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# Stable isotopes in water indicate sources of nutrients that drive algal blooms in the tributary bay of a subtropical reservoir

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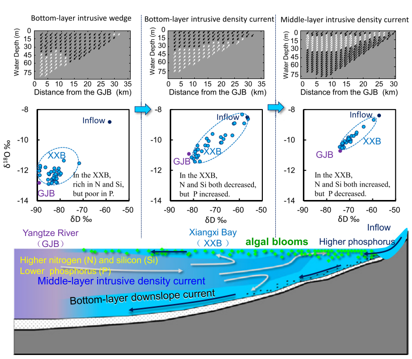
## HIGHLIGHTS

- A mass balance method was established to determine nutrients transportation.
- The nutrients in the tributary bay were mainly from the Yangtze River.
- Efforts to control pollution in one or two tributary basins could be meaningless.
- Phytoplankton succession and biomass could be controlled through changes in density currents.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Eutrophication has become a severe environmental problem in some tributaries of the Three Gorges Reservoir (TGR) in China. A two-year field investigation of nutrients, oxygen stable isotopes ($\delta^{18}O$), and hydrogen stable isotopes ($\delta D$) was performed from January 2010 to December 2011 to determine the sources of nutrients in Xiangxi Bay (XXB). The results showed that nitrogen, phosphorus and silicon varied seasonally depending on hydrodynamic changes. The bottom-layer intrusive density current decreased nitrogen and silicon concentrations and increase phosphorus concentrations in XXB, while the middle-layer intrusive density current increased nitrogen and silicon concentrations and decrease phosphorus concentrations. The differences in $\delta^{18}O$ and $\delta D$ among the Yangtze River (YR), XXB and the region upstream of XXB were significant, and according to the tracer method, the estimated contribution ratios of nitrogen, phosphorus and silicon from the YR to XXB were much larger than those from the region upstream of XXB. These findings suggest that water quality in the TGR can be improved by reducing the pollution load throughout the upstream basin of the YR but not through decentralized efforts in only one or two tributary basins.



## 1. Introduction

Algal blooms have become one of the most important ecological problems in the tributary bays of the Three Gorges Reservoir (TGR) in China (Stone, 2008; Zhou et al., 2009). Generally, regional nutrient enrichment is a critical factor leading to eutrophication and algal blooms, but nutrient concentrations have shown slight declines in the main

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stream since the Three Gorges Dam (TGD) was built (Fu et al., 2010). This suggests that nutrients are not the factor limiting algal blooms in the TGR, and the slower flow caused by the TGD is considered the driving factor of eutrophication (Fu et al., 2010; Xu et al., 2010). In fact, although there were previously no algal blooms in the Yangtze River (YR), the water was rich in nutrients both before and after the TGD was completed (Huang et al., 2014; Lou and Yin, 2016; Ran et al., 2017), and subsequent research has found a significant relationship between phytoplankton in some tributary bays and the levels of nitrogen (N) and phosphorus (P) during the rainy season (Ye et al., 2007; Zheng et al., 2006). Silicon (Si) is one of the most important nutrients affecting the metabolism of diatoms (Darley and Volcani, 1969), and its levels have also been shown to significantly correlate with chlorophyll *a*, especially when the phytoplankton biomass is dominated by diatoms (Ye et al., 2007). Therefore, the N:Si and N:P ratios could determine spring algal blooms in the TGR (Ye and Cai, 2012; Ye et al., 2007), but the mechanism driving nutrient enrichment in the tributary bays, especially the identity of the main source, remains controversial.

Nutrients in the tributary bays were first considered to originate from point and non-point sources of pollution in the basins (Ye et al., 2009). For example, some scholars have shown that almost 95% of the P in Xiangxi Bay (XXB) comes from upstream inflow, as does 61% of the N (Li et al., 2008), and increases in those nutrients due to changes in land use and management were thought to cause eutrophication in XXB (Li et al., 2009; Ye et al., 2009). However, other researchers have noted that nutrient levels in some tributary bays are more affected by the main stream of the YR (Holbach et al., 2014; Luo et al., 2007; Yang et al., 2015), and the contribution of nutrient flux from the basin of the tributary has been estimated to be <3% (Huang et al., 2014). The recently discovered layered bidirectional density currents (LBDCs) provide powerful evidence for use in identifying effects from the YR (Ji et al., 2017; Yang et al., 2010). However, the effects of different types of LBDCs on nutrient transport and phytoplankton succession as well as the associated mechanisms remain unclear.

In the present study, field observations of nutrient levels, oxygen isotopes ($\delta^{18}O$), and hydrogen isotopes ($\delta D$) were carried out for two years in XXB. As stable water isotopes can be used as natural conservative tracers to identify water sources (Bogaard et al., 2007), a method using hydrogen and oxygen isotope tracers (Yang et al., 2015) was applied to directly estimate the contribution rates of different water sources to XXB and to indirectly determine their nutrient contribution rates. The aims of this study were to 1) determine the specific relationships between the nutrient variations and different types of density currents and 2) to provide management recommendations for pollution control in the TGR.

## 2. Materials and methods

### 2.1. Research area and sampling sites

The Xiangxi River (XXR) is the largest tributary in the region near the TGD (Fig. 1a); it originates from Shenlongjia Mountain and flows into the main stream of the TGR in Guojiaba. This is an area with a subtropical continental monsoon climate with large temperature differences in spring, frequent cloudy/rainy weather in autumn, concentrated and heavy rains in the summer and occasional snowy conditions in the winter. The average annual temperature is approximately 16.6 °C, and the average annual rainfall and river discharge are 1015.6 mm and 40.18 $m^3 \cdot s^{-1}$, respectively. When the TGR is operated at a water level of 175 m, a covered reach (XXB) caused by the backwater of the TGR extends approximately 40 km from the estuary to Zhaojun Town.

From January 2010 to December 2011, eleven sampling sites (at intervals of approximately 3 km) were established to monitor the temporal and spatial variations in environmental parameters in XXB, and they are designated XX00-XX10 in succession from the estuary to the end of the backwater (Fig. 1b). Another site (abbreviated as GJB) was located at the main stream of the TGR, and there was a site in the upstream natural inflow river of XXB (designated "Inflow").

### 2.2. Monitoring and testing methods

From January 2010 to December 2011, nine parameters, namely, water flow velocity (FV), water temperature (WT), water depth (WD), turbidity (Turb.), total N (TN), nitrate ($NO^-_3$-N), total P (TP), phosphate ($PO^-_4$-P), and dissolved silicate (Si), as well as oxygen isotopes ($\delta^{18}O$) and hydrogen isotopes ($\delta D$), were monitored monthly at the sampling sites XX00-XX10, GJB and Inflow. In addition, the parameters WT, WD, TN, TP, Si, and Turb. were measured once every two days at XX06 for a more detailed analysis.

Two 350-ml bottles of water were collected using a water sampler (QCC15-2.5, Beijing, China) at depths of 0.5 m and 2 m and then at 10-m intervals to the bottom. One was sent to a local laboratory to measure the TN, $NO^-_3$-N, TP, $PO^-_4$-P and Si concentrations according to national standards (China, 1995; Wei, 2002). The other bottle was filtered through a Whatman GF/C filter, and both the water and filter were then stored in a cold box (<5 °C) and transported to the laboratory. The water was used to measure $\delta D$ and $\delta^{18}O$ using a laser absorption water isotope spectrometer analyzer (LWIA V2, Liquid Water Isotope Analyzer; LRG Company, USA) relative to the Vienna Standard Mean Ocean Water (VSMOW) (Graig, 1961). The measurement precision was 0.19‰ and 0.06‰ for $\delta D$ and $\delta^{18}O$, respectively. The parameters WT and Turb. were measured using a Hydrolab DS5X multiprobe sensor (Hydrolab, USA) from the river surface to the bottom at 1-m intervals.

### 2.3. Stable isotope tracing method

(1) Hydrogen and oxygen isotope tracers

In natural water molecules, there are two possible hydrogen (H) isotopes, $^1H$ and D (deuterium), and three possible oxygen (O) isotopes, $^{16}O$, $^{17}O$ and $^{18}O$. These isotopes do not undergo radioactive decay and are therefore widely used to research sources of pollution, the migration of elements and food webs (Bogaard et al., 2007). In this study, D and $^{18}O$ were measured in the water samples and used as tracers to determine water exchange and the supply of nutrients in XXB of the TGR.

As D/H or $^{18}O/^{16}O$ ratios are very low in nature, it is difficult to determine isotopic differences using the data measured in this study. Therefore, relative micrometer differences in D/H or $^{18}O/^{16}O$ between the collected sample and the standard are based on internationally stipulated values and denoted by δ as follows (Hoefs, 2015):

$$\delta X(‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \quad (1)$$

where $R_{sample}$ is the abundance ratio of D/H or $^{18}O/^{16}O$ in the sample; $R_{standard}$ is the abundance ratio of D/H or $^{18}O/^{16}O$ in the international standard; and X indicates D or $^{18}O$. In the present study, the average ocean water was used as the standard material for the water O isotopes.

(2) Two-compartment linear mixing model

The main stream of the TGR (GJB) and the upstream region of XXB (Inflow) are the two main water sources for XXB (Chen et al., 2013; Yang et al., 2015), so according to the mass balance principle, a two-compartment linear mixing model (Clark and Fritz, 1997) can be used