Supporting Information

Tracking Nitrogen Sources, Transformation and Transport at a Basin Scale With Complex Plain River Networks

Qitao Yi[2,3], Qiuwen Chen[1,2*], Liuming Hu[1], Wenqing Shi

[1] Center for Eco-Environment Research, Nanjing Hydraulic Research Institute, Nanjing 210098, China

[2] Research Center for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing 100085, China

[3] School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, China

[*]Corresponding author: Hujuguan 34, Nanjing 210098, China. Tel./Fax: +86 25 85829765, E-mail: qwchen@nhri.cn

Number of pages: 17

Number of additional text: 1

Number of figures: 10

Number of table: 4

MATERIALS AND METHODS

Study area. The basin includes parts of Jiangsu Province, Zhejiang Province and Shanghai City. The topography of the basin is composed of 80% low alluvial plains and 20% mountains or hills. The Taihu basin has a typical subtropical monsoon climate, with distinct seasons and abundant rainfall. The annual average temperature and precipitation is 16 ^{o}C and 1177 mm respectively. The rainy season is concentrated in the summer months of June, July and August, and the dry season is in winter in December, January and February.

The basin is divided into eight parts in terms of hydraulic characteristics (Figure.1b). The northern and western parts, including the Huxi part, Zhexi part and Wu-Xi-Chen part, are upstream areas flowing into Lake Taihu; while the others in the eastern and southern parts are the downstream areas flowing out of the lake. The river network is well developed and more than 200 main rivers crisscross the basin. The total river length is 120,000 km and the river density is 3.2 km/km^2.

The lake water table is fully regulated by hydraulic structures, serving flooding control, navigation and ecological functions. In the stud area,the main rivers are composed of natural rivers and man-made canals between cities. There are a number of gates installed to regulate water exchange between the Yangtze River and Lake Taihu through coastal rivers. Storm water from the study areas was discharged into the Yangtze River during the high flow period, and water was diverted from the Yangtze River into Lake Taihu during the low flow periods.

Water quality analysis. Temperature (T), pH, dissolved oxygen (DO), and electricity conductivity (EC), were measured in-situ using YSI electrodes (Xylem Company, New York, USA). The water samples were stored in an icebox, brought to the laboratory and analyzed immediately. TN, total dissolved nitrogen (TDN) and the dissolved inorganic nitrogen (DIN) forms of nitrate (NO_3-N), nitrite (NO_2-N), and ammonium (NH_4-N) were analyzed in the lab. Samples for TDN and DIN, and chloride (Cl^-) were filtered through pre-rinsed 0.45-µm cellulose ester filters. TN analyses were examined using a UV colorimetric method after alkaline persulfate digestion for TN and TDN with raw and filtered water samples, respectively. The NO_2-N was determined using diazotization with sulfanilamide dihydrochloride. The NO_3-N, NH_4-N, and Cl^- were analyzed by ion chromatography (ICS-2000, Dionex Company, USA).

Table S1 List of rivers and sampling sites in the study area for the analysis of water quality and dual stable isotopes of nitrate in the upstream river network of Lake Taihu, China.

General flow direction	Rivers	Traditional Chinese name	Sampling sites
West to East	The Yangtze River	The Changjiang River	YZR1, YZR2, YZR3, YZR4, YZR5 (green)
	The Beijing-Hangzhou Grand Canal	The Jinghangyunhe River	J1, J2, J3, J4, J5 (dark brown)
	The north part of the Yixing-Liyang City Canal	The Beixihe River	B1, B2, B3 (yellow)
	The south part of the Yixing-Liyang Canal	The Nanxihe River	N1, N2, N3, N4, N5 (yellow)
	The Xiaxihe River	-	XX (black)
	The Lake Taihu-Lake Gehu Canal	The Taigeyunhe River	TG (black)
North to South	The Danyang-Jintan-Liyang Canal	The Danjinlicaohe River	D1, D2, D3 (red)
	The Biandan-Mengjin River	-	BD, MJ (purple)
	The Wujin-Yixing Canal	The Wuyiyunhe River	W1, W2 (brilliant blue)
	The Wuxi-Liyang Canal	The Xilicaohe River	XL (brilliant green dot)
	The Yonganhe River	-	YA (black dot)
Coastal Rivers along the Yangtze River (Regulated by gates)	The Xichen Canal	The Xichengyunhe River	G1 (Gate 1, blue), XC (black)
	The Caoganghe River	-	G2 (Gate 3, blue)
	The Deshenghe River	-	G3 (Gate 4, blue)
	The Xinmenghe River	-	G4 (Gate 4, blue)
	The Jiuquhe River	-	G5 (Gate 5, blue)
Lake Taihu inflowing river mouths	The ports of Wuxi, Hangdu, Dapu, Chengdong, Hongxiang, Guandu, Jiaodu, Shedu, Hengtang, Shaoxiang, Yincun, Caoqiao, and Taige inflowing rivers in sequence		M1~M13 (grey)

Note: The colors in brackets of last column refer to Figure 1 for differ sampling sites among rivers.

Table S2 Proportion of land use at each category for statistics of dual isotopes of nitrate

Category	Grassland	Building land	Arable land	Forest	Waters	Unused land
AGR	0.10%	11.4%	70.7%	6.9%	10.4%	0.49%
HBR	0.15%	19.1%	57.4%	9.4%	13.5%	0.48%
UBR	0.12%	36.5%	49.6%	8.4%	5.2%	0.12%

Note: The land use data was obtained from the Land Cover data of the GlobeLand30 product (http://www.globallandcover.com/). It is at the spatial resolution of 30 m and covers the area within 80°N and 80°S. Land use was easily categorized into three types related to the spatial patterns of isotopic data: the agricultural areas (AGR) in the upstream, hybrid areas (HBR) of agricultural land and small cities or populated towns in the midstream, and highly urbanized areas (UBR) in the downstream; they have averaged proportions of building areas of 11.4%, 19.1% and 36.5% in average, respectively.

Table S3 End-members of $\delta^{15}N$ and $\delta^{15}O$ designated for the mixing models estimating pollution sources of nitrate.

Sources	June of 2015	October of 2015	January of 2016
Soils	$\delta^{15}N$ = +4.1 ± 0.8‰ (n=10); $\delta^{18}O$ = +0.6 ± 1.1 ‰ (n=9)	$\delta^{15}N$ = +4.1 ± 0.8‰ (n=10)	$\delta^{15}N$ = +4.1 ± 0.8‰ (n=10)
Sewage/Manure	$\delta^{15}N$=+13.3± 3.8‰(n=9); $\delta^{18}O$ = +0.6 ± 1.1 ‰ (n=9)	$\delta^{15}N$=+13.3± 3.8‰ (n=9)	$\delta^{15}N$=+13.3± 3.8‰ (n=9)
Atmospheric deposit	$\delta^{15}N$ = +0.7 ± 1.3 ‰ (n=7); $\delta^{18}O$ = +58.0 ± 3.1 ‰ (n=7)	-	-

Note: n is the number of samples for statistics; "-" indicated that atmospheric deposit nitrate was not included in the mixing model. During summer, nitrate arises from atmospheric deposit, sewage/manure-derived nitrate that has been nitrified or partially denitrified, and microbial nitrate derived from ammonium in fertilizer/rain and soil nitrogen. During winter, only soils and sewage/manure are counted due to negligible rainfall impacts. During autumn, nitrate sources from soils, sewage/manure and the Yangtze River were counted due to a large amount of diverted water from the Yangtze River. In this period, the soil source and Yangtze River source were grouped together because of their similar $\delta^{15}N$ signatures. The end-member of $\delta^{15}N$ and $\delta^{18}O$ for sewage source was obtained by counting three samples of raw sewage and six samples of treated sewage together, with signatures of $\delta^{15}N$ = +18.0 ± 1.1‰ and $\delta^{18}O$ = +1.9 ± 0.6 ‰, and +10.9± 0.6 ‰ and $\delta^{18}O$ = +0.0 ± 0.7 ‰, respectively[28]. This end-member considered an average scale for mixing treated and untreated sewage.

Table S4 Water quality and nitrogen forms during three sampling campaigns in the upstream river networks of Lake Taihu.

Season	Stat	T (°C)	pH	DO (mg L^{-1})	EC (us cm^{-1})	Cl^- (mg L^{-1})	TN (mg L^{-1})	TDN (mg L^{-1})	NH_4-N (mg L^{-1})	NO_2-N (mg L^{-1})	NO_3-N (mg L^{-1})
Jun 2015	Min	25.1	7.0	1.9	284	16	2.2	1.3	0.0	0.1	0.0
	Max	26.6	7.8	6.0	630	115	6.9	5.8	0.6	0.9	2.6
	Mean	26.1	7.5	4.1	409	41	3.4	2.4	0.2	0.2	1.0
Oct 2015	Min	21.0	7.8	3.3	311	15	1.7	0.3	0.0	0.0	0.3
	Max	24.9	8.8	8.5	854	212	9.4	8.9	0.9	0.6	3.9
	Mean	22.4	8.2	6.3	488	67	3.5	2.7	0.2	0.2	1.6
Jan 2016	Min	6.4	8.2	5.7	206	13	2.4	2.0	0.1	0.0	0.2
	Max	14.4	9.4	10.5	704	183	9.3	7.7	2.1	0.3	4.9
	Mean	8.0	8.6	9.2	391	63	5.1	4.4	0.9	0.1	2.0

Note: stat, statistical values; Min, minimum values; Max, maximums values; Mean, average values. T, temperature; DO, dissolved oxygen; EC, electricity conductivity; TN, total nitrogen; TDN, total dissolved nitrogen.

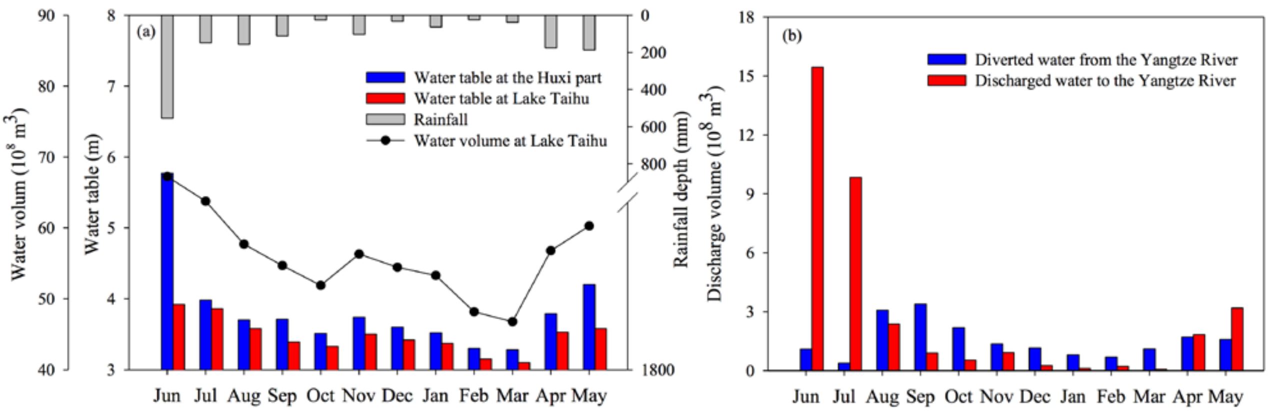

Figure S1. Water regime in the study area during the period from June of 2015 to May of 2016. (Note: Water storage at Lake Taihu corresponded to the rainfall depth and water table is shown in panel a, and water exchange with the Yangtze River through water gates at coastal rivers is shown in panel b. The monthly data at the end of each month was collected from open access reports at the official website of the Taihu Basin Authority.)

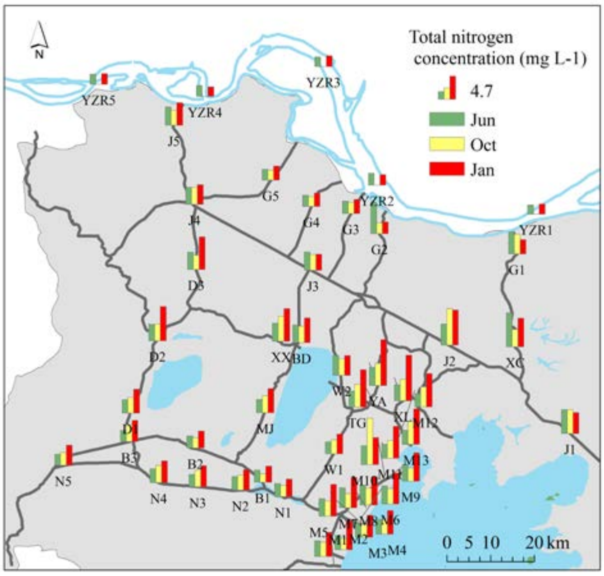

Figure S2. Spatial distribution of total nitrogen concentration in June, October of 2015 and January of 2016.

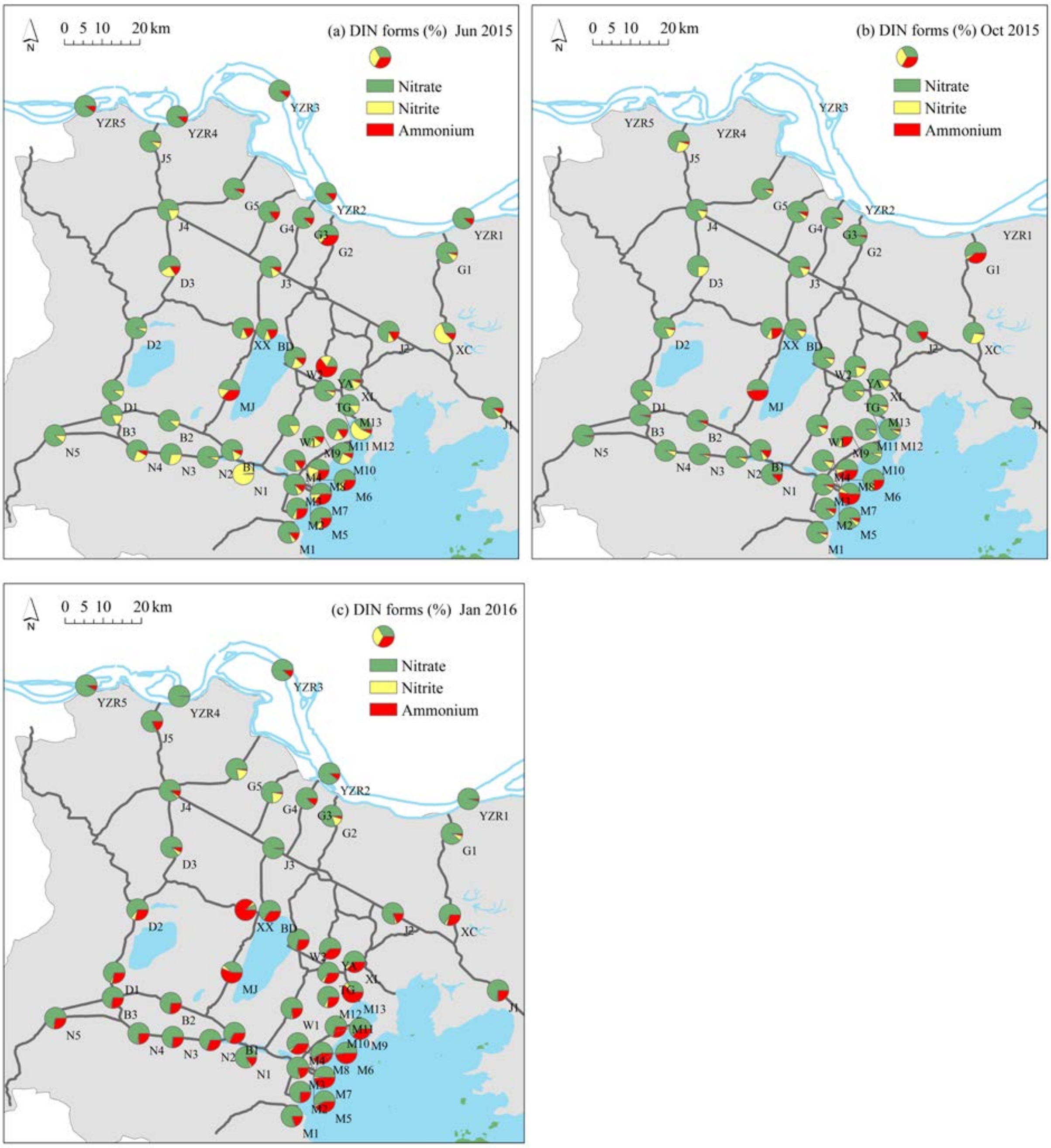

Figure S3 Spatial distribution of dissolved inorganic (DIN) forms in June of 2015 (a), October of 2015 (b) and January of 2016 (c).

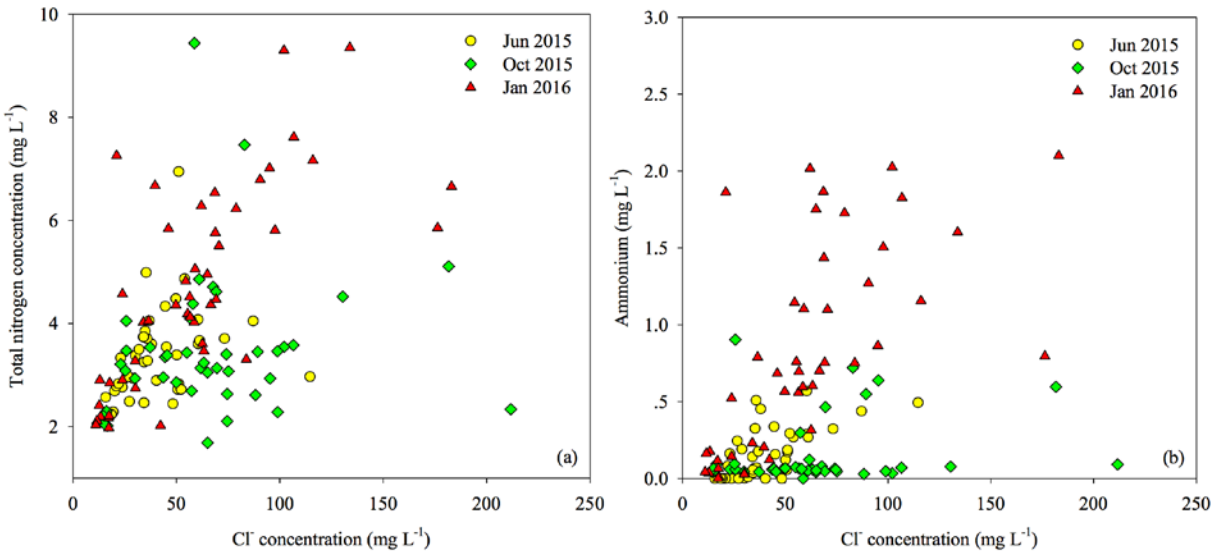

Figure S4. Relationships between chloride ion and total nitrogen (a), and ammonium (b) in water samples in June of 2015, October of 2015, and January of 2016. (Note: the linear equations of total nitrogen and ammonium versus chloride in January of 2016 are: y=0.025x+2.45, R=0.436 (p<0.01); and y=0.0059x-0.077, R=0.588 (p<0.01), respectively. There are no significant relationships in June and October of 2015. R is the Pearson correlation coefficient at confidence levels of 99% (p<0.01).)

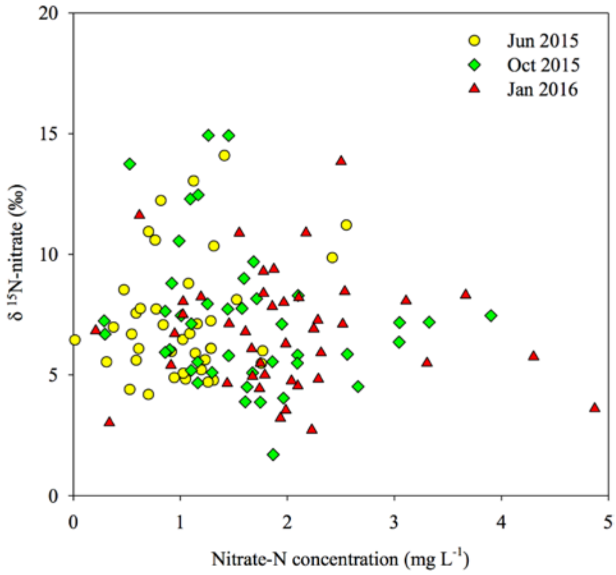

Figure S5. δ^{15}N-nitrate versus nitrate concentration for all samples in June, October of 2015 and January of 2016 (Note: there is no significant relationships between nitrate and δ^{15}N-nitrate according to the Pearson correlation analysis at confidence levels of 95% (p<0.05) or 99% (p<0.01).)

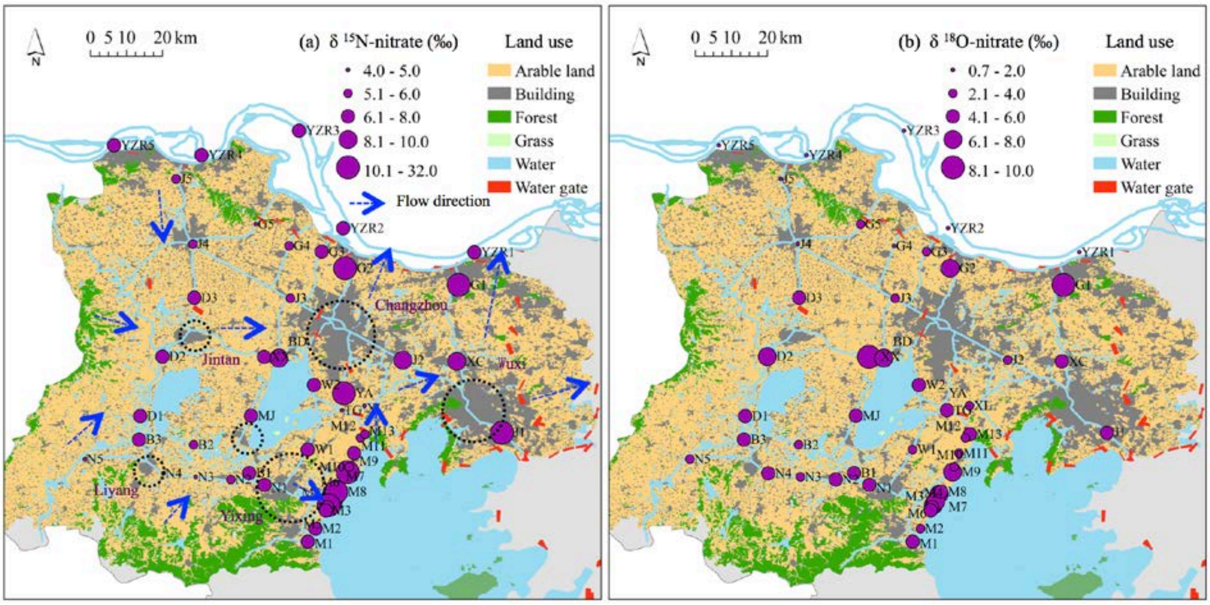

Figure S6. Spatial distribution of δ^{15}N-nitrate (a) and δ^{18}O-nitrate (b) in the upstream river network of Lake Taihu during the high flow in June of 2015.

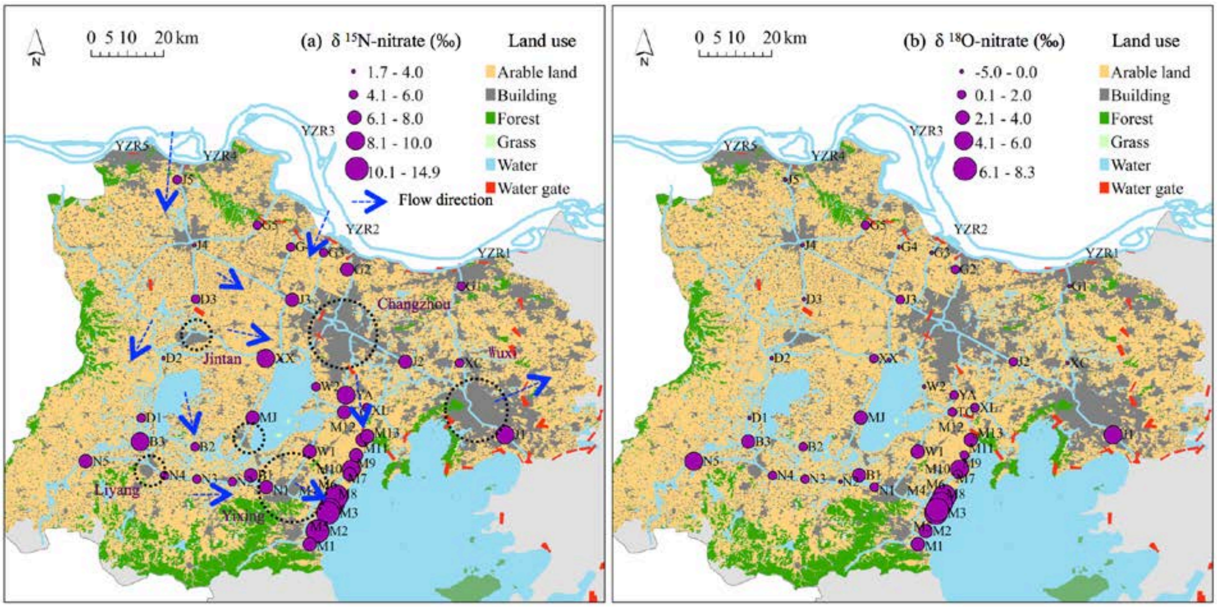

Figure S7. Spatial distribution of δ^{15}N-nitrate (a) and δ^{18}O-nitrate (b) in the upstream river network of Lake Taihu during low flow in October of 2015. (Note: Water diversion from the Yangtze River occurred during the sampling campaign.)

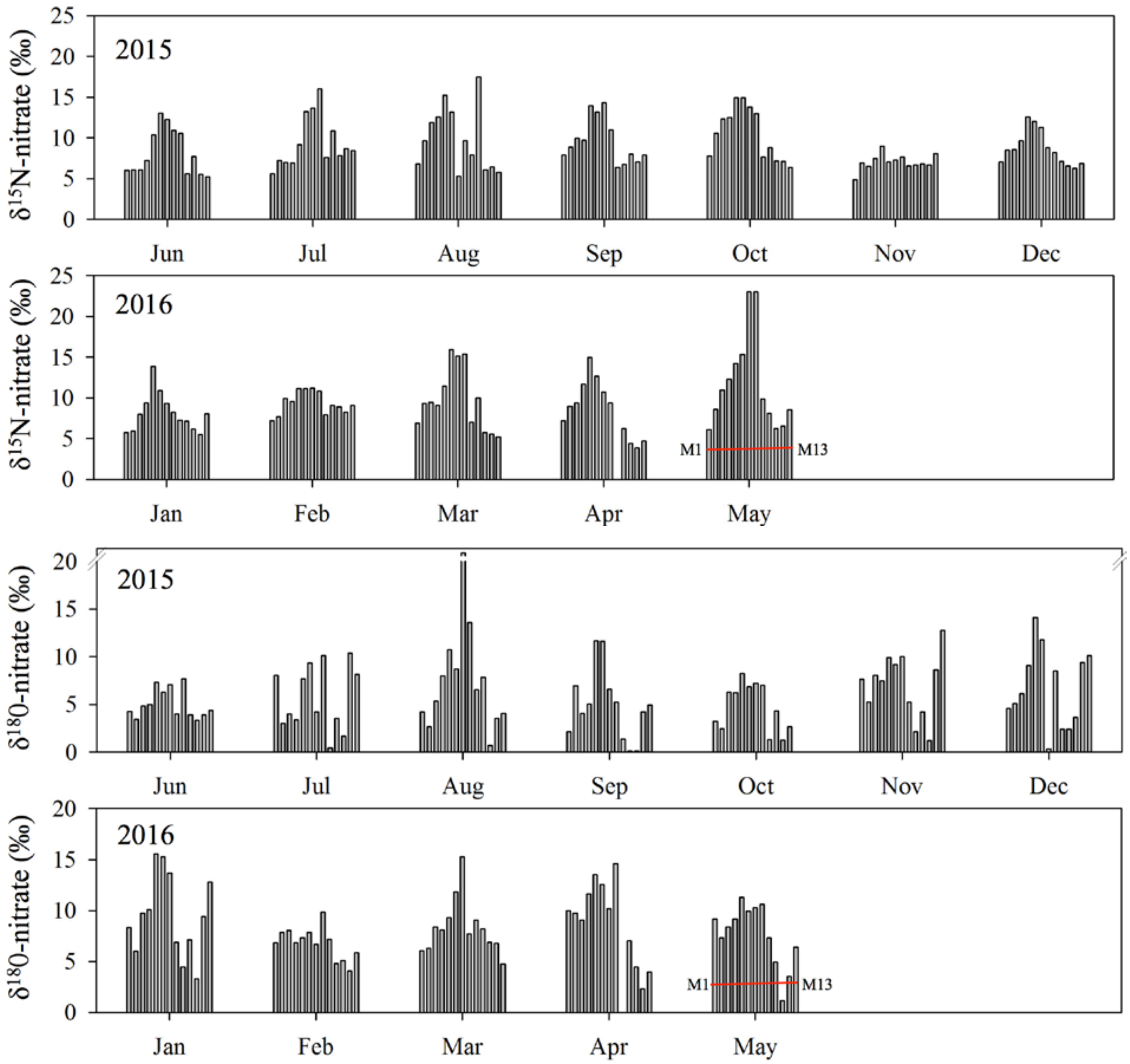

Figure S8. Monthly data of δ^{15}N-nitrate and δ^{18}O-nitrate in the inflowing rivers from June of 2015 to May of 2016. (Note: there is inverse flow out of the lake at M13 in June of 2015 due to high water level in the lake and discharge towards the Yangtze River.)

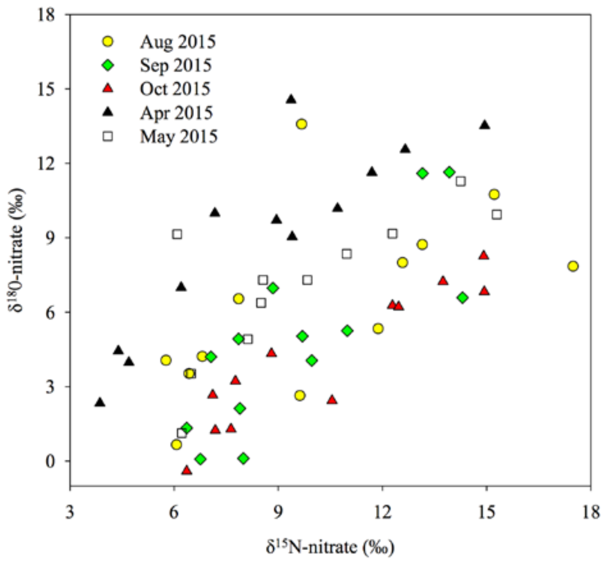

Figure S9. δ^{15}N-nitrate versus δ^{18}O-nitrate plots for water samples in the inflowing rivers in August, September and October of 2015, April and May of 2016. (Note: the linear equations of δ^{18}O versus δ^{15}N are: y=0.60x+0.62, R=0.590 (p<0.05) in August; y=1.10x-5.67, R=0.812 (p<0.01) in September; y=0.80x-4.13, R=0.892 (p<0.01) in October; y=0.98x+0.61, R=0.916 (p<0.01) in April; y=0.70x+0.33, R=0.746 (p<0.01) in May. R is the Pearson correlation coefficient at confidence levels of 95% (p<0.05) or 99% (p<0.01).)

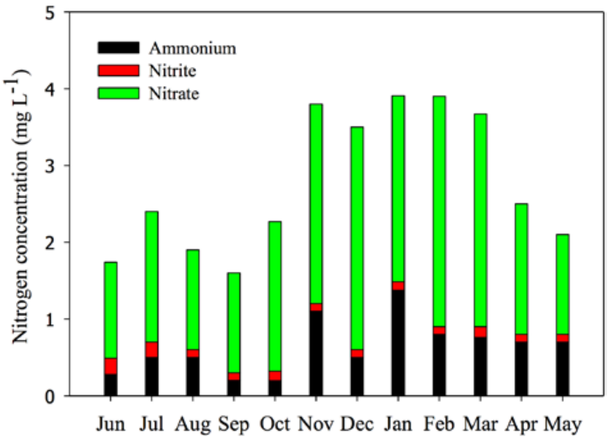

Figure S10 Monthly change of dissolved inorganic nitrogen during the sampling period from June of 2015 to May of 2016.