

The oxygen isotopic composition of phosphate as an effective tracer for phosphate sources in Hongfeng Lake

Yongxue Ji^{1,2} · Jingan Chen¹ · Runyu Zhang¹ · Yong Liu^{1,2} · Jingfu Wang¹

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Abstract In order to characterize the oxygen isotopic composition of internal phosphate and explore the possibility of using these data to identify phosphate sources, we measured oxygen isotopic compositions of phosphate ($\delta^{18}\text{O}_p$) in sediment pore water in Hongfeng Lake, a typical deep-water lake in a mountainous area. These data, in combination with $\delta^{18}\text{O}_p$ in surface water samples and water column samples, were successfully used to identify phosphate sources. The $\delta^{18}\text{O}_p$ value of sediment pore water ranged from 15.2‰ to 15.8‰, with an average value of 15.5‰—the $\delta^{18}\text{O}_p$ value of internal phosphate. The $\delta^{18}\text{O}_p$ values decreased gradually through the water column from 19.4‰ in surface water to 16.4‰ in deeper water, implying that internal phosphate had more negative $\delta^{18}\text{O}_p$ values than external phosphate. This finding was substantiated by horizontal variations in $\delta^{18}\text{O}_p$ values, which decreased with increasing distance from inflowing rivers. All collected evidence suggests that external and internal phosphate have distinctly different isotopic signatures and that these signatures have not been considerably altered by biological mediation in Hongfeng Lake. Therefore, $\delta^{18}\text{O}_p$ can be used to distinguish phosphate sources. A two-endmember mixing model showed that internal phosphate had an average contribution of 40%, highlighting the influence of internal phosphorus loading on aqueous phosphate and eutrophication. This study illustrates the need to reduce the internal

phosphorus load from sediment and provides guidance for nutrient management and in-lake restoration treatment in Hongfeng Lake. The data presented here are limited, but serve to highlight the great potential of $\delta^{18}\text{O}_p$ as an effective tracer for identifying phosphate sources. Systematic investigations of the oxygen isotopic compositions of external phosphate, internal phosphate, and phosphate through the water column, in combination with in-lake P biogeochemical cycle study, would be desirable in further research.

Keywords Phosphate source · $\delta^{18}\text{O}_p$ · Eutrophication · Hongfeng Lake

1 Introduction

Lakes are an important source of drinking water. In the past 20 years, lake eutrophication has become one of the most concerning environmental problems in China. A large number of studies have shown that excessive nitrogen and phosphorus (P) inputs are the main causes of eutrophication, and that P is a limiting nutrient in many fresh-water ecosystems (Jickells 1998). Reducing P loading plays a crucial role in controlling eutrophication (Qin 2009; Wu et al. 2008). However, only when the sources are identified and quantified can effective measures be taken to reduce the total P load. Sources of P include external input and internal release from sediment. Despite significant reduction of external P loading, in many lakes the water phosphate levels have not noticeably declined. Phosphorus release from sediment is assumed to be the primary source of P (Marsden 1989; Vandermolen and Boers 1994; Sondergaard et al. 1999, 2003; Rockwell et al. 2005; Burger et al. 2007; Elsbury et al. 2009; Qin 2009).

✉ Jingan Chen
chenjingan@vip.skleg.cn

¹ State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

² University of Chinese Academy of Sciences, Beijing 100049, China

Phosphorus exists in water mainly in three forms: particulate organic phosphorus (POP), dissolved organic phosphorus (DOP) and dissolved inorganic phosphorus (DIP). DIP, mainly consisting of phosphate (PO_4^{3-}), is the most easily utilized component for organisms. Therefore, concentrations and sources of phosphate have always been the focus of eutrophication researchers. So far, there are three widely used methods for the estimation of P release flux from lake sediments: sediment core incubation, in situ benthic chambers, and a diffusive model based on Fick's laws of diffusion (Tengberg et al. 1995; Burger et al. 2007; Ozkundakci et al. 2011). However, all these methods have the following shortcoming: it is difficult to extrapolate their results to whole-lake basins because the tested area is very small relative to the bed of the lake, across which there tends to be high spatial variability (Ozkundakci et al. 2011), especially for deep-water lakes in mountainous areas.

In this study, Hongfeng Lake was selected to systematically investigate the oxygen isotopic composition of phosphate ($\delta^{18}\text{O}_p$) in lake water and sediment pore water. The aims of this work were to: (1) characterize $\delta^{18}\text{O}_p$ for internal phosphate; and (2) explore the possibility of identifying phosphate sources by their oxygen isotopes.

2 Materials and methods

2.1 Study sites

Hongfeng Lake ($26^\circ 26'$ to $26^\circ 35' \text{N}$, $106^\circ 19'$ to $106^\circ 28' \text{E}$) is a typical deep-water lake located in a mountainous area of Guizhou Province, Southwestern China. The surface area is 57.2 km^2 , with a total capacity of $6.01 \times 10^8 \text{ m}^3$ and mean depth of 10.5 m (max 45 m). It has six inflowing rivers including the Maxian, Yangcang, Maibao, Houliu, and Taohuayuan, and one outlet, the Maotiao River. It is monomictic and strongly stratified during the summer, with anoxic hypolimnion from June to September.

Hongfeng Lake supplies drinking water to the provincial capital, Guiyang City, with a population over three million. A slight deterioration in the water quality can cause serious social problems. Previous study found algae blooms have become more frequent in the past ten years due to high P loading. However, it remains unknown how much internal phosphate contributes to the total phosphate load in the lake.

2.2 Sample collection

Surface sediments and lake water were sampled in March 2016. To ensure sufficient sediment pore water for analysis, more than 25 L of surface sediments were collected using a

dredge bucket at Huayudong (HYD) (Fig. 1) at a water depth of 22 m. Seven 20-L water column samples were synchronously taken from the surface to the bottom in 3-m intervals using hydrophore. Surface water samples were collected in a different region of the lake (Fig. 1). Pore water was extracted from the surface sediments through centrifugation immediately after sampling.

2.3 Measurement of the oxygen isotopic composition of phosphate

All water samples, including lake water and sediment pore water, were processed according to the method of McLaughlin et al. (2004, 2006). Briefly, a series of dissolution and precipitation reactions were utilized to isolate and purify dissolved phosphate as silver phosphate. On the basis of reduplicate experiments, we made minor modifications to the McLaughlin et al. method. First, a pH electrode replaced pH-indicator to more precisely monitor pH in situ and ensure enough silver phosphate was formed. Second, the process of dislodging cerium ion and organic matter was repeated twice in the treatment of sediment pore water to reduce impurities. The detailed procedures are shown in Fig. 2.

The $\delta^{18}\text{O}$ value of silver phosphate was measured using an elemental analyzer coupled to an isotope ratio mass spectrometer (EA-IRMS) at the Third Institute of Oceanography, State Oceanic Administration. The $\delta^{18}\text{O}$ value of water was measured by MAT253 mass spectrometer at the Institute of Geochemistry, Chinese Academy of Sciences. All $\delta^{18}\text{O}$ isotopic values are reported using standard delta notation relative to the Vienna Standard Mean Ocean Water and the analytical precision is better than 0.3‰.

3 Results and discussions

$\delta^{18}\text{O}_p$ in sediment pore water was, for the first time, determined in this study. Huayudong sediment pore water $\delta^{18}\text{O}_p$ values ranged from 15.2‰ to 15.8‰, with an average value of 15.5‰, and represent $\delta^{18}\text{O}_p$ of the internal P load. Variations of $\delta^{18}\text{O}_p$ in the water column are shown in Fig. 3. $\delta^{18}\text{O}_p$ decreased gradually from 19.4‰ at the surface to 16.4‰ at a depth of 9 m, and then fluctuated between 14.5‰ and 17.2‰, with an average value of 16.0‰. Since internal phosphate is released from sediment and diffuses into the overlying water, phosphate from sediment can be expected to have a greater impact on $\delta^{18}\text{O}_p$ deeper in the water column than on surface water. Profile variations of $\delta^{18}\text{O}_p$ indicate that internal phosphate should have more negative values than external phosphate. This inference was supported by the spatial variations of

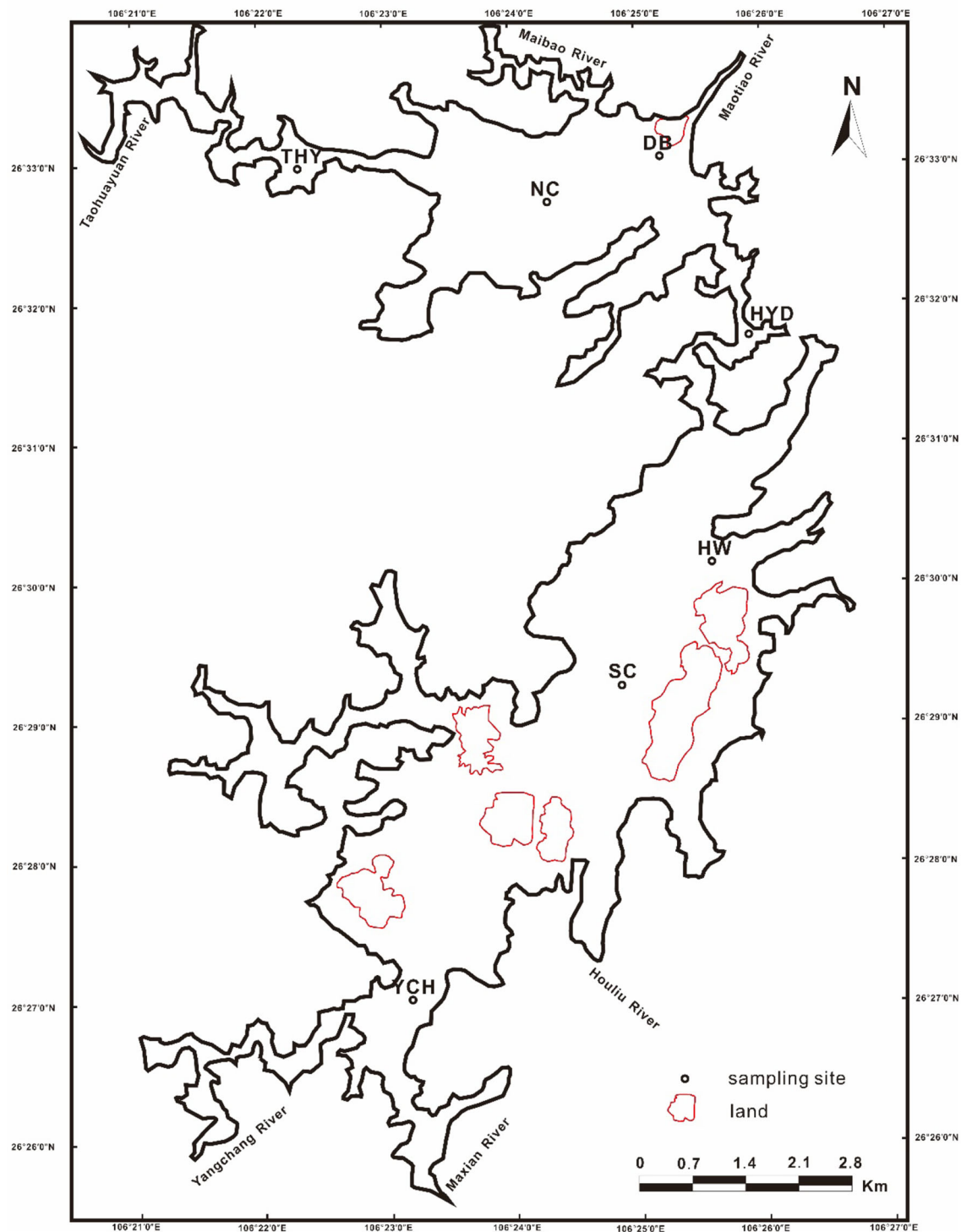


Fig. 1 Location of sampling sites in Hongfeng Lake

$\delta^{18}\text{O}_\text{P}$ values in the surface water of Hongfeng Lake (Fig. 4). In the southern part of Hongfeng Lake, $\delta^{18}\text{O}_\text{P}$ values decreased gradually from upstream to downstream: 21.0‰ at YCH, 20.7‰ at SC, 19.7‰ at HW, 19.4‰ at HYD, and 16.0‰ at DB. $\delta^{18}\text{O}_\text{P}$ values in the north

exhibited similar variation, declining gradually from 20.9‰ at THY to 16.0‰ at DB. Internal phosphate as a percentage of total phosphate increased with increasing distance from the inflowing rivers, thus the decreasing trend of the $\delta^{18}\text{O}_\text{P}$ values from upstream to downstream

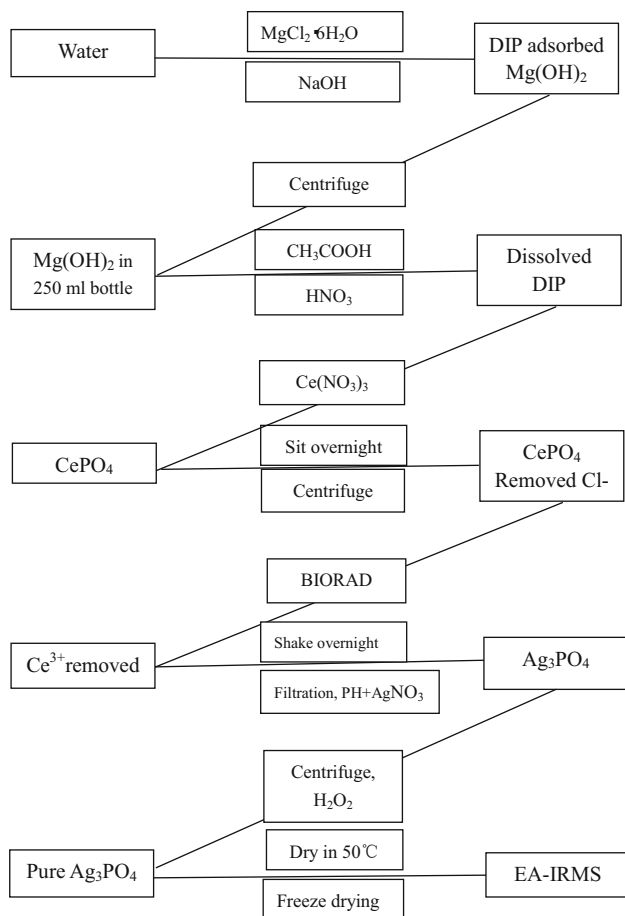


Fig. 2 Procedures for processing dissolved phosphate (modified from the method of McLaughlin et al. 2004)

indicate that the external phosphate has more positive $\delta^{18}\text{O}_\text{P}$ values than the internal phosphate in Hongfeng Lake.

It is well known that the phosphorus-oxygen bond in phosphate is resistant to inorganic hydrolysis at surface water temperatures and pressures and that phosphate only exchanges oxygen with ambient water through biological mediation (Kolodny 1983; Shemesh 1983; Shemesh et al. 1988; Dahms and Boyer 1973; Lecuyer et al. 1999; Paytan et al. 2002; O'Neil 2003; Elsbury et al. 2009). Therefore, $\delta^{18}\text{O}_\text{P}$ truly records the oxygen isotopic signature of the primary phosphate and can be used to trace the phosphate source where biological uptake and recycling through biomass are low (Elsbury et al. 2009). However, two requisites need to be checked before application. First, that $\delta^{18}\text{O}_\text{P}$ values differ greatly across phosphate sources. Second, that there is no significant oxygen exchange between phosphate and ambient water.

The $\delta^{18}\text{O}_\text{P}$ values near the inlets of the inflowing rivers are 21.0‰ at YCH and 20.9‰ at THY. External phosphate has significantly higher $\delta^{18}\text{O}_\text{P}$ values than the internal phosphate in Hongfeng Lake. Previous study has revealed

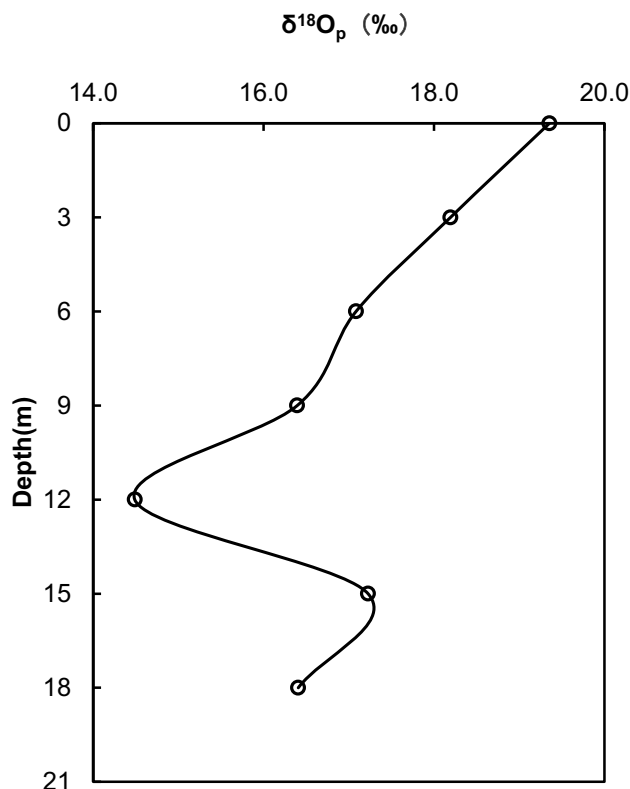


Fig. 3 $\delta^{18}\text{O}_\text{P}$ variations in the water column of Hongfeng Lake

that as biological uptake and recycling increase, $\delta^{18}\text{O}_\text{P}$ will shift toward an equilibrium value between water and phosphate through enzyme-mediated biochemical reactions. At equilibrium, the magnitude of fractionation between water and phosphate is only a function of temperature, and $\delta^{18}\text{O}_\text{P}$ can be calculated based on temperature, the oxygen isotopic composition of ambient water, and a well-established empirically derived fractionation equation (Longinelli et al. 1976; Blake et al. 1997):

$$T(^{\circ}\text{C}) = 111.4 - 4.3(\delta^{18}\text{O}_\text{P} - \delta^{18}\text{O}_\text{w}) \quad (1)$$

where T is the temperature of the water, and $\delta^{18}\text{O}_\text{P}$ and $\delta^{18}\text{O}_\text{w}$ are the oxygen isotopic compositions of phosphate and water, respectively.

The expected $\delta^{18}\text{O}_\text{P}$ equilibrium value is calculated to range from 13.9‰ to 14.7‰ according to the $\delta^{18}\text{O}_\text{w}$ values between -7.5 ‰ and -6.3 ‰ in Hongfeng Lake. Measured $\delta^{18}\text{O}_\text{P}$ values varied from 16.4‰ to 20.7‰, clearly distinct from the equilibrium value and with a large variation. This implies the $\delta^{18}\text{O}_\text{P}$ values are less influenced by biological uptake and recycling in Hongfeng Lake. In fact, many studies have revealed that the oxygen isotopes have not reached equilibrium between phosphate and water in most natural water, especially where residence times are short and phosphate not extensively recycled by the biomass

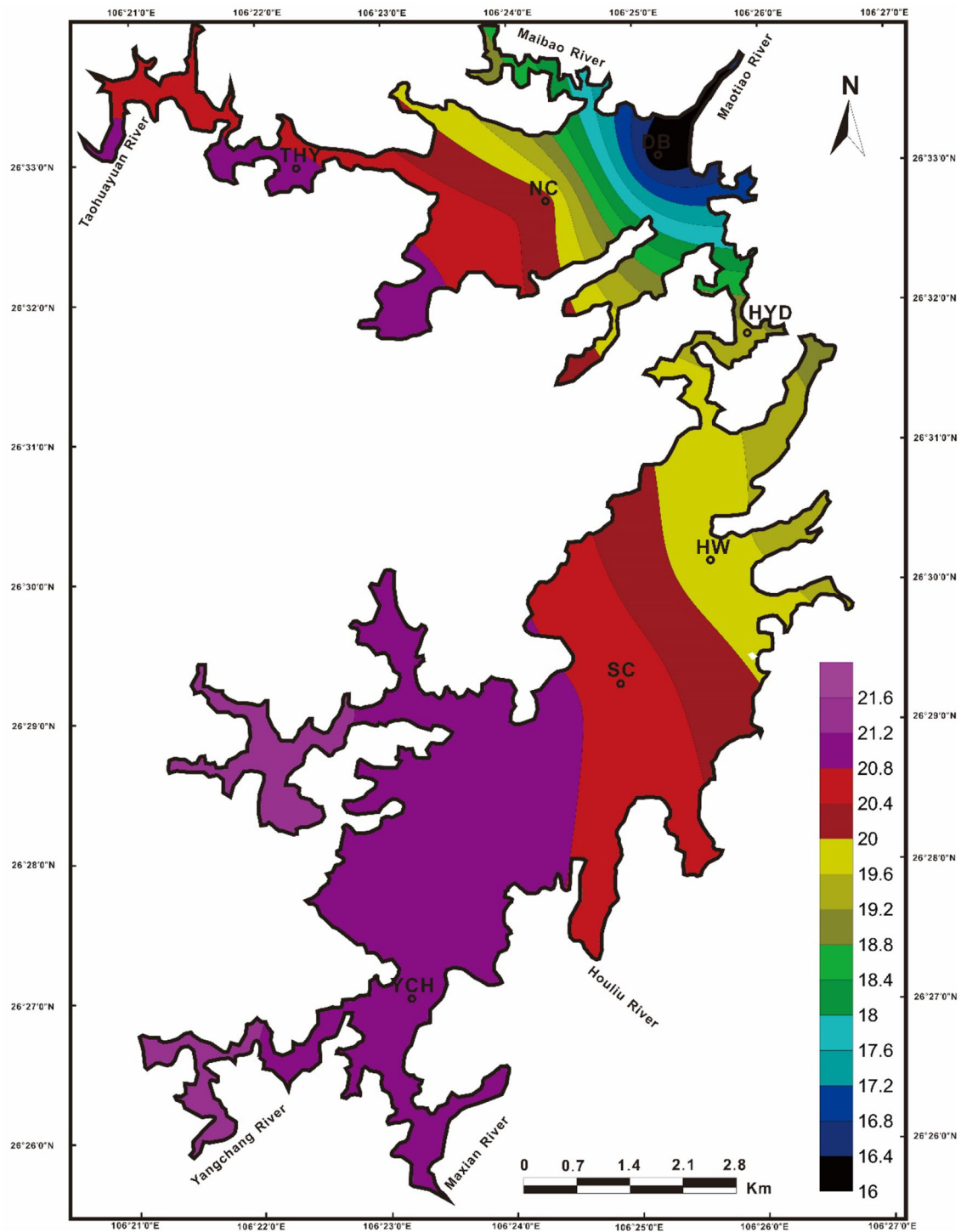


Fig. 4 Spatial variations of $\delta^{18}\text{O}_p$ values in the surface water of Hongfeng Lake

(McLaughlin et al. 2006; Elsbury et al. 2009; Young et al. 2009).

From the above discussion, it is clear that internal phosphate has sufficiently different isotopic signatures from external phosphate and that these signatures are not considerably altered by biological mediation in Hongfeng

Lake. Therefore, $\delta^{18}\text{O}_p$ can be used to quantitatively distinguish phosphate sources and their relative contribution percentage. A two-endmember mixing model was used to calculate the relative contribution percentage of internal phosphate (F_{internal}) at HYD:

$$F_{\text{internal}} = (\delta^{18}\text{O}_{\text{p-lake}} - \delta^{18}\text{O}_{\text{p-external}}) / (\delta^{18}\text{O}_{\text{p-internal}} - \delta^{18}\text{O}_{\text{p-external}}) \quad (2)$$

where $\delta^{18}\text{O}_{\text{p-lake}}$, $\delta^{18}\text{O}_{\text{p-external}}$, and $\delta^{18}\text{O}_{\text{p-internal}}$ represent $\delta^{18}\text{O}_{\text{p}}$ of lake water, of external phosphate, and of internal phosphate, respectively.

The calculations show that the average contribution percentage of internal phosphate reached 40%, highlighting the importance of the internal P load to water phosphate and eutrophication in Hongfeng Lake. Although Elsbury et al. (2009), based on limited $\delta^{18}\text{O}_{\text{p}}$ data, speculated that there was a likely phosphate source from sediment recycling in Lake Erie, no direct measurement of $\delta^{18}\text{O}_{\text{p}}$ of internal phosphate has been reported until now. Here, we have presented the first dataset of oxygen isotopic composition of phosphate in sediment pore water, and quantified the relative contribution of internal phosphate on the water phosphate in Hongfeng Lake.

Many previous studies have estimated the internal P flux in Hongfeng Lake by other methods. Based on the Zr-oxide diffusive gradient in thin films technique, Luo et al. estimated the phosphorus flux from the sediments in summer and other seasons were 6.3–8.0 t (Luo et al. 2015) and 8.8–10.0 t (Luo 2015), respectively, accounting for 33%–39% of the total P in Hongfeng Lake. A diffusive model by Wang (2013) showed that sedimentary P emission for the whole lake was about 14.5 t/year, making up 31% of the total P. Using the sediment core incubation method, Yang (2013) reported the P release flux was 19–27 t/year, accounting for about 41%–59% of the total P. As a whole, our result is in concert with these previous studies, although they are based on different methods. This supports the reliability of $\delta^{18}\text{O}_{\text{p}}$ as a tracer for phosphate sources.

4 Conclusions

In this initial attempt to characterize the oxygen isotopic composition of internal phosphate, we have made the first oxygen isotopic measurements of phosphate in sediment pore water in Hongfeng Lake. These data, in combination with the oxygen isotopic compositions of phosphate in surface water and column water samples, have been successfully used to identify phosphate sources. The $\delta^{18}\text{O}_{\text{p}}$ value of sediment pore water ranged from 15.2‰ to 15.8‰, with an average value of 15.5‰. The $\delta^{18}\text{O}_{\text{p}}$ values decreased gradually from surface water to deeper water in the water column, indicating that internal phosphate had more negative $\delta^{18}\text{O}_{\text{p}}$ values than external phosphate. This was supported by the horizontal variations of the $\delta^{18}\text{O}_{\text{p}}$ values, decreasing with increasing distance from the

inflows. External and internal phosphate had sufficiently distinct isotopic signatures and these signatures were not altered considerably by biological mediation in Hongfeng Lake, allowing the use of $\delta^{18}\text{O}_{\text{p}}$ in distinguishing phosphate sources. The two-endmember mixing model showed that the average contribution of internal phosphate reached 40%, highlighting the influence of the internal P load on water phosphate and eutrophication and illustrating the need to control the internal P load from sediments.

This study is far from comprehensive and the $\delta^{18}\text{O}_{\text{p}}$ data are limited, but it serves to highlight the great potential of $\delta^{18}\text{O}_{\text{p}}$ as an effective tracer for identifying phosphate sources. Systematic investigations of oxygen isotopic compositions of external phosphate, internal phosphate, and phosphate in the water column, and of the in-lake P biogeochemical cycle, would be desirable in further research.

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