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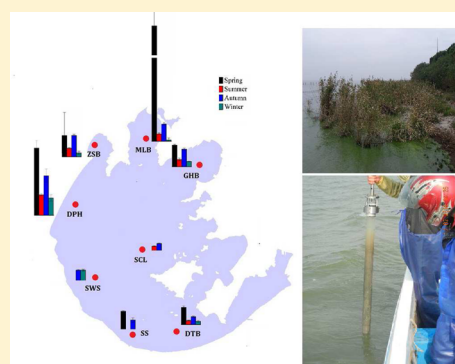
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S Supporting Information

ABSTRACT: The seasonal occurrence and distribution of phosphite (HPO_3^{2-} , P) in sedimentary interstitial water from Lake Taihu was monitored from 2011 to 2012 to better understand its possible link to P cycle in the eutrophic shallow lake. Phosphite concentrations ranged from < MDL to $14.32 \pm 0.19 \mu\text{g P/kg}$ with a mean concentration of $1.58 \pm 0.33 \mu\text{g P/kg}$, which accounts for 5.51% total soluble P (TSP_s) in surficial sediments (0–20 cm). Spatially, the concentrations of sedimentary phosphite in the lake's northern areas were relatively higher than those in the southern areas. Higher phosphite concentrations were always observed in seriously polluted sites. Generally, phosphite in the deeper layers (20–40 cm and 40–60 cm) showed minor fluctuations compared to that in the surficial sediments, which may be associated with the frequent exchange at the sediment–water interface. Phosphite concentrations in surficial or core sediments decreased as spring > autumn > summer > winter. Higher phosphite levels occurred in the areas with lower redox (Eh), higher P contents, and particularly when metal bonded with P to form Al–P_s and Ca–P_s. Phosphite may be an important media in the P biogeochemical cycle in Lake Taihu and contribute to its internal P transportation.



1. INTRODUCTION

Phosphorus (P), the 11th most common element on earth, has been commonly recognized as a limiting nutrient affecting biological productivity for most ecosystems. It is critical to understand P behavior since P chemistry controls key aspects of eutrophication, microbial nutrition, corrosion, and other environmental processes.¹ However, prior work in P environmental chemistry presumed phosphate (with a +5 oxidation state) is the dominant P carrier.² Increasing concerns have recently been given to a new pattern in the P biochemical cycle since some special P species with an oxidation state lower than +5 such as phosphine (PH_3 , −3), hypophosphite (HPO_2^{2-} , +1), and phosphite (HPO_3^{2-} , H_2PO_3^- , +3) have been identified in natural environments.^{3,4}

Phosphite is largely used in numerous products such as fungicide, P fertilizers,⁵ plastic stabilizers, water treatment agents, and organophosphorous pesticides. Phosphite could be introduced into the environment from industries (during the production and usage of these products) and from natural sources such as iron corrosion,^{1,6,7} lightning or volcanism,⁸ and biotic processes.⁹ As a result, micromolar levels of phosphite have been found in various matrices including drinking water,¹ natural geothermal pools,¹⁰ apatites,¹¹ fulgurites,⁸ lakes,⁴ and industrial wastewater.⁷ Phosphite introduced into aquatic ecosystems may have potentially adverse effects on aquatic life and eutrophication.¹² However, knowledge on the distribution of phosphite into the environment is limited

although research does indicate that aquatic sediment and extreme environment are potential natural sources of phosphite.⁸

Lake Taihu, a large shallow freshwater lake in eastern China, has become hypereutrophic, and algal blooms frequently. It has previously been demonstrated that P is a vital limiting nutrient for eutrophication in Lake Taihu.¹³ Sediments act as an important P reservoir inducing bioreductive or abiotic-reductive generation by transferring phosphate to phosphite in the anaerobic environment, which may transport phosphite into ground and surficial waters.⁴

The bioavailability of phosphite has long been a topic of interest,^{14–16} demonstrating that phosphite could be involved in the biogeochemical P cycle. Phosphite could be oxidized to phosphate and then be utilized; moreover, it is readily available for biological uptake without being recognized as the component of dissolved reactive P (DRP). Recent research indicating appreciable concentrations of reduced P in the environment has brought new contributions to the understanding of the overall P cycle. Phosphite from Lake Taihu water ranges from $0.31 \pm 0.31 \mu\text{g P/L}$ to $5.27 \pm 0.31 \mu\text{g P/L}$, which correlates to 1%–10% of the DRP, suggesting that the

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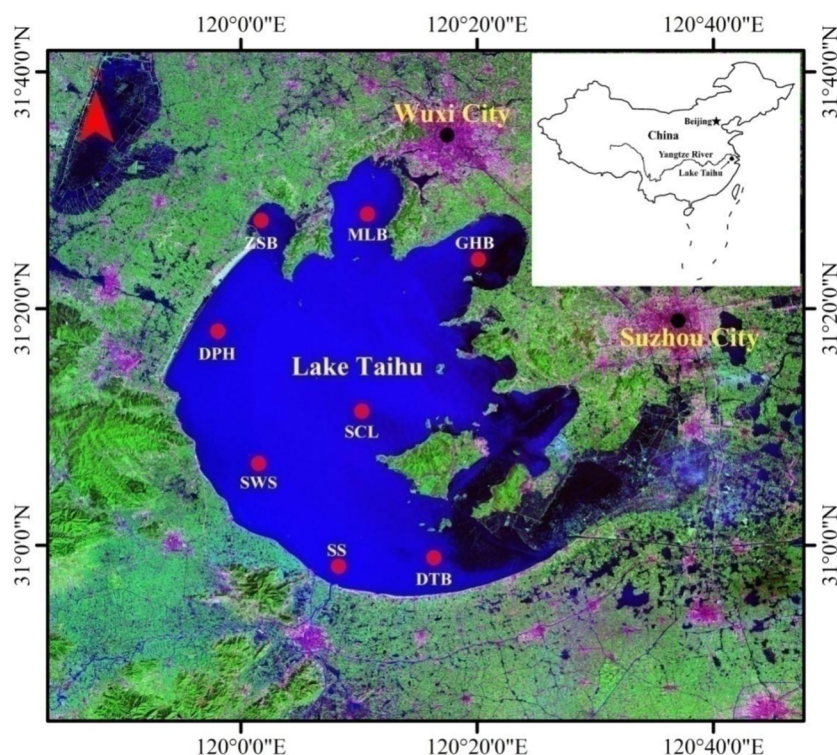


Figure 1. Location of sampling sites in Lake Taihu, China. northern Lake Taihu area (DPH, ZSB, MLB, GHB), central Lake Taihu area (SCL), and southern Lake Taihu area (SWS, SS, DTB).

phosphite represents a significant fraction of the DRP .⁴ A concentration of $10 \mu\text{g/L}$ DRP can be sufficient to meet phytoplankton growth, while, a higher concentrations of $30\text{--}100 \mu\text{g/L}$ would potentially promote algal blooms.¹⁷ This level of phosphite would be significant as a P nutrient carrier and would provide substantial support to algal growth.¹²

Monitoring the occurrence and distribution of phosphite and its possible link to P cycle is important to the understanding of the P biogeochemical process in Lake Taihu. The goals of this study are (1) to gain an overview of the seasonal and spatial distribution of phosphite in sediments of interstitial water from Lake Taihu; (2) to discuss the main environmental factors controlling phosphite distribution; and (3) to explore the potential link of phosphite to the P geochemistry cycle. This work will be helpful in reevaluating the P cycle and stimulating a novel discussion on the relationship between P species and eutrophication.

2. MATERIALS AND METHODS

Study Area. Lake Taihu lies in the Yangtze Basin on the border of Shanghai, Jiangsu and Zhejiang provinces in eastern China, which covers an area of 2338 km^2 . In this basin, more than 25 rivers flow through the developed industrial and agricultural regions before finally entering Lake Taihu (Figure 1). It is an important resource of drinking water, fishing, transportation, and tourism. Within the northern basin of Lake Taihu, the three largest inflow water fluxes are Chengdong Harbor, Dapu Harbor and Liangxi River.¹⁸ In recent years, more than a million tons of municipal and industrial wastewater discharge from the upper rivers have caused severe lake eutrophication. To compare the potential site-specific variation of phosphite in the entire lake, eight representative sampling sites were selected based on the limnological and geographical characteristics of Lake Taihu. The study area and sample site

are shown in Figure 1. According to the average concentrations of total N, total P, and chlorophyll-a in Lake Taihu, north Lake Taihu including MLB, ZSB, and DPH are set at a hyper-eutrophic level, central Lake Taihu including SCL and west Lake Taihu including SS and SWS are at an eutrophic level, and east Lake Taihu including DTB are at a light to medium eutrophication level.¹⁹ Sites MLB and ZSB are located in the northern lake region where the sediments are polluted by sewage emission. Site DPH located in the northwest lake region, close to the Dapu Harbor is considered as the most polluted area in Lake Taihu. Site GHB, located in northeast region, is an important drinking water resource to the cities of Wuxi and Suzhou. Site SCL, located near central lake often has less enriched nutrients and low water transparency due to wind-driven sediment resuspension. SS and SWS site, located in the southwest region, account for about one-third of the total runoff into Lake Taihu. Site DTB, located in southeast region is an important base of freshwater aquaculture for Lake Taihu.

Sample Collections. Eight surficial sedimentary samples (0–20 cm) in Lake Taihu were taken with a Peterson grab sampler (purchased from Nanjing Institute of Geography and Limnology) from the summer of 2011 to the spring of 2012 during all four seasons. Besides, four sedimentary cores about 60 cm deep were collected from the seriously polluted northern Lake Taihu region including MLB, GHB, DPH, and ZSB with a $9.1 \times 70 \text{ cm}$ cylindrical sediment sampler (purchased from Nanjing Institute of Geography and Limnology). Sediment cores were divided immediately into three layers: (1) surficial layer of 0–20 cm; (2) interim layer of 20–40 cm; and (3) bottom layer of 40–60 cm. All the samples were packed into plastic bags and stored at 4°C in darkness prior to extraction within 24 h. Details of physicochemical properties of waters from the investigated locations during four seasons are shown

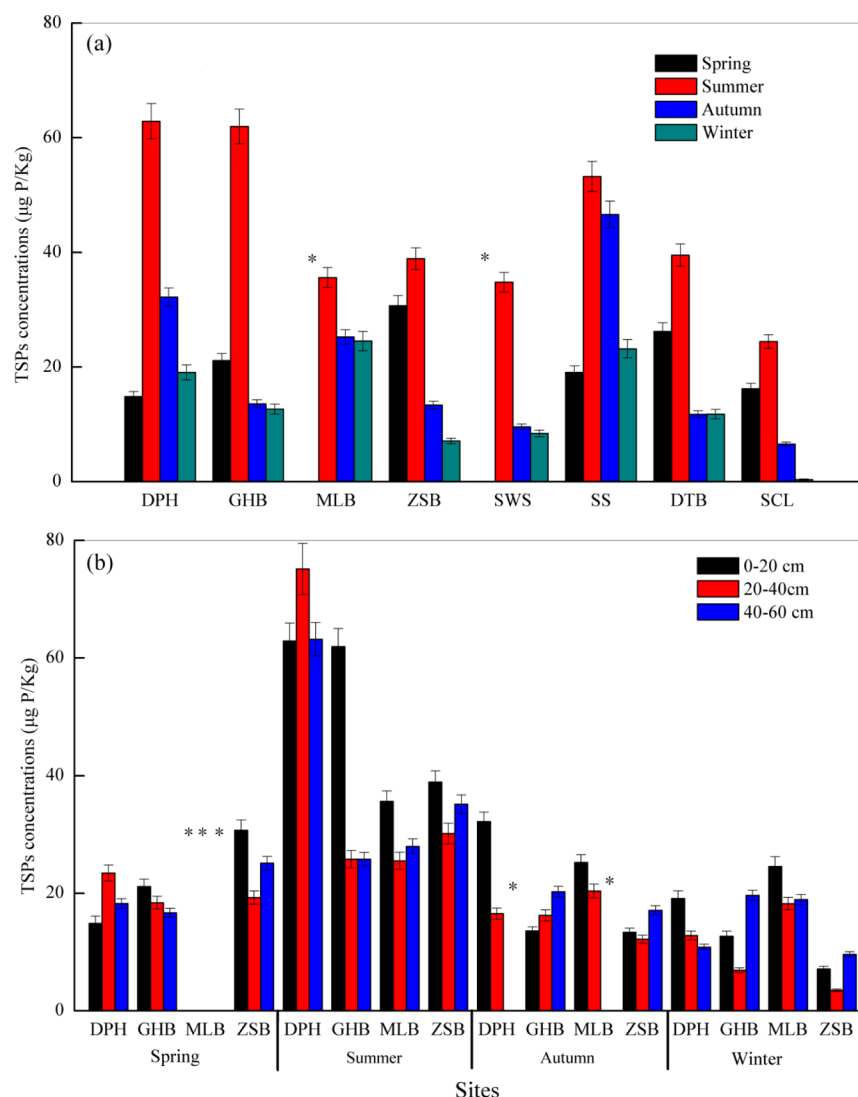


Figure 2. (a) Seasonal distribution of TSP_s in surficial sedimentary interstitial water in Lake Taihu; (b) Vertical distributions of phosphite from four representative sites in northern Lake Taihu during four seasons. Note: some abnormal data (*) were eliminated from the figure.

in Supporting Information (SI) Table S1 and Figure S1. Details on the cleaning and sampling protocol are given in SI S1.

Sample Preparation and Phosphite Determination. All sediment samples were centrifuged within 24 h at 8000 rpm for 25 min to extract interstitial water by a CT15RT versatile refrigerated centrifuge (China). Interstitial waters preserved at 0–4 °C in the dark and analyzed within 14 days. Our preliminary investigation verified that phosphite was stable for at least 14 days under above preservation protocols. Subsamples of interstitial water were filtrated through 0.22 μm membranes, and then treated with OnGuard II Ag cartridges (2.5 cc P/N 057090, Dionex) and OnGuard II RP columns (2.5 cc P/N 057084, Dionex) to remove the excessive chloride and organic substances before analysis.

All of the extracts were analyzed for phosphite using suppressed ion chromatography (IC) coupled with multiple gradient procedure for potassium hydroxide (KOH) eluent: 1 mM from 0 to 13.5 min; 1 to 18 mM from 13.5 to 15.5 min; 18 mM from 15.5 to 24 min; 18 to 40 mM from 24 to 27 min; 40 mM from 27 to 34 min; and 40 mM to 1 mM from 34.1 to 35 min. In brief, chromatographic separation of phosphite was performed on a Dionex model 2000 ion chromatography

system (Dionex, Sunnyvale, CA) equipped with an IonPac AG11-HC (50 mm \times 4 mm) guard column and an IonPac AS11-HC (250 mm \times 4 mm) analytical column. Operating conditions of IC system and verification of determination method of phosphite, quality assurance and quality control (QA/QC) of the analyses have been described by Han et al.,⁴ as well as in SI S3, Figure S3, and Figure S4. The estimated method detection limit (MDL) of phosphite for the 500 μL injection volumes is 0.062 $\mu\text{g P/L}$. All concentrations of phosphite in sedimentary interstitials are reported based on a wet weight (ww) basis.

Physicochemical Analysis of Sediment. Subsamples of sediments were also subjected to various physicochemical analyses. About 10 g of sedimentary samples were freeze-dried, ground and homogenized by passing through an 80 mesh sieve. Total P (TP_s), total inorganic P (TIP_s) and total organic P (TOP_s) in sediments were measured as described previously.²⁰ By the chemical sequential extraction scheme, sedimentary P fractions were divided into exchangeable P (EP_s), dissolved P (DP_s), P bound to Al (Al-P_s), P bound to Fe (Fe-P_s), P bound to Ca (Ca-P_s), occluded P (OP_s), and organic P (Org-P_s).²¹ For metal determination, all sedimentary samples were

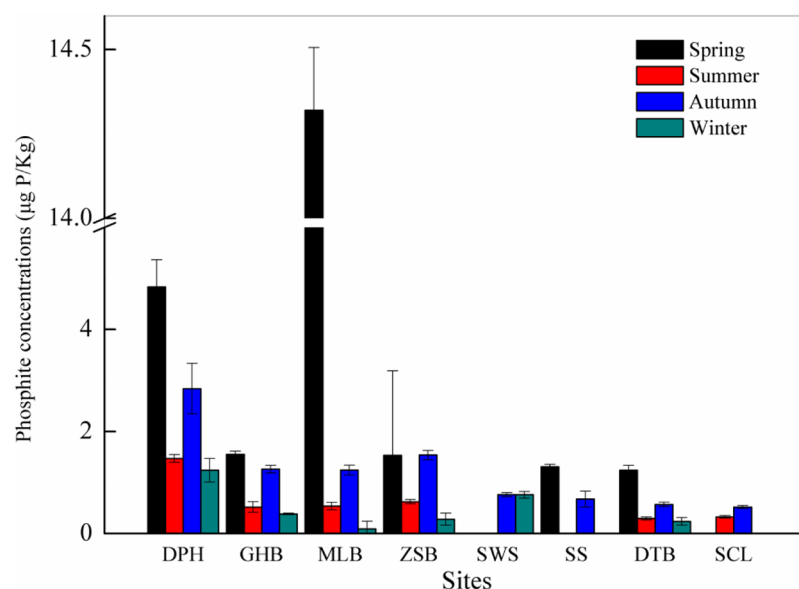


Figure 3. Seasonal distribution of phosphite in surficial sedimentary interstitial water in Lake Taihu.

digested with a four-acid mixture and determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Fisher Scientific).²² Soluble reduced P including soluble phosphite is regarded as a part of the total soluble P (TSP_s) in sedimentary interstitial water. In order to evaluate the proportion of phosphite in TSP_s, the TSP_s in eight surficial sedimentary samples and four sedimentary cores during four seasons was measured simultaneously by the ascorbic acid-molybdate blue colorimetry.²³ Sedimentary redox potential (Eh_s) was measured using calibrated combined redox electrodes.

Statistical Analysis. All samples were analyzed at least three times, and the results were represented as “geometric mean \pm geometric standard deviation.” Correlation analyses were performed to determine relationships between phosphite concentrations and environmental variables. Data from different sites and seasons were compared by a one-way analysis of variance (ANOVA), and statistically different treatments were identified by the LSD-*t* test. All statistical analyses were conducted using SPSS software (SPSS, Inc.). Differences were regarded as significant at $P < 0.05$ (symbolized as *) and very significant at $P < 0.01$ (symbolized as **).

3. RESULTS AND DISCUSSION

Total Soluble P (TSP_s) in the Sedimentary Interstitial Waters from Lake Taihu. Figure 2 represents the distribution of TSP_s in interstitial waters in the surficial sediments and sediment cores. TSP_s ranged from 0.35 ± 0.12 to 75.14 ± 8.45 $\mu\text{g P/kg}$ with a mean concentration of 28.70 ± 16.00 $\mu\text{g P/kg}$ during the four periods. In summer, the TSP_s concentrations were between 24.43 ± 2.91 and 75.14 ± 8.45 $\mu\text{g P/kg}$ with a mean of 39.81 ± 16.03 $\mu\text{g P/kg}$, which was significantly higher than those in the other three seasons ($P < 0.05$), while relatively lower concentrations were observed in winter ranging from 0.35 ± 0.12 $\mu\text{g P/kg}$ to 24.53 ± 3.46 $\mu\text{g P/kg}$ with a mean of 10.76 ± 7.27 $\mu\text{g P/kg}$.

Phosphite in Surficial Sediments during Four Seasons. Concentrations of phosphite in interstitial water are shown in Figure 3. In general, phosphite was found with concentrations ranging from $< \text{MDL}$ to 14.32 ± 0.19 $\mu\text{g P/kg}$.

Maximum phosphite concentration was found at MLB site in the spring. While phosphite concentrations from the southern Lake Taihu region were mostly lower than the MDL, the annual average concentration of phosphite in Lake Taihu was 1.58 ± 0.33 $\mu\text{g P/kg}$. The levels of phosphite reported here are of the same order of magnitude (about submicromole level) as found in natural matrices,^{10,24,25} suggesting that sediment is an important source of phosphite in the environment.

The spatial distribution of phosphite in surficial sediment was site-specific. It seems that the phosphite concentrations may be related to the sediment contaminant status, and that higher phosphite concentrations were normally found in seriously polluted areas. Annual average phosphite concentrations in northern Lake Taihu (DPH: 2.60 ± 1.65 $\mu\text{g P/kg}$; MLB: 4.05 ± 6.86 $\mu\text{g P/kg}$) were almost 10 times higher than those in less contaminated areas such as central Lake Taihu (SCL: 0.28 ± 0.26 $\mu\text{g P/kg}$) or southern Lake Taihu (SWS: 0.38 ± 0.44 $\mu\text{g P/kg}$; SS: 0.49 ± 0.63 $\mu\text{g P/kg}$). Two higher annual average phosphite concentrations were measured at MLB (4.05 ± 6.87 $\mu\text{g P/kg}$) and DPH (2.60 ± 1.65 $\mu\text{g P/kg}$), respectively, which were close to industrial and agricultural effluents and had serious eutrophication.¹⁸ The lowest annual concentration was observed at SCL of 0.425 ± 0.134 $\mu\text{g P/kg}$, where the water quality was good. Similar spatial distribution had been observed for PH₃ in sediments of Lake Taihu.^{26,27}

Seasonally, phosphite levels changed significantly ($P < 0.05$) (Figure 3). Generally, the seasonal average phosphite concentrations in Lake Taihu decreased as spring (4.13 ± 5.18 $\mu\text{g P/kg}$) $>$ autumn (1.18 ± 0.77 $\mu\text{g P/kg}$) $>$ summer (0.63 ± 0.43 $\mu\text{g P/kg}$) $>$ winter (0.45 ± 0.43 $\mu\text{g P/kg}$). The highest phosphite concentration for each site was found in the spring, while the lowest concentration was in winter. Seasonal phosphite differences may be related to the variable production and elimination process, which suggests that a series of weather-related biochemical and geochemical reactions are involved in phosphite presence in an anaerobic sediment or soil culture (see SI S2).^{7,8,15,28}

Phosphite in the Sedimentary Profiles during Four Seasons. The vertical and seasonal distributions of phosphite in sediments profiles at four representative sites including DPH,

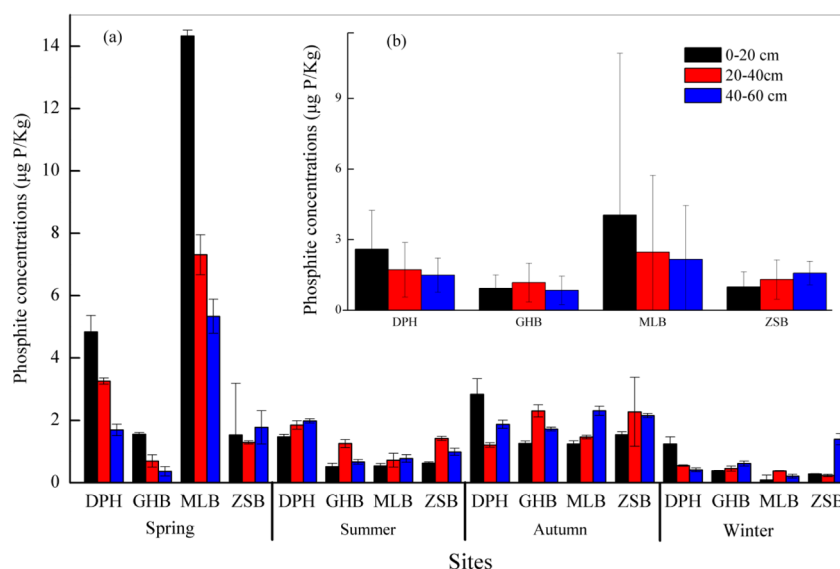


Figure 4. (a) Vertical distributions of phosphite from four representative sites in northern Lake Taihu during four seasons; (b) Annual distributions of phosphite in sediment profiles at four sites.

ZSB, MLB, and GHB in northern Lake Taihu were also studied to investigate the possible migration of sedimentary phosphite (Figure 4). In general, the overall phosphite concentrations in the surficial layers (0–20 cm) ranged from $0.09 \pm 0.15 \mu\text{g P/kg}$ to $14.33 \pm 0.19 \mu\text{g P/kg}$ with a mean of $2.14 \pm 3.45 \mu\text{g P/kg}$, which fluctuated significantly due to frequent exchange at the water-sediment interface. Phosphite in the deeper two layers (20–60 cm) were relatively comparable with less variations ($0.23 \pm 0.04 \mu\text{g P/kg}$ to $7.31 \pm 0.64 \mu\text{g P/kg}$, mean: $1.67 \pm 1.71 \mu\text{g P/kg}$ for 20–40 cm layers; $0.21 \pm 0.06 \mu\text{g P/kg}$ to $5.33 \pm 0.55 \mu\text{g P/kg}$, mean: $1.51 \pm 1.23 \mu\text{g P/kg}$ for 40–60 cm layers, $P > 0.05$). Lower levels of phosphite were found in deeper layers, where sediments were hardly disturbed by external sources. Similar to the spatial variation in surficial sediments, the relative higher concentrations of phosphite in sedimentary profiles were found in MLB (annual concentrations: $2.89 \pm 4.23 \mu\text{g P/kg}$) and DPH (annual concentrations: $1.94 \pm 1.22 \mu\text{g P/kg}$), which may be partly attributed to the high phosphite concentration in spring. As is also visible in Figure 4a, the phosphite content in sedimentary profiles fluctuates in depth. Generally, the overall decreasing trend in phosphite concentrations was found with increasing depth at MLB and DPH (Figure 4b). Conversely, the vertical profiles were quite different in ZSB, which could be attributed to strong disturbances caused by the regular occurrence of dredging activity.

There are distinct seasonal patterns in profiles of phosphite (Figure 4a). Generally, the seasonal variation of annual phosphite in core sediments decreased as spring ($3.67 \pm 3.97 \mu\text{g P/kg}$) > autumn ($1.85 \pm 0.53 \mu\text{g P/kg}$) > summer ($1.07 \pm 0.52 \mu\text{g P/kg}$) > winter ($0.52 \pm 0.40 \mu\text{g P/kg}$), which is consistent with the variation of surficial sediments. Interestingly, the highest phosphite was measured during spring at DPH and MLB, whereas ZSB and GHB experienced the highest concentrations during autumn. The lowest for all sites were in winter.

Distribution of phosphite may be affected by multiple environmental variables. Results in Table 1 present the evaluation of the influence of environmental conditions and sedimentary properties on the concentrations of phosphite. A

Table 1. Regression Analyses of Phosphite with Different P fractions and Environmental Factors

environmental factor (x)	phosphite concentrations (y) ($\mu\text{g P/kg}$)			
	regression equation	R	P	N
TP _s (mg/kg)	$y = 0.029x + 0.344$	0.339 ^(a)	0.005	68
Al-P _s (mg/kg)	$y = 0.004x + 0.002$	0.556 ^(b)	0.000	68
Fe-P _s (mg/kg)	$y = 0.006x + 0.094$	0.229	0.062	68
Ca-P _s (mg/kg)	$y = 0.011x + 0.095$	0.285 ^(a)	0.020	68
Eh _s (mV)	$y = -28.93x + 48.05$	-0.283 ^(a)	0.031	68

^a: $P < 0.05$. ^b: $P < 0.01$.

significant negative correlation exists between phosphite concentrations and Eh_s ($P < 0.05$), indicating that phosphite levels could be related to lower redox potential of the local environment. The phosphite concentration could be balanced by its possible formation (depending on P-containing precursor levels as well as temperature) and depletion (oxidation or utilization). Reductive environment is favorable for the production and preservation of phosphite in sediment. Phosphite is readily measured in a reducing environment.^{8,29} According to the calculated equilibrium distributions of the various P species in water as both functions of pH and Eh depicted in SI Figure S2, the P redox process is clearly relevant to Eh in the environment. Phosphate (P, +5) is the dominate P form under oxidized condition; reduced P such as phosphite, hypophosphite and elemental P maybe the dominate P forms under reducing conditions. Similarly, it has been demonstrated that reducing conditions would also favor the evolution of PH₃.³⁰

Significance of Phosphite in P cycle. It is estimated that this observed phosphite which accounts for 5.51% TSP_s in sedimentary interstitial waters, should be an indispensable component of P fractions. Significant positive correlations between sedimentary phosphite and TP_s, Al-P_s, and Ca-P_s were observed (Table 1). This indicates to some extent that the contents of phosphite in sediments are related high P contents, especially metal bonded P fractions. Phosphite could be produced in an abiotic way from inorganic phosphate minerals

such as apatite and brushite. Furthermore, it has been proposed that a significant portion of the minute concentration of phosphite in minerals may be converted to phosphite.³¹ It also has been shown that some inorganic P minerals, especially phosphide minerals such as schreibersite, $(\text{Fe, Ni})_3\text{P}$, could react with water to form phosphite as a primary product.³² Most P in sediment was stored in P-containing minerals, and the vast majority of these contain P in the +5 oxidation state, which is not readily soluble in water. Phosphite is believed to be more mobile and soluble (1000 times higher at similar pH and temperature).³³ This implies that soluble phosphite may be liberated from insoluble inorganically bonded phosphate through reduction. This research shows that phosphite could be an important media in the P biogeochemical cycle in Lake Taihu. Current evidence from geochemistry and cosmochemistry also indicates that the detection of phosphite in primitive systems on modern-day earth may elucidate the mechanisms by which P can be transformed in prebiota from a mineral into a biologically active form.²⁵ Phosphite introduced into the aquatic systems could be oxidized into the reactive phosphate, which may have a significant positive effect on algae blooms.¹² Previous research on the microbiological and algae-related importance of reduced P compounds has been unequivocally established.^{14,15,34}

Comparison of Phosphite Concentrations in Lake Taihu with Those Reported Previously. Our results are compared with published results of phosphite concentrations in different environmental matrices (Table 2). Phosphite can be

Table 2. Phosphite Concentrations in Sediments from Lake Taihu and Other Matrices

matrix	phosphite concentration	reference
process water and wastewater with P production plants	$(2.30 \pm 0.26)-(1550 \pm 100)$ mg P/L	7
drinking water contacting cast iron	0.17–0.92 mg P/L	7
natural geothermal water	1.86 μg P/L	10
various apatites under relatively crude conditions	$(0.3 \pm 0.4) \times 10^2$ $(30.0 \pm 9) \times 10^2 \mu\text{mol}/\text{mg}$	11
fulgurites from North America, Africa and Australia	90–820 ppm	8
liquid fertilizer	$(27.6 \pm 0.5) \% - (30.3 \pm 0.9) \% \text{ (w/w)}$	36
plant samples	above 3–5 ppm	37
Sediments from Lake Taihu	$0-(14.32 \pm 0.19) \mu\text{g}$ P/kg (ww)	this study

detected in a wide variety of circumstances. It appears that excessive amounts of artificial phosphite are produced from industry, such as in P production plants¹ and high-tech industries,³⁵ and from iron corrosion.^{6,7} Lower levels of natural phosphite are liberated from P-containing minerals under extreme environments such as volcanic eruptions^{11,31} and cloud-to-ground lightning discharges⁸ or under naturally occurring reducing environments, such as geothermal waters²⁴ and oceanic vents.³³ The phosphite concentrations in the interstitial waters are similar to those detected in natural geothermal waters, but significantly lower than others. It should be noted that the amount of phosphite detected in this study is likely to represent only a portion of the total phosphite content existing in sediments. We suspect that there are some phosphite fractions adsorbed or bound to the minerals in sediments.

This work demonstrates the wide presence of phosphite and its possible link to the P cycle in Lake Taihu. The quasi-

equilibrium between sedimentary phosphite of higher levels and overlying waters' phosphite are easily affected by multiple factors, which can result in the release of phosphite from sediments to the water column via various processes (suspension, diffusion, extraction, and hydrolysis, etc.). This investigation was limited to an analysis of the concentrations at specific locations within Lake Taihu. Identifying the serious influence of external sources, especially from nonpoint sources such as agricultural runoffs, was not the focus of this research—but can be traced through previous studies and will be the subject of future studies by our research group. This study shows that the role of sedimentary phosphite in regulating P cycle at sediment–water interface has significant implications on eutrophic lakes' functions and processes. Overall, further studies are necessary focusing on transport pathways and remobilization as well as annual trends of phosphite in Lake Taihu ecosystem.

■ ASSOCIATED CONTENT

Supporting Information

Further information on physic-chemical properties of waters and sediments from the investigated locations during four seasons (Table S1 and Figure S1); and details on the cleaning and sampling protocol (S1); details on some biochemical and geochemical reactions for the production and elimination of phosphite (S2); Eh-pH diagram for P species in water (Figure S2); and secondary confirmation of phosphite by 2D-CIC and IC-ESI-MS (S3). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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