshang	13-Jul	2.5	30.2	−5.8	−48.0	−1.4	93.0	105.8

(*continued*)

Table 1 | continued

Water system	Type		Sampling site	Date	Precipitation (mm)	T (°C)	δ^{18}O (‰)	δD (‰)	*d* (‰)	Cl (mg/L)L)	SO_4 (mg/L)L)
Guo River (GR)	North Trib	30	Taikang	11-Jul	0.4	29.9	−5.8	−53.6	−7.0	94.8	177.3
		31	Bozhou	13-Jul	0	30.1	−5.7	−53.0	−7.6	184.9	243.6
		32	Mengcheng	13-Jul	0	30.2	−5.6	−50.3	−5.9	159.3	169.4
		33	Huaiyuan	14-Jul	0	30.6	−4.8	−43.9	−5.3	114.3	160.2
Southern section of the East Line of SNWTP (SNWTP (S))	South Sec.	34	Jiangdu	19-Jul	0.2	31.1	−6.5	−54.4	−2.4	31.4	41.2
		35	Gaoyou	19-Jul	0.2	28.5	−4.3	−37.8	−3.5	32.1	41.5
		36	Baoyin	19-Jul	0.2	29.8	−3.9	−34.9	−3.6	32.8	40.9
		37	Huai'an	19-Jul	0	29.5	−3.1	−33.5	−8.5	51.7	52.7
Northern section of the East Line of SNWTP (SNWTP (N))	North Sec.	38	Siyang	17-Jul	0	29.2	−3.6	−41.0	−12.1	81.7	116.6
		39	Suqian	16-Jul	0.4	29.8	−4.4	−41.5	−6.5	82.1	126.9
		40	Pizhou	14-Jul	0	29.5	−5.5	−45.7	−1.5	81.7	153.9
		41	Tai'e'zhuang	18-Jul	0	28.3	−5.8	−46.7	−0.2	102.8	200.2
		42	Jining	16-Jul	0.9	28.5	−6.5	−54.7	−2.9	180.4	373.8
		43	Liangshan	16-Jul	0.9	31.6	−6.8	−56.8	−2.5	47.3	185.0
Tributaries of Nansi lake (TRI_NSL)	Trib	44	Jishu	16-Jul	0.9	29.3	−7.0	−61.7	−5.4	184.2	180.6
		45	Sunzhuang	16-Jul	0.9	30.6	−6.8	−59.3	−4.8	175.7	259.9
		46	Liangshanza	16-Jul	0.9	33.4	−6.4	−60.5	−9.6	211.5	302.9
		47	Yanzhou	17-Jul	0.9	28.5	−6.9	−60.6	−5.0	155.7	178.2
Nansi Lake (NSL)	Lake	48	Weishandao	17-Jul	0	29.1	−4.0	−43.0	−11.2	120.6	206.4
		49	Erjibashang	17-Jul	0	30.3	−3.9	−39.9	−8.9	150.9	220.4
		50	Erjibaxia	15-Jul	9.8	27.6	−3.7	−39.4	−9.9	147.0	223.1
		51	Dushandao	15-Jul	9.8	27.7	−3.0	−37.4	−13.6	104.8	132.2
		52	Nanyanghu	17-Jul	0	29.2	−2.4	−36.5	−17.2	145.4	241.0

Tri, tributary; Sec, section; precipitation is the daily data at the sampling sites (data from China Meteorological Data Sharing Service Database, http://www.cdc.cma.gov.cn); T is the water temperature in sampling; d = deuterium excess, calculated as δD-8δ^{18}O.

field. Filtered 100 mL water samples were placed in high-density polyethylene (HDPE) bottles and stored in an ice box for lab analyses. Water temperature was measured *in situ* using a handheld meter. Stable isotope and ion (Cl^- and SO_4^{2-}) analyses were performed in the laboratory of the Institute of Geographic Sciences and Natural Resources Research (Beijing), Chinese Academy of Sciences. Isotopic analyses were done using a Thermo Finnigan TC/EA with GC-PAL autosampler attached to a Thermo Finnigan MAT-253 continuous flow mass spectrometer via a Conflo III interface. Isotopic values are reported using the standard δ notion relative to the NIST/IAEA reference materials V-SMOW. The analytical precision was ±0.1‰ and ±1.5‰ for δ^{18}O and δD, respectively. Water Cl^- and SO_4^{2-} were measured using a Shimadzu Ion Chromatograph (IC) meter (Shimadzu HIC-SP, Japan), and the precision was ±0.1 mg/L. Reagent and procedural blanks were determined in parallel for the sample treatment using identical procedures. Statistical package SPSS (version 11.5, IMB Ltd) and analysis of variance (ANOVA) tests were used in the analysis.

RESULTS

The surface water δ^{18}O and δD compositions from different sampling sites of the Huai River basin are listed in Figure 1 and Table 1. The δ^{18}O value of the whole basin varied from −7.8‰ to −2.4‰ with an average value of −5.4‰. The δD value for the whole basin varied from −61.7‰ to −33.5‰ with an average value of −47.5‰. The δ^{18}O values of the tributaries waters showed clear spatial differences; northern waters were enriched while the southern water systems were depleted (Figure 1). The northern δ^{18}O values ranged from −5.1‰ to −6.9‰ in the Shaying River and −4.8‰ to −5.8‰ in the Guo River. The southern δ^{18}O values ranged from −6.4‰ to −6.7‰ in the Shi River and from

−7.5‰ to −7.8‰ in the Pi River. Similar trends were observed for δD values as well.

The Cl and SO_4 concentrations in northern Shaying River (up to 266.8 and 124.9 mg/L for Cl and SO_4, respectively) and Guo River (up to 184.9 and 243.6 mg/L for Cl and SO_4), respectively (Table 1), were obviously higher than those from the southern Shi River and Pi River (up to 7.9 and 17.5 mg/L for Cl and SO_4). Tables 2 and 3 show the results of isotopic ($\delta^{18}O$ and δD) and anionic (Cl and SO_4) ANOVAs of the different water systems, respectively. Due to the limited sampling sites ($n = 2$, not of a Gaussian distribution), the data from Shi River was not included in the one-way ANOVA analysis. It was found that the isotopic ($\delta^{18}O$ and δD) and anionic (Cl and SO_4) values from the Pi River sites are significantly different ($p < 0.01$) when compared with northern waters (Shaying River, Guo River, Northern SNWTP, Nansi Lake and its tributaries). In addition, tributary $\delta^{18}O$ and δD values also showed an increase in the direction of water flow for all rivers studied here (Figure 1).

The $\delta^{18}O$ and δD values for the four southern sites of SNWTP increased from south to north, while isotopic

Table 2 | The one-way ANOVA of the $\delta^{18}O$ (lower triangle) and δD (upper triangle) among nine water systems (Shi River is not included, due to only two samples on the river) of the Huai River basin

	HRMC	HZL	PR	SYR	GR	SNWTP (S)	SNWTP (N)	TRI_NSL	NSL
HRMC		0.001**	0.073	0.669	0.637	0.013*	0.753	0.000**	0.004**
HZL	0.000**		0.000**	0.001**	0.002**	0.674	0.007**	0.000**	0.858
PR	0.009**	0.000**		0.144	0.230	0.001**	0.059	0.171	0.000**
SYR	0.300	0.000**	0.002**		0.901	0.007**	0.500	0.002**	0.002**
GR	0.203	0.007**	0.002**	0.665		0.014*	0.495	0.007**	0.005**
SNWTP (S)	0.002**	0.333	0.000**	0.020*	0.093		0.040*	0.000**	0.808
SNWTP (N)	0.122	0.003**	0.001**	0.561	0.939	0.078		0.000**	0.015*
TRI_NSL	0.196	0.000**	0.003**	0.043	0.035*	0.000**	0.018*		0.000**
NSL	0.000**	0.317	0.000**	0.000**	0.001**	0.070	0.000**	0.000**	

For abbreviations of water system see Table 1.
**The difference is significant at the 0.01 level (two-tailed).
*The difference is significant at the 0.05 level (two-tailed).

Table 3 | The one-way ANOVA of Cl (lower triangle) and SO_4 (upper triangle) among nine different water systems (Shi River is not included) of the Huai River basin

	HRMC	HZL	PR	SYR	GR	SNWTP (S)	SNWTP (N)	TRI_NSL	NSL
HRMC		0.216	0.639	0.000**	0.000**	0.505	0.000**	0.000**	0.000**
HZL	0.244		0.182	0.026*	0.000**	0.700	0.000**	0.000**	0.000**
PR	0.531	0.154		0.002**	0.000**	0.358	0.000**	0.000**	0.000**
SYR	0.000**	0.000**	0.000**		0.003**	0.019*	0.000**	0.000**	0.000**
GR	0.000**	0.001**	0.000**	0.670		0.000**	0.850	0.155	0.547
SNWTP (S)	0.534	0.712	0.309	0.000**	0.001**		0.000**	0.000**	0.000**
SNWTP (N)	0.001**	0.033*	0.002**	0.136	0.100	0.024*		0.169	0.640
TRI_NSL	0.000**	0.000**	0.000**	0.030*	0.123	0.000**	0.001**		0.362
NSL	0.000**	0.001**	0.000**	0.957	0.731	0.001**	0.167	0.051	

For abbreviations of water system see Table 1.
**The difference is significant at the 0.01 level (two-tailed).
*Difference is significant at the 0.05 level (two-tailed).

values for the six northern sites increased from north to south (Figure 1). Thus, the δ^{18}O and δD of both sections increase along the direction of the water flow, likely due to higher evaporation rates on hot summer days (Figure 2). Similar results were seen in the Huai River main channel and its four main tributaries excluding the Shaying River that was influenced by a rainfall event on 12 July. Moreover, we saw significant differences between the two sections; the northern SNWTP section Cl and SO_4 were obviously higher than those of the southern SNWTP section (Tables 2 and 3).

DISCUSSION

Isotopic variations in waters in the Huai River basin

In a previous study (Tan *et al.* 2009), the average δ^{18}O for precipitation, surface water, and groundwater at Wudaogou (close to site 7 in this study) were recorded as −9.15‰ ($n = 3$), −6.76‰ ($n = 4$), and −8.01‰ ($n = 6$), respectively; the average δD for precipitation, surface water, and groundwater were −50.38‰, −48.81‰, and −57.32‰, respectively. Li *et al.* (2010a) also indicated that the main channel of the Huai River could discharge riverine groundwater on two sides in both the rainy and dry seasons. Microcystins can only be produced by river algae but cannot be produced in groundwater; however, Tian *et al.* (2013) even detected microcystins in the groundwater (maximum microcystin concentration 0.446 μg/L) discharged from the Shaying River main channel (maximum microcystin concentration 1.846 μg/L) in December 2008 and December 2009 (dry season). All the rivers and lakes surrounding levees in our sampling areas are constantly monitored by the government (in rainy season every year) to prevent water flowing out of rivers or lakes (Hongze Lake, Nansi Lake, etc.). Consequently, it can be excluded that the surface waters in our sampling period (July in the rainy season of 2008) and areas were recharged from groundwater.

The International Atomic Energy Agency maintains a database containing oxygen and hydrogen isotopic contents of precipitation from around the world (IAEA/WMO 2010). These contain two GNIP (Global Network of Isotopes in Precipitation) stations, one within the Huai River basin (Zhengzhou, upriver of Shaying River) and one close to the south-eastern border (Nanjing) (Figure 1). In order to present the δ^{18}O and δD relations between precipitation and surface waters of this region, the two GNIP stations' (Zhengzhou and Nanjing) precipitations monthly δ^{18}O and δD variations (from IAEA/WMO 2010) are shown in Figure 3. Although the precipitation isotopic data of Zhengzhou and Nanjing

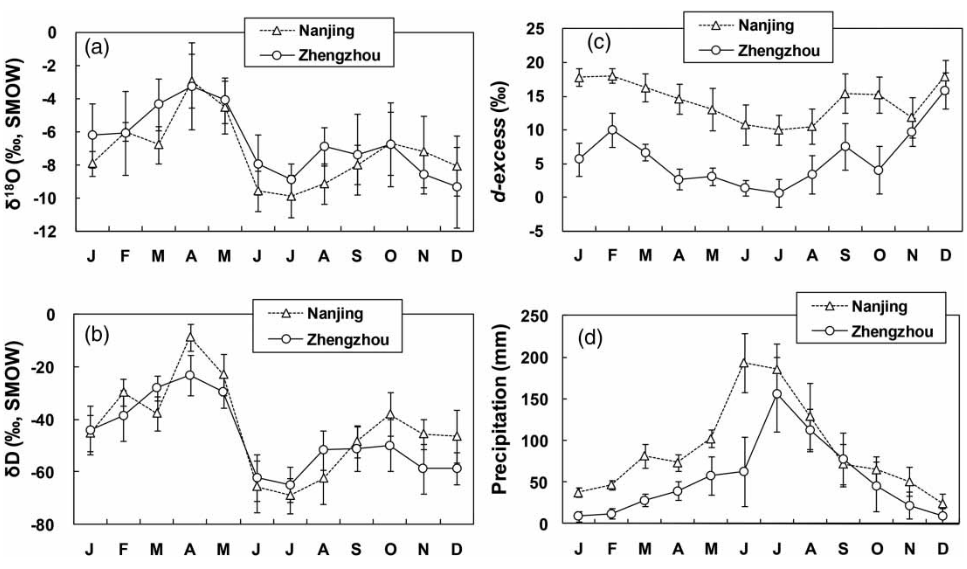


Figure 3 | Monthly average and SD variations (eight-year average) of δ^{18}O, δD, *d*-excess, and precipitation of the two IAEA monitoring sites Nanjing and Zhengzhou (see locations in Figure 1). Original data were obtained from the IAEA database (IAEA 2010).

show extremely large seasonal variation throughout the year (Figure 3), the precipitation in the northern Huai River basin (Zhengzhou) during the summer months (June to September) has consistently higher $\delta^{18}O$ (1‰ to 2‰) and deuterium (7‰ to 9‰) values than those of the southern basin (Nanjing). Furthermore, $\delta^{18}O$ and δD values of Zhengzhou and Nanjing in the summer months are consistently lower than the rest of the year, indicating that the summer precipitation of the Huai River basin (between Zhengzhou and Nanjing) is mostly derived from the moisture masses from the Pacific Ocean (Yamanaka *et al.* 2004).

Our sampling at each site was scheduled to occur before the rainfall event on a certain day, but certain samplings could not avoid the effects of the day-before precipitation events. On the northern tributary of the Shaying River, for example, $\delta^{18}O$ and δD values for sites 27 and 28 were more depleted than upriver sites 25 and 26, which were influenced by a rainfall event on 12 July 2008 (Table 1). This is similar to previous isotopic findings on the precipitation and river waters in this region (Tan *et al.* 2009). However, the rainfall event on 17 July did not decrease the $\delta^{18}O$ and δD values of site 10 (sampling time occurred before the rainfall on 18 July at this site) relative to sites 8 and 9 on the Huai River's main channel. This may be the result of the precipitation not being sufficient enough to change the Huai River's main channel waters (only 2.3 mm on 17 July at upriver sites 8 and 9); also, the high air temperatures on 17 and 18 July (29.6°C to 30.6°C, Table 1) might cause the intensive evaporation of river water and decreased the water $\delta^{18}O$ and δD values at site 10.

As lakes and reservoirs have more intensive evaporation than their confluent rivers and streams, the $\delta^{18}O$ and δD in lake/reservoir waters always have more enriched values than those of their confluent waters (Telmer & Veizer 2000; Gammons *et al.* 2006). In this study, Hongze Lake and Nansi Lake had distinctly higher isotopic values than the Huai River and Nansi Lake's tributaries, respectively (Table 1), and the differences were significant (Table 2). However, the Cl and SO_4 concentrations in these waters did not show significant variance in the comparison (Table 3). These indicate that oxygen and hydrogen isotopes are more sensitive than chemical ions, and thus, it highlights the advantages to using $\delta^{18}O$ and δD as tracers in hydrological studies (Schotterer *et al.* 1993; Kendall & Coplen 2001).

Traditionally, the Huai River main channel serves as a geographic division between southern and northern China in terms of temperature (south-side is subtropic and north-side is warm temperate zone), precipitation (more or less than 750 mm/year), and vegetation (rice and wheat cultivated) distribution. Currently, the northern plain areas in this region have more intensive agricultural and industrial activities than the southern areas, which also produce more pollution in northern areas in this region (Wang & Ongley 2004; Hu *et al.* 2009; Tian *et al.* 2013). In the present study, the surface water $\delta^{18}O$ and δD variations also exhibit apparently spatial differences between south and north areas. Northern waters were enriched while the southern water systems were depleted (Figure 1). In addition, the northern and southern $\delta^{18}O$ and δD differences also exist in the man-made channel of the SNTWP (Figure 1 and Table 1). These surface water isotopes spatial differences, certainly, are affected by the northern and southern differences of temperature, precipitation, evaporation, etc. The Cl and SO_4 concentrations in northern tributaries (Shaying River and Guo River) were obviously higher than those in southern tributaries (Shi River and Pi River) (Table 1). Similar north and south variations also exist in the SNWTP water Cl and SO_4 (Tables 1–3). These results might be mostly due to higher pollution in the northern plain (intensive agricultural and industrial activities) of this region (Wang & Ongley 2004; Hu *et al.* 2009; Tian *et al.* 2013).

River water isotopic variations along the flow direction

It is expected that upriver waters have lower $\delta^{18}O$ and δD values than downriver waters (Simpson & Herczeg 1991; Ramesh & Sarin 1992; Telmer & Veizer 2000; Dalai *et al.* 2002; Yuan & Miyamoto 2008), but different studies addressed this with various explanations. For instance, Simpson & Herczeg (1991) concluded that the increasing $\delta^{18}O$ and δD from upriver to downriver portions of the Murray River (a river in the semi-arid area in Australia) mostly resulted from river water evaporation and heavy isotopic irrigation inflows. Ramesh & Sarin (1992) indicated the increasing $\delta^{18}O$ and δD in upper Ganges River (in India) was due to altitude increases (altitude effect), but lowland isotopic increases resulted from evaporation effects. Dalai et al. (2002) demonstrated the altitude effects resulted in the δ^{18}O variations in the Yamuna River (in India) and its tributaries in high mountain areas. The increasing δ^{18}O and δD from upriver to downriver in the Ottawa River (a river in a humid continental climate area in Canada) are addressed mainly by water evapotranspiration (Telmer & Veizer 2000). The δ^{18}O and δD variations in the Pecos River (a river in the southern Rocky Mountains in the United States) were also mainly caused by evaporation-induced isotopic enrichments, and only two creeks were dominated by groundwater which was also affected by the seepage of the surrounding reservoir (Yuan & Miyamoto 2008).

Since irrigation diversions are always associated with water evaporation, the evaporation process can lead to water δ^{18}O and δD increasing (Simpson & Herczeg 1991; Yuan & Miyamoto 2008; Ahmad et al. 2012). Here we discuss only the evaporation and altitude effects on river isotopic variation. In order to compare the evaporation and altitude effects, we compared our data from the Huai River basin with the published data of other large rivers from different countries (Table 4). Altitude effects on δ^{18}O changes varied between 0.7‰ and 37.8‰ per 1,000 m in those rivers, whereas the evaporation effects on δ^{18}O changes only ranged between 0.4‰ and 3.1‰ per 1,000 km (upper section of Table 4). In the Huai River basin waters, the altitude effects ranged between 7.9‰ and 3,200.0‰ per 1,000 m, but evaporation effects varied between 2.6‰ and 20.0% per 1,000 km (lower section of Table 4). Moreover, the studies on the Murray River (Simpson & Herczeg 1991), Ganges River (Ramesh & Sarin 1992), and Yellow River (Su et al. 2004) revealed that the river waters seasonal δ^{18}O and δD changed as well, and that the evaporation effects on δ^{18}O changes were consistently higher in the hot/warm season and lower in the cold/cool season (Table 4). Thus, these studies indicate the high evaporation effects on river δ^{18}O changes in hot/warm seasons and the contrast in cold/cool seasons. Similar findings on evaporation and temperature effects on river δ^{18}O changes were also reported in US national surface waters' samplings (Kendall & Coplen 2001). These δ^{18}O variations in river waters from different continents, along with this study, indicate that evaporation is a more suitable explanation than altitude effect for δ^{18}O increase from upriver to downriver waters.

LSWL upon δ^{18}O and δD

The δ^{18}O and δD composition of meteoric water and surface waters have been known to vary in a systematic manner (Craig 1961; Ramesh & Sarin 1992; Kendall & Coplen 2001; Dutton et al. 2005). However, the exact relationship between δ^{18}O and δD of precipitation and surface water varies from geographical region to region (Kendall & Coplen 2001; Dalai et al. 2002; Yuan & Miyamoto 2008). Our δ^{18}O and δD data (Figure 4(a) and 4(b)) show a clear linear trend ($\delta D = 5.36\delta^{18}O - 18.39$; $r^2 = 0.84$, $p < 0.01$) that represents the LSWL for the Huai River basin, eastern China. The slope (5.36) and intercept (−18.39) of the Huai River basin LSWL are both between that of the summer Yellow River LSWL ($\delta D = 4.71\delta^{18}O - 22.64$; $r^2 = 0.92$, $p < 0.01$; derived from Su et al. 2004) and the summer Yangtze River LSWL ($\delta D = 7.68\delta^{18}O + 1.59$; $r^2 = 0.98$, $p < 0.01$; derived from Li et al. 2010b). Most points of these three rivers fall below the global meteoric water line (GMWL, $\delta D = 8\delta^{18}O + 10$; Craig 1961), representing the strong summer evaporation effects on δ^{18}O and δD surface waters, which are similar to other river basins that have intensive evaporation in the hot season (Gammons et al. 2006; Yuan & Miyamoto 2008; Ahmad et al. 2012).

Figure 4(b) shows the comparison of internal Huai River basin LSWL with local meteoric water lines (LMWL) of two IAEA stations (Zhengzhou and Nanjing). Theoretically, the LMWL of the Huai River basin should be found between Zhengzhou LMWL and Nanjing LMWL, because Zhengzhou and Nanjing are located near the northern and southern borders of the Huai River basin, respectively (Figure 1). In our study, however, all surface water isotopic data points fall below both Zhengzhou and Nanjing LMWLs. In addition, most northern sites (Shaying River, Guo River, Nansi Lake and its tributaries) fall even below the Huai River basin LSWL. All of this once again highlights the evaporation effects in the Huai River basin with higher evaporation effects seen in the northern waters relative to southern. The high evaporation of northern waters in the Huai River Basin may be due to natural landforms of plains which are cultured as farms (Shao et al. 1989;

Table 4 | Comparison between the upriver and downriver $\delta^{18}O$ values of surface waters in the Huai River basin and other rivers from different continents

River	Country	River flow direction	Total length (km)	$\delta^{18}O$ (‰) Upriver	$\delta^{18}O$ (‰) Downriver	In research Length (km)	In research Drops (m)	$\delta^{18}O$ changes Evaporation effects (‰/10³ km)	$\delta^{18}O$ changes Elevation effects (‰/km)	Sampling period	Data source
Murray River	Australia	E to W	2,370	−7.94	−1.84	2,215	180	2.8	33.9	Jan 1989	Simpson & Herczeg (1991)
				−7.84	−1.03	2,215	180	3.1	37.8	Apr 1989	Simpson & Herczeg (1991)
				−8.30	−5.32	2,215	180	1.3	16.6	Jun 1989	Simpson & Herczeg (1991)
Ottawa River	Canada	W to E	1,160	−11.10	−10.10	900	360	0.9	2.8	Sep 1991	Telmer & Veizer (2000)
			1,160	−12.70	−11.40	900	360	1.2	3.6	May 1992	Telmer & Veizer (2000)
Yangtze River	China	W to E	6,380	−13.80	−8.30	4,090	1,470	1.3	3.7	Aug 2006	Li *et al.* (2010b)
Yellow River	China	W to E	5,460	−13.10	−7.00	3,910	3,290	1.6	1.4	Aug–Sep 2000	Su *et al.* (2004)
				−11.80	−8.80	3,910	3,290	0.8	0.7	Mar–Apr 2001	Su *et al.* (2004)
Danube River	Europe	W to E	2,857	−10.83	−9.65	2,204	300	0.5	3.9	Aug–Sep 2007	Rank *et al.* (2009)
Ganges River	India	W to E	2,700	−9.20	−3.80	2,100	213	1.2	25.4	Mar 1982	Ramesh & Sarin (1992)
				−11.50	−10.60	2,100	213	2.6	4.2	Sep 1982	Ramesh & Sarin (1992)
Yamuna River	India	N to S	1,376	−9.40	−7.80	1,376	1,450	0.4	1.1	Jun 1999	Dalai *et al.* (2002)
Indus River	Pakistan	NE to SW	2,900	−12.8	−7.5	2,000	2,430	2.7	2.2	Jan–Jun 2003	Ahmad *et al.* (2012)
Missouir River	United States	NW to ES	3,690	−17.60	−10.90	3,246	950	2.1	7.1	1984–1987	Winston & Criss (2003)
Pecos River	United States	N to S	1,400	−6.00	−3.90	1,400	1,800	1.5	1.2	Mar 2005	Yuan & Miyamoto (2008)
				−4.80	−3.10	1,400	1,800	1.2	0.9	May 2005	Yuan & Miyamoto (2008)
Huai River	China	W to E	1,000	−7.5	−5.0	600	52	4.2	48.1	Jul 2008	This study
Shayin River	China	N to S	620	−6.9	−5.0	150	15	12.7	126.7	Jul 2008	This study
Guo River	China	N to S	420	−5.8	−4.8	300	31	3.3	32.3	Jul 2008	This study
Shi River	China	S to N	220	−6.7	−6.4	90	6	3.3	50.0	Jul 2008	This study
Pi River	China	S to N	260	−7.8	−7.5	130	38	2.6	7.9	Jul 2008	This study
North part of SNWTP	China	N to S	390	−6.5	−3.1	390	23	8.7	147.8	Jul 2008	This study
South part of SNWTP	China	S to N	160	−6.8	−3.6	160	1	20.0	3,200.0	Jul 2008	This study

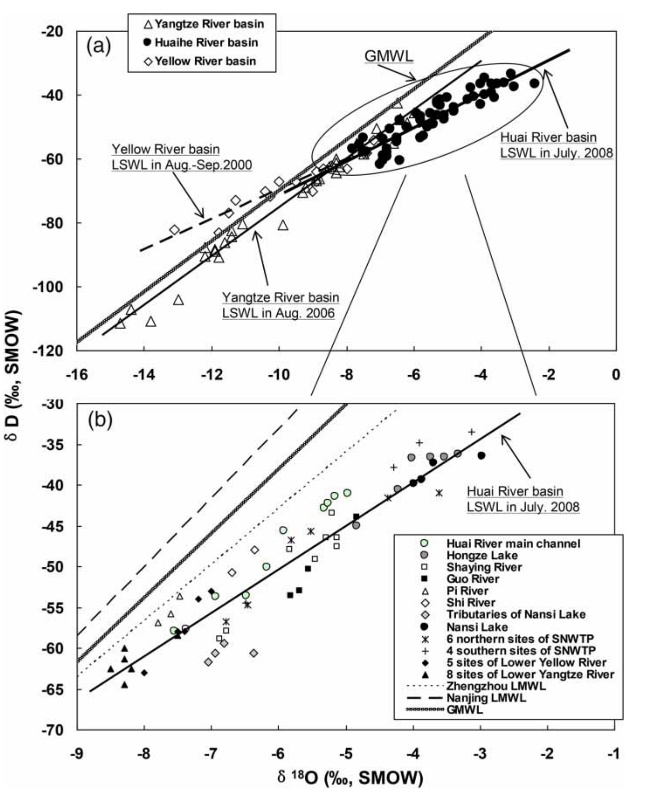


Figure 4 | Local surface water line (LSWL) for the Huai River basin. (a) GMWL (Craig 1961) and LSWLs of the Yellow River basin and Yangtze River basin (data from Su *et al.* (2004) and Li *et al.* (2010a, 2010b)) are shown for reference. (b) Comparison of different waters around the Huai River basin LSWL ($\delta D = 5.36\delta^{18}O - 18.39$; $r^2 = 0.84$), and GMWL and LMWLs of Zhengzhou and Nanjing (data from IAEA (2010)) are shown for reference.

Ge *et al.* 2006). Also, it could be due to less forest cover percentages in the northern plains than the southern mountainous areas in this region (Wang & Ongley 2004).

The Huai River basin LSWL (slope and intercept) falls between the southern Yangtze basin LSWL and the northern Yellow River basin LSWL, and there are obvious isotopic differences that exist between south and north waters inside this region (Figures 1 and 4). These may be an indication that the Huai River main channel is the $\delta^{18}O$ and δD 'boundary' between southern and northern China, and the three LSWLs show a progression of increasing slope and intercept, moving from southern to northern China. Based on these results, along with those of our report on the spatial differences in ionic chemistry of this region (Zhang *et al.* 2011), we suggest that the main channel of the Huai River is likely the geographic division line of surface water isotopic and ionic chemistry for eastern China in addition to its already acknowledged role as a geographic division line for temperature, precipitation, and vegetation distribution (Wang & Ongley 2004).

Characteristics of deuterium excess

Deuterium excess (*d*-excess) was defined by Dansgaard (1964) as $d = \delta D - 8\delta^{18}O$, and the *d* value is typically close to +10‰ for precipitation samples in temperate climates (i.e., the δD intercept of the GMWL). Sites dominated by continental vapor (e.g., Mongolia) have decreasing *d*-excess with decreasing $\delta^{18}O$, whereas *d*-excess decreases with increasing $\delta^{18}O$ in sites dominated by oceanic moisture masses (Schotterer *et al.* 1993; Araguás-Araguás *et al.* 1998). In the present study, the surface waters' $\delta^{18}O$ show a significantly negative correlation to *d*-excess ($r = 0.76$, $p < 0.01$; Figure 5), which indicates that this region is dominated by the Pacific oceanic moisture masses in the summer (Araguás-Araguás *et al.* 1998; Yamanaka *et al.* 2004).

Surface water *d*-excess values can vary significantly from geographical region to region because the surface water in a given place can be influenced by various issues. For example, the river waters from arid western US areas have much lower *d*-excess values (below −2) compared to the humid eastern US river waters (above 10) (Kendall & Coplen 2001). The *d*-excess values of the Kachura site on the Indus River were obviously lower than other sampling sites, exhibiting the evaporation effects of Kachura Lake (Ahmad *et al.* 2012). Eastern Canadian surface water

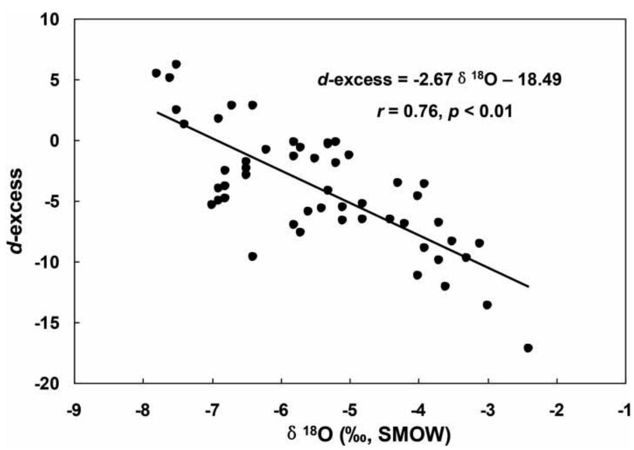


Figure 5 | Relationship between the *d*-excess and $\delta^{18}O$ in the surface waters of the Huai River basin.

d-excess values were higher in coastal areas (Newfoundland and Nova Scotia) but lower in the waters from western inland areas (Labrador and Quebec), because the two areas are controlled by recycled moisture and land evaporation, respectively (Timsic & Patterson 2014). In this study, only five sites from two southern rivers (Shi River and Pi River) and four sites from the upriver Huai River main channel had positive *d*-excess values (1.3 to 6.2). All 43 of the remaining sites had negative *d*-excess values and much lower *d*-excess values in Hongze Lake (−9.7 to −4.6) and Nansi Lake (−17.2 to −8.9) compared with their water source rivers (Table 1). These low *d*-excess values in this region and much lower values found in lake samples demonstrate the intensive evaporation of this region in the summer season. Our current regional study can be comparable to previous large-scale surface water isotopic research (Kendall & Coplen 2001; Ahmad *et al.* 2012). However, the water *d*-excess values of the southern section of the SNWTP (sites 34 to 37) were lower than the values from the two southern rivers (Shi and Pi, sites 17 to 21). These findings are the converse to previous studies in eastern Canadian waters, in which *d*-excess values were higher in coastal water but lower in inland areas waters (Timsic & Patterson 2014). It suggests that oceanic moisture effects above the SNWTP south section (sites 34 to 37) may not be as strong as the moisture effects above the Shi River and Pi River (sites 17 to 21), or the evaporation effects in former areas are greater than the latter area.

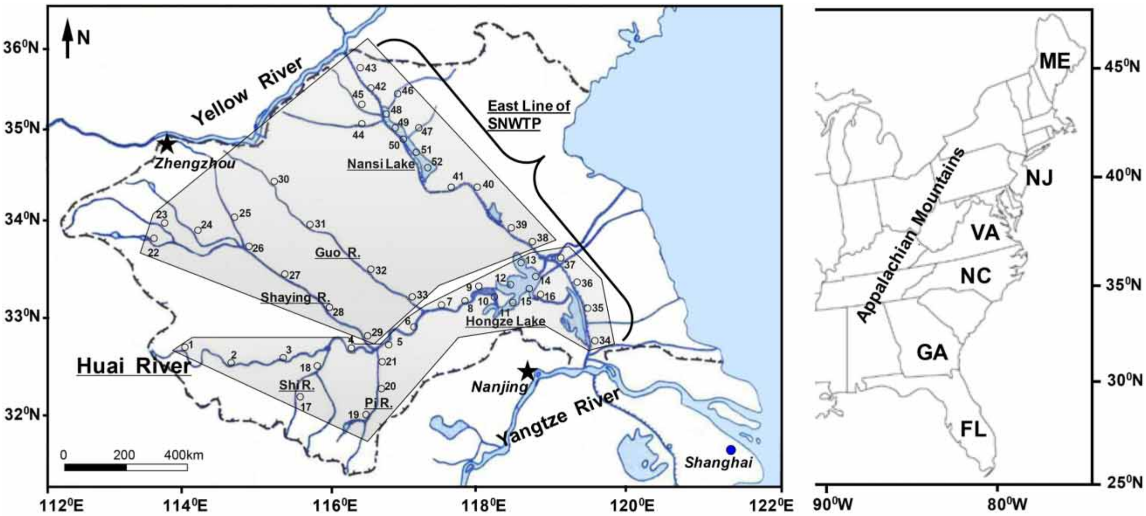
Latitude effects on the slopes of LSWLs

Based on more than 4,800 river water samples across 50 states of the United States, Kendall & Coplen (2001) published the slopes and intercepts of the local river water lines (LSWL, $\delta D = (\text{slope})\ \delta^{18}O + \text{intercept}$. Note: although Kendall & Coplen (2001) used the term 'LWML', they clearly indicated that regressions were calculated from river water isotopic data, which is the same as LSWL in our study). Rivers in the eastern United States, which are derived from the Appalachian Mountains and flow into the Atlantic Ocean, are largely controlled by the North American monsoon (Kendall & Coplen 2001) and can be compared with eastern Chinese rivers that are derived from the western mountains and controlled by the East Asian monsoon. Here, we compare the LSWLs of rivers in eastern China and the eastern United States and present the results in Figure 6. Given the preceding discussion of spatial differences between northern and southern waters in the Huai River basin, we separated the northern waters (Shaying River, Guo River, northern six sites of the East Line of the SNWTP, Nansi Lake and its tributaries) and the southern waters (Huai River, Shi River, Pi River, Hongze Lake and four southern sites of the East Line of the SNWTP) of the Huai River basin. This national scale comparison shows that river elevation slopes of LSWLs of both eastern China and the eastern United States increased northward (Figure 6). This is independent of the comparison between separate Chinese rivers or larger-scale areas in China (northern and southern halves of the basin) or the United States (state by state). Kendall & Coplen (2001) speculated that the extent of evaporative fractionation of rainwater could impart a distinctive LSWL within a certain area/region, and although they indicated the 'latitude effects' on large-scale (e.g., national) river water $\delta^{18}O$ variations, they did not point out that the slopes of LSWLs in the eastern USA (east of the Appalachian Mountains) increased northward.

Comparing the slopes of LSWLs of rivers from both eastern China and the eastern United States, our study proposes a new hypothesis of latitude effects on the river water line slopes on a large scale (using $\delta^{18}O$ and δD values). The slopes of regional LSWLs increase with increasing latitude when regions have similar surrounding landforms. It is rare to be able to couple regions from across the globe; however, due to the similarity in landforms, latitudes, and coastlines, the plains of eastern China and the eastern United States can be coupled together as monsoon-influenced areas. This novel hydrological theory may be tested in other comparable areas, such as eastern Africa and eastern South America if corresponding large-scale data can be found.

CONCLUSIONS

The results of this study show the stable isotope composition of surface waters from the Huai River basin in China. The isotopic and anionic data indicate the difference between northern and southern waters in this region. Northern



Inside Huai River basin

Area	LSWL Slope	LSWL Intercept	r^2	n
North Areas	5.80	-18.15	0.88	27
South Areas	5.22	-16.89	0.94	25

East China (N ↓ S)

River	LSWL Slope	LSWL Intercept	r^2	n
Lower Yellow River[a]	10.35	19.61	0.97	5
Huai River Main channel	7.03	-5.67	0.97	10
Lower Yangtze River[b]	6.89	-5.09	0.96	8

East United States[c] (N ↓ S)

State	LSWL Slope	LSWL Intercept	r^2	n
ME	7.1	3.6	0.94	76
NJ	6.9	6.6	0.89	5
VA	6.7	4.3	0.97	53
NC	6.3	2.9	0.96	87
GA	5.5	0.5	0.89	63
FL	5.4	1.3	0.97	73

Figure 6 | Spatial changes in the slopes of LSWLs of eastern China and eastern United States surface waters: lower table shows the comparison in the slopes of LSWLs from north to south in the two countries. Superscript letters a, b, c in the lower table stand for Su *et al.* (2004), Li *et al.* (2010a, 2010b), and Kendall & Coplen (2001), respectively.

waters (Shaying River, Guo River, the six northern sites of the East Line of SNWTP and Nansi Lake and its tributaries) having higher δ^{18}O, δD, Cl, and SO_4 values than southern waters (Shi River and Pi River). The differences are mostly derived from southern and northern precipitation variation, intensive evaporation and irrigation, with little influence from groundwater recharge. The two big lakes in this region, Hongze Lake and Nansi Lake, also exhibited higher δ^{18}O and δD composition values than their confluent waters, which also indicate their sensitivity to evaporation relative to that of rivers.

The δ^{18}O variations of eight rivers from different continents and those of the Huai River basin indicate that evaporation is a more plausible interpretation than latitude effect for the seen δ^{18}O increases from upriver to downriver waters. Latitude affects the rough tendency of δ^{18}O values for a number of rivers in a large area, but not for any given river in isolation. The *d*-excess variations in the surface water also point towards the high evaporative enrichments in the Huai River basin in the summer and highlights that lakes are more sensitive to evaporation than rivers. The significant negative correlation between *d*-excess and δ^{18}O also attests that the Huai River basin is dominated by the Pacific oceanic moisture masses in the summer.

Our δ^{18}O and δD composition data define the LSWL for the Huai River basin, which is one of the first presented LSWL for surface waters in eastern China. Compared with published data from the Yellow River and Yangtze River, the Huai River basin LSWL slope and intercept hold the middle positions from all three rivers/basins, suggesting that the Huai River could be the geographic division between southern and northern China. Furthermore, the comparison between the LSWLs of eastern China and the eastern United States raises a hypothesis that slopes of LSWLs increase as a result of increasing latitude. This novel hydrological theory may be tested in other coupled comparable areas in the world if corresponding large-scale data can be found.

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