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1 **Effects of elevated sulfate in eutrophic waters on the internal**  
2 **phosphate release under oxic conditions across the sediment-water**  
3 **interface**

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## 18 **Abstract**

19 Eutrophication in freshwater environments may be enhanced by the elevation of  
20 sulfate in waters, through the release of internal phosphorus (P) from anoxic sediments.  
21 However, the influence of increasing but modest sulfate concentrations (less than 3,000  
22  $\mu\text{M}$ ) on P release under oxic conditions across the sediment-water interface (SWI) in  
23 **eutrophic freshwater** is poorly understood. In this study, the profiles of P, iron (Fe), and  
24 sulfur (S) **and physicochemical parameters** were measured in a simulated lacustrine  
25 system with varying concentrations of sulfate (970-2,600  $\mu\text{M}$ ) **in overlying water**. The  
26 results indicated that elevated concentrations of sulfate increased the soluble reactive P  
27 in overlying waters under oxic conditions across the SWI. A 100  $\mu\text{M}$  increase of sulfate  
28 was found to induce a  $0.128 \text{ mgm}^{-2}\text{d}^{-1}$  increase of P flux from surface sediments into  
29 overlying waters under oxic conditions. Higher sulfate concentrations in the overlying  
30 waters increased the concentrations of labile S(-II) in the deep sediments, due to sulfate  
31 penetration and subsequent reduction to S(-II). We also found the fluxes of labile Fe  
32 and P from deep to surface sediment were both positive and greater than the  
33 corresponding fluxes from surface sediment to the overlying water, suggesting that  
34 reduction of P-bearing Fe(III)(oxyhydr)oxides in deep anoxic sediment acted as a major  
35 source of internal P release. In addition, the upward flux of Fe(II) was significantly  
36 lower under higher sulfate conditions, indicating that the Fe(II) flux could be **blocked**  
37 **mitigated** by formation of Fe(II) sulfides in the deep sediment. Under these conditions,  
38 less Fe(II) from deep sediments could be re-oxidized and combine with P in the surface,

39 oxic sediment, thereby reducing the retention capacity for P and leading to higher  
40 release of internal P to the water column.

41 **Key words:** Eutrophication, Internal P loading, Sulfate, Freshwater, DGT

## 42 **1. Introduction**

43 Eutrophication and the consequent formation of harmful algal blooms (HABs)  
44 represents a global challenge and poses serious threats to ecosystem services and human  
45 health (Conley et al. 2009, Paerl et al. 2011, Smith 2003). Phosphorus (P) is regarded  
46 as one of the primary limiting factors for the control of eutrophication in freshwater  
47 (Carpenter 2008, Schindler et al. 2008). Measures aimed at reducing inputs of external  
48 phosphorus have resulted in large-scale declines of phosphorus concentrations in many  
49 water bodies around the world (Huser et al. 2018, Tong et al. 2017). However, lakes  
50 typically show a delayed recovery in response to decreasing external P loads (Coveney  
51 et al. 2005), due to release of internal P from sediments (Paytan et al. 2017). Thus,  
52 understanding the processes of P release from sediments is important for the successful  
53 management of eutrophic waters.

54 The process of internal P release is influenced by many factors, such as  
55 temperature, pH and redox conditions (Christophoridis and Fytianos 2006). Iron (Fe) is  
56 a redox-sensitive element and the biogeochemical cycling of Fe regulates the mobility  
57 of internal phosphorus (Mortimer 1942). Under anoxic conditions, the reductive  
58 dissolution of P-bearing Fe(III)(oxyhydr)oxides is recognized as a major mechanism  
59 for internal P release (Rydin 2000). However, comparison of 23 different aquatic

60 systems did not show a strong correlation between internal P release rate and the bottom  
61 water oxygen concentration (Caraco et al. 1989). In addition, the sulfate concentration  
62 of the water was regarded as an extremely important variable controlling sediment P  
63 release in multiple systems, and showed a strong correlation with P release rate under  
64 both oxic and anoxic conditions (Caraco et al. 1989). Thus, the amount of P released  
65 from the sediment depended on the availability of sulfate (Caraco et al. 1989).

66 It has been found that the sulfide produced during sulfate reduction promote P  
67 mobilization from marine sediment through its dual effect on the cycling of Fe  
68 (Lehtoranta et al. 2009, Roden and Edmonds 1997, Rozan et al. 2002). Firstly, sulfide  
69 is a powerful reductant for the reduction of solid Fe(III) minerals to dissolved Fe(II)  
70 ion with concurrent P release (Bostrom et al. 1988). Secondly, sulfide could displace P  
71 from solid-phase Fe(II)-P compounds and trap the dissolved Fe(II) ion to iron sulfide  
72 precipitation (Roden and Edmonds 1997), which significantly promotes P release and  
73 reduces P retention capacity (Lehtoranta et al. 2009). For freshwater lakes with low  
74 concentrations of sulfate, it is commonly accepted that sulfate has slight effect on  
75 internal P release and Fe cycling (Caraco et al. 1989, Hansel et al. 2015). During recent  
76 decades, sulfate concentrations have increased in freshwater systems due to acid  
77 deposition and industrial wastewater inputs (Yu et al. 2013, Zak et al. 2006). For  
78 example, sulfate concentration in Lake Taihu has undergone a rapid increase ( $>12 \mu\text{M}$   
79  $\text{L}^{-1}\text{y}^{-1}$ ) over the past 60 years and now attains concentrations close to  $1,000 \mu\text{M}$  (Yu et  
80 al. 2013). Caraco et al. (1989) proposed that freshwater systems with intermediate

81 sulfate concentration (~100-300  $\mu\text{M}$  sulfate) tended to have high P release rates under  
82 anoxic condition. Some researchers showed that increasing sulfate levels could  
83 significantly promote the internal P release in freshwater lakes under anoxic conditions  
84 (Chen et al. 2016a, Roden and Edmonds 1997, Zhao et al. 2019). So far, anoxic  
85 conditions in the bottom water could be considered as an essential prerequisite for  
86 sulfate-stimulated release of P from sediments in freshwater systems.

87 Under natural conditions, oxygen distribution across the sediment-water interface  
88 (SWI) in shallow freshwater lakes, like Lake Taihu in China, is heavily influenced by  
89 hydrodynamic disturbance, accelerating the oxygen diffusion rate from the atmosphere  
90 to the water column (Chatelain and Guizien 2010). Thus, anoxia in bottom waters is  
91 hardly persistent during most seasons, except in the summer months. In the oxygenated  
92 water column and oxic surface sediments, Fe(II) may be rapidly converted to  
93 Fe(III)(oxyhydr)oxides, which provide fresh adsorption sites on which to retain  
94 available P (Mortimer 1942). Although oxic conditions across the SWI may increase  
95 the P adsorption capacity in surface sediment, P release is still observed in some oxic  
96 bottom waters (Gächter and Müller 2003, Kraal et al. 2013). These observations suggest  
97 that other mechanisms may also affect internal P release. For example, P can be released  
98 by dissolution of vivianite by interaction with hydrogen sulfide in deep sediments  
99 where oxygen cannot diffuse (Gächter and Müller 2003). Thus, higher concentrations  
100 of hydrogen sulfide in deep sediments may influence P release from surface sediments  
101 under oxic SWI conditions. Hansel et al. (2015) found that even when the sulfate

102 concentration was as low as 200  $\mu\text{M}$ , sulfate reduction was still a dominate force for  
103 the reduction of Fe(III) oxide. Increasing concentration of the sulfate in freshwater lakes  
104 has the potential to promote the mobilization of P through its effect on the cycling of  
105 iron under oxic condition across the SWI. However, to date no quantitative analysis has  
106 been undertaken on the contribution of elevated sulfate in shallow freshwaters to  
107 internal P release under oxic SWI conditions. Work to date has only been undertaken  
108 on sulfate rich waters such as a lowland river (2,600-7,800  $\mu\text{M}$  sulfate) polluted by  
109 mining activities and an estuary (28,000  $\mu\text{M}$  sulfate) (Kraal et al. 2013, Zak et al. 2006),  
110 neither of which has wide applicability for freshwater systems. In addition, a  
111 comprehensive evaluation of the impact of sulfate on the dynamic cycling of S-Fe-P,  
112 and their interactions, is crucial to the understanding of how eutrophication conditions  
113 change with oxic-anoxic variations.

114 In this study, an incubation experiment was conducted in a continuous dynamic  
115 shallow water simulation system under three sulfate levels. Diffusive gradients in thin  
116 films (DGT) and microelectrode techniques were employed to collect the vertical  
117 dynamic features of labile of P, Fe, S, as well as the related environmental factors at a  
118 fine scale. Based on the DGT profiles, the apparent fluxes of labile P and Fe from both  
119 surface sediment to water, and from deep sediment to surface sediment, were calculated.  
120 The objective of the study was to explore the effects of elevated sulfate inputs to the  
121 water column under oxic SWI conditions on internal P release.

## 122 **2. Materials and methods**

### 123 *2.1. Sample Collection*

124 The sampling sites were in Meiliang Bay (120°9 E, 31°31 N), the northern part of  
125 Lake Taihu. Lake Taihu is the third largest freshwater lake in China and is experiencing  
126 eutrophication and algal blooms. Sulfate concentrations here have undergone a rapid  
127 increase over the past 60 years and now attain about 1,000  $\mu\text{M}$  (Yu et al. 2013).  
128 Sediments and lake water were collected from Lake Taihu using an Ekman grab sampler  
129 and Plexiglas hydrophore, respectively. The collected samples were transported to the  
130 laboratory immediately and stored at 4 °C for less than 24 h before pre-treatment.

### 131 *2.2. Preparation of sediment-water columns*

132 Sediments were sieved through a 0.5 mm pore-size mesh to remove occasional  
133 macrofauna and large particles, and then completely homogenized to eliminate the  
134 horizontal heterogeneity of the natural sediment (Ding et al. 2015, Zilius et al. 2016).  
135 The pre-treated sediments and overlying water (filtered with 0.45  $\mu\text{m}$  filters) were used  
136 to fill perspex cylinders (8.4 cm in diameter and 50 cm in height) and 48 cylinders were  
137 produced in this study. Each cylinder contained 20 cm of sediment and 25 cm of  
138 overlying water. This sediment pretreatment method has been used extensively in other  
139 incubation experiments focused on exchange across the SWI (Chen et al. 2016b, Sun  
140 et al. 2017, Wang et al. 2017).

### 141 *2.3. Microcosm set-up*

142 Water flow over sediment has a significant influence on oxygen consumption

143 (Higashino 2011) and water-sediment interaction (Qin et al. 2007), which play key roles  
144 in Fe-S-P cycling. Taking this into consideration, we designed a dynamic microcosm  
145 system. The microcosm system consisted of six units, each including a water reservoir  
146 tank (12.3 cm in diameter and 20 cm in height) and six perspex cylinders (Figure.S1a  
147 and b). All of the cylinders were sealed with rubber plugs and silicone sealant. A micro  
148 pump and an aeration unit were installed in each reservoir tank (Figure.S1c). Water  
149 from each of the reservoir tanks was separately pumped into the inlet of the first  
150 cylinder of each unit, at 5 cm above the surface of sediment, and flowed out through  
151 the outlet of the cylinder, into the inlet of the next cylinder in the unit. All six cylinders  
152 in one unit were connected in series via their inlets and outlets, to simulate the **regular**  
153 water movement **in shallow lakes** and uniform initial conditions **among cylinders**. The  
154 water in the final cylinder of a unit flowed into the reservoir tank of the next unit. Water  
155 in each reservoir tank was initially sparged with N<sub>2</sub> at a flow rate of 0.4 L min<sup>-1</sup> for 24  
156 h to remove oxygen from each unit and then air was pumped into each tank for 5 min  
157 h<sup>-1</sup> to maintain the oxic environment across the SWI. The pre-incubation period lasted  
158 for 2 weeks.

159 At the end of pre-incubation, the concentrations of dissolved oxygen (DO), redox  
160 potential (Eh), DGT-labile P and Fe, and the soluble reactive P (SRP) in water-sediment  
161 profiles were measured from three randomly selected cylinders (Figure.S2). The  
162 profiles exhibited very consistent distributions for all the parameters, suggesting that  
163 the sediment was homogeneous in chemical distribution across different cylinders prior

164 to the main experiments.

#### 165 *2.4. Incubation Experiment*

166 After pretreatment, the water in each of the final cylinders in a unit was directed  
167 back to that unit's own reservoir tank, and the entire microcosm was separated into  
168 eight independent units (Figure.S1b). We choose six units (36 cylinders) at random on  
169 which to perform the experiment.  $\text{Na}_2\text{SO}_4(\text{s})$  was subsequently dissolved in the  
170 corresponding reservoir tank to obtain the desired concentration values as follows: no  
171 addition (Control; group C), 1,770  $\mu\text{M}$  (low sulfate; group B), and 2,600  $\mu\text{M}$  (high  
172 sulfate; group A). Control group (970  $\mu\text{M}$ ) represented the background concentration  
173 of sulfate found in the water column of Lake Taihu. According the work of Caraco et  
174 al. (1989), the background concentration of sulfate ( $\sim 1000 \mu\text{M}$ ) in Lake Taihu is higher  
175 than the typical freshwater type ( $\sim 10\text{-}300 \mu\text{M}$ ). However, it is still much less sulfate  
176 rich than the sites (a lowland river (2,600-7,800  $\mu\text{M}$  sulfate) polluted by mining  
177 activities and an estuary (28,000  $\mu\text{M}$  sulfate)) studied previously (Kraal et al. 2013, Zak  
178 et al. 2006). As no mandatory standards of sulfate are declared for surface waters  
179 worldwide, we chose the quality standard of sulfate in drinking water (2,600  $\mu\text{M}$ ) in  
180 China (GB3838-2002, China) for the high sulfate group (group A), which was very  
181 close to lower limiting values of salt waters ( $\sim 3,000\text{-}30,000 \mu\text{M}$ ). The set value in group  
182 B was a median value between those for groups A and C. All three units were incubated  
183 at room temperature ( $20\pm 2 \text{ }^\circ\text{C}$ ) for 45 days in the dark. Sampling was performed on the  
184 10th, 20th, 30th, 32nd, 37th and 45th day after the onset of incubation.

185 *2.5. Analyses of samples*

186 On the planned sampling day, two columns for each treatment (treated as duplicates)  
187 were randomly selected for sediment and water sampling. The distribution of DO and  
188 Eh in water-sediment profiles were measured using needle-type microelectrodes (OX-  
189 100 and RD-100; Unisense, Denmark) and the overlying water was then collected.  
190 Subsequently, ZrO-Chelex and AgI DGT (Easysensor Ltd., China) probes bound back  
191 to back were inserted into the sediments (Han et al. 2015). 24 hours later, these DGT  
192 probes were retrieved from sediments for processing.

193 After that, the sediment samples were transferred to a glove box containing a dry  
194 nitrogen atmosphere and sliced at a vertical resolution of 1cm to a depth of 10cm. An  
195 aliquot of each sliced sediment sample was transferred to a 50 ml plastic centrifuge tube  
196 which was then capped, removed from the glove box and centrifuged at 2500 g for 30  
197 min. After centrifugation, tubes were returned to the glove box to sample the pore water.  
198 The supernatant water in each centrifuge tube was dispensed via a 10 ml plastic syringe,  
199 fitted with a 0.45 $\mu$ m pore-size cellulose nitrate membrane filter, collected in a 5 ml  
200 plastic centrifuge tube, and finally stored at -20 °C. (Modified from Jilbert et al. (2011)).

201 The deployed ZrO-Chelex DGT was analyzed following the procedure detailed in  
202 Xu et al. (2013). The ZrO-Chelex gel was sliced at a resolution of 2 mm. Each sliced  
203 gel was sequentially eluted using HNO<sub>3</sub> and NaOH and the labile P and Fe in the eluates  
204 were determined using a microplate spectrophotometer (Multiskan FC; Thermo  
205 Scientific, Waltham, USA). The concentrations of labile S contained in the binding  
206 layer of the AgI DGT were determined by computer imaging densitometry (CID). The

207 image of the AgI gel was scanned using a flat-bed scanner (Canon 5600F, Canon Inc.,  
208 Japan) at a resolution of 600 dpi (0.0423 mm×0.0423 mm) and then converted to  
209 grayscale intensities with Image J (Version 1.48, NIH, USA) (Ding et al. 2012). The  
210 concentrations of the labile P, Fe and S measured by the DGT were calculated by  
211 methods listed in the Supporting Information.

212 The concentration of SRP in the water was determined using the molybdenum blue  
213 method (Murphy and Riley 1962). The concentration of sulfate in water was measured  
214 using a turbid metric method (Tabatabai 1974).

## 215 2.6. Data processing

216 ~~To reflect the diffusion direction of Fe and P across the sediment-water interface~~  
217 ~~and oxic-anoxic interface.~~To assess the effect of elevated sulfate in overlying water on  
218 internal P release under oxic condition across the SWI, the apparent fluxes at two depths  
219 were calculated in this study. Oxygen penetration depths in the sediment were measured  
220 as being less than 1cm (Fig.2.b). Therefore, this depth (-1 cm) was used to divide  
221 sediment profiles into surface oxic sediment and deeper anoxic sediment.

222 The ~~net~~-apparent fluxes of P and Fe at a specific depth were calculated from the  
223 DGT-labile P and labile Fe profiles using the following procedure:

224 (i)  $C = f(x)$  :get the regression equation between the measured concentrations (C) of  
225 P or Fe(II) and the corresponding depth (x).

226 So, the concentration gradients at the depth of i:  $\left. \frac{\partial c}{\partial x} \right|_{x=i} = f'(i)$  and the mean

227 concentration gradients from depth of m to depth of n:  $\left. \frac{\partial c}{\partial x} \right|_{mn} = \frac{\sum_{i=m}^n f'(i)}{m-n}$ . Based on the

228 depth-distributions of DGT-labile P and Fe, the concentration gradients were assessed

229 separately at the depths from 0 to 1 cm (overlying water), 0 to -1 cm (surface oxic  
230 sediment), -1 to -10 cm (deep anoxic sediment)

231 (ii) Taking the main mechanisms that could influence the internal P release into  
232 consideration, the ~~net~~ apparent fluxes of P or Fe(II) at the SWI were calculated as the  
233 sum of fluxes from surface sediment to the SWI, and from bottom water to the SWI  
234 using equation (1) (Ding et al. 2015, Gao et al. 2016).

$$235 \quad F_0 = F_s + F_w = (-\phi D_s \frac{\partial c_s}{\partial x_s}) + (-D_w \frac{\partial c_w}{\partial x_w}) \quad (1)$$

236 Where  $F_0$  is the apparent flux ( $\text{mg m}^{-2}\text{d}^{-1}$ ) at the SWI.  $F_s$  and  $F_w$  represent the labile  
237 P or Fe fluxes from surface sediment to the SWI, and from bottom water to the SWI,  
238 respectively.  $\frac{\partial c_s}{\partial x_s}$  and  $\frac{\partial c_w}{\partial x_w}$  are the concentration gradients in surface sediment and

239 overlying water, respectively.  $\phi$  is the porosity in sediment.  $D_w$  is the diffusion  
240 coefficient in water ( $\text{cm}^2 \text{s}^{-1}$ ) calibrated by the actual temperature (Li and Gregory 1974).

241 The diffusion coefficient in sediment ( $D_s$ ) ( $\text{cm}^2 \text{s}^{-1}$ ) were calculated from the diffusion  
242 coefficient in water ( $D_w$ ) and porosity ( $\phi$ ) in sediment (Ullman and Aller 1982).  ~~$D_s$  is~~

243 ~~the bulk sedimentary diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) (Ullman and Aller 1982).  $D_w$  is the~~  
244 ~~bulk sedimentary diffusion coefficient in water, and the porosity is  $\phi$  (Han et al. 2015,~~

245 ~~Li and Gregory 1974);  $\frac{\partial c_s}{\partial x_s}$  and  $\frac{\partial c_w}{\partial x_w}$  are the concentration gradients in surface~~

246 ~~sediment and overlying water, respectively.~~

247 (iii) Similarly, the ~~net~~ apparent fluxes of P or Fe(II) at 1 cm below the SWI (-1 cm)  
248 were calculated using equation (2)

$$249 \quad F_1 = F_{s1} + F_{s2} = (-\phi D_{s1} \frac{\partial c_{s1}}{\partial x_{s1}}) + (-\phi_2 D_{s2} \frac{\partial c_{s2}}{\partial x_{s2}}) \quad (2)$$

250 Where  ~~$F_1$  is the apparent flux at 1 cm below the SWI (-1 cm)~~.  $F_{s1}$  and  $F_{s2}$  represent  
251 the labile P or Fe fluxes from surface sediment to -1 cm, and from deep sediment to -1

252 cm, respectively.  $F_1$  is the and apparent flux at 1 cm below the SWI (-1 cm), which is  
253 the sum of  $F_{s1}$  and  $F_{s2}$ .  $D_{s1}$ ,  $\varphi_1$ ,  $\frac{\partial c_{s1}}{\partial x_{s1}}$ ,  $D_{s2}$ ,  $\varphi_2$ , and  $\frac{\partial c_{s2}}{\partial x_{s2}}$  were the mean values of  
254 sedimentary diffusion coefficients, porosity, and concentration gradient in surface  
255 sediment or deep sediment, respectively.

256 To comprehensively and quantitatively assess the concentration effect of sulfate on  
257 the internal P release in natural eutrophic waters (for instance, Lake Taihu in China),  
258 four linear regression equations were established, based on the functional relationships  
259 between the apparent fluxes ( $F_1$ ,  $F_0$  of labile Fe and P) and the concentrations of sulfate  
260 in overlying water. In addition, we extended the applied scope of the regression  
261 equations to predict the change of apparent fluxes of labile Fe and P over a wider  
262 concentration range of sulfate in freshwater systems. Here, four critical values for  
263 sulfate were determined by equations according to the following two scenarios:

264 Scenario 1: When the apparent diffusive flux of labile P or labile Fe across the SWI  
265 was zero ( $F_0=0$ )

266 Scenario 2: When the apparent diffusive fluxes of labile P or labile Fe were equal  
267 at the SWI and at 1 cm below the SWI ( $F_{10}=F_1-F_0$ ).

268 Based on the four critical values of sulfate derived here, we selected two of the  
269 critical values, which did not belong to the concentration range (~3,000-30,000  $\mu\text{M}$ ) of  
270 salt waters (Caraco et al. 1989) and divided the concentration range (0-3,000  $\mu\text{M}$ ) into  
271 different parts.

272 All of the statistical analyses were performed using SPSS software (V25.0; SPSS,  
273 USA). The differences of DO, Eh, SRP in overlying water and oxygen penetration depth  
274 (OPD) in sediment between different treatments were determined by pairwise

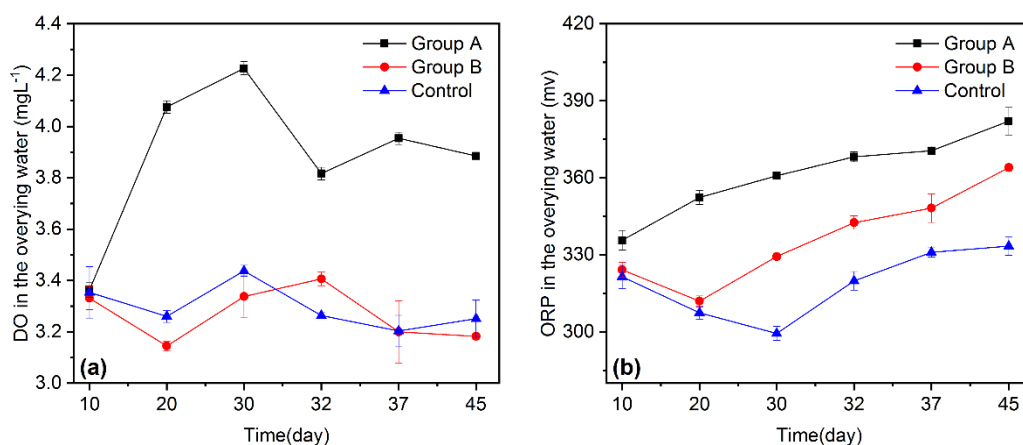
275 comparisons using one-way analysis of variance (ANOVA) and the Duncans multiple  
276 range test were used to perform means comparison. Besides, the differences of labile S,  
277 labile Fe and labile P between different sampling times were also assessed. The  
278 differences between the mean values at significance probability ( $p$ )<0.05 were  
279 considered statistically significant. ~~One-way analysis of variance (ANOVA) was~~  
280 ~~employed to detect differences of DO, Eh, SRP in overlying water and oxygen~~  
281 ~~penetration depth (OPD) in sediment between different treatments. The difference of~~  
282 ~~labile S, labile Fe and labile P between different sampling times were also assessed by~~  
283 ~~ANOVA. A  $P$ <0.05 was considered significant.~~ The functional relationships between  
284 sulfate concentration in the overlying water and fluxes of labile Fe and P were  
285 established using linear fitting.

### 286 **3. Results**

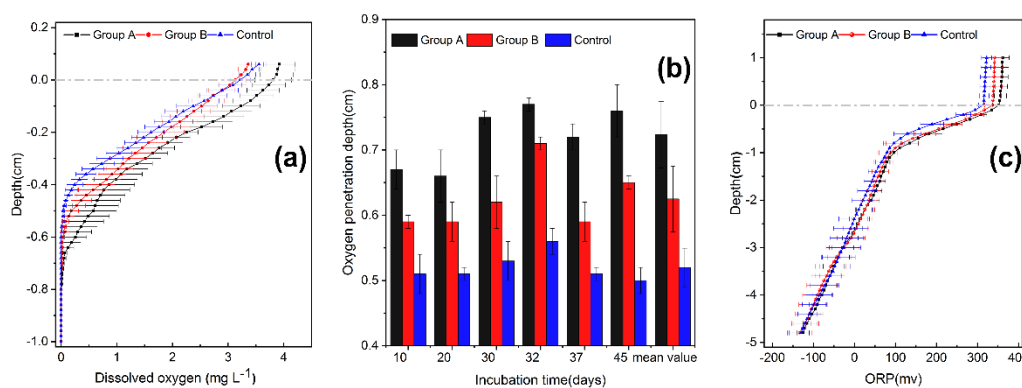
#### 287 *3.1. Vertical distribution of DO and Eh in sediment-water interface*

288 Sulfate addition induced an apparent change in the DO profiles, including DO level  
289 (Figure.1a.) and DO penetration depth (Figure.2a) in the surficial sediment. The highest  
290 DO concentrations in bottom water and at each depth along the vertical water-sediment  
291 profiles were always found in the group A. The sediment oxygen concentrations in the  
292 group B were also higher at depths of -0.05 to -0.7 cm than those in the Control  
293 (Figure.1a). Furthermore, higher sulfate concentrations led to a significant increase in  
294 the vertical oxygen penetration depth (OPD) in the order of group A>group B>Control  
295 (one-way ANOVA,  $p$ <0.05) (Figure.2b).

296 The redox potential (ORP) showed a similar trend to DO (Figure.1b, Figure.2c).  
 297 Sulfate addition significantly increased the ORP values in bottom water and followed  
 298 the order group A>group B>Control (one-way ANOVA,  $p<0.05$ ). From the SWI to the  
 299 depth of -3 cm, the ORP values in the group A and group B units were significantly  
 300 higher than those in the Control group (one-way ANOVA,  $p<0.05$ ).



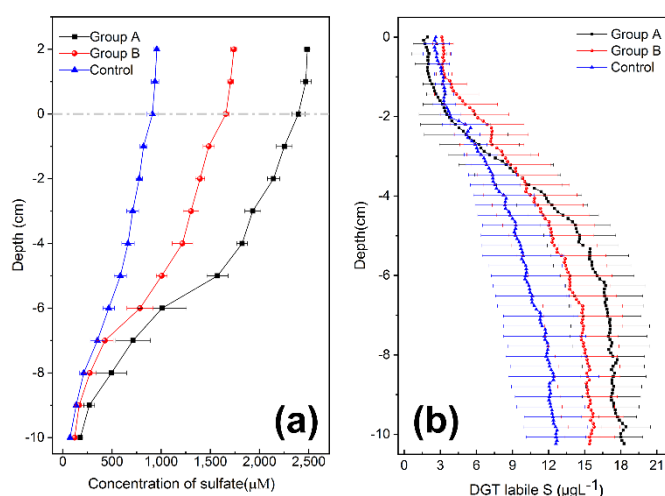
301  
 302 Figure 1. Variation of dissolved oxygen (DO) (a) and redox potential (ORP) (b) in bottom water  
 303 from the three treatment groups during the 45-days incubation (data shown by mean  $\pm$  SD, n =  
 304 2). Control: 970  $\mu$ M; group B: low sulfate, 1,770  $\mu$ M; group A: high sulfate, 2,600  $\mu$ M.



305  
 306 Figure 2. Dissolved oxygen profiles (DO) (a), oxygen penetration depth (OPD) (data shown by  
 307 mean  $\pm$  SD, n = 2) (b) and redox potential (ORP) profiles (c) from the three treatment groups  
 308 (data of DO and OPD were shown by the mean values during the 45-days incubation period  $\pm$   
 309 SD, n=12). The horizontal dashed line indicates the sediment-water interface (SWI). Control:  
 310 970  $\mu$ M; group B: low sulfate, 1,770  $\mu$ M; group A: high sulfate, 2,600  $\mu$ M.

311 3.2. Vertical distribution of sulfate and DGT-labile S in the sediment-water profiles

312 The concentrations of sulfate in overlying water were  $2,394 \pm 67$  in group A,  
313  $1,658 \pm 33$  in group B, and  $911 \pm 55$   $\mu\text{M}$  in the Control (Figure. 3a). In all groups, the  
314 sulfate concentration in pore water decreased slightly with increase in sediment depth.  
315 In addition, the concentration of sulfate in pore water at each depth followed the order  
316 group A > group B > Control (Figure. 3a).



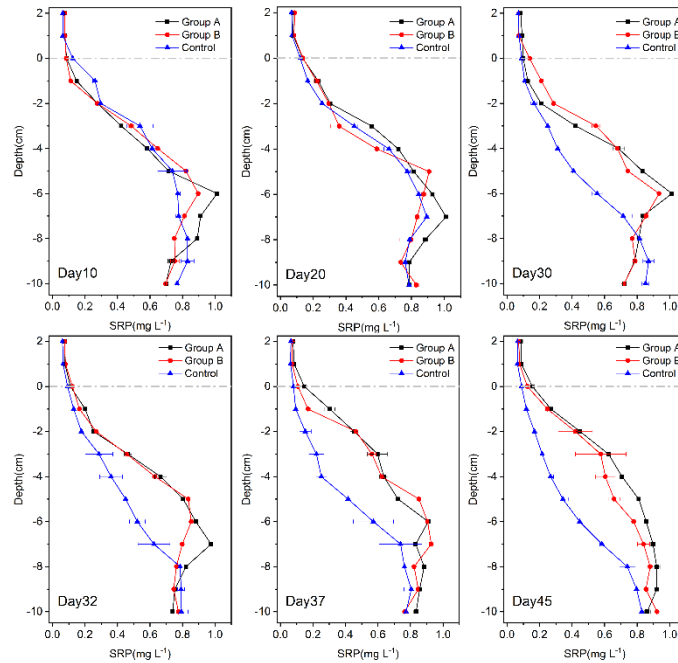
317 Figure 3. Changes in the concentration of sulfate with depth in the sediment-overlying water  
318 profiles (a) (data of sulfate was shown by the mean values of all sampling times during the 45-  
319 days incubation period  $\pm$ SD,  $n=12$ ), one-dimensional distributions of DGT-labile S in profiles  
320 as determined by AgI DGT (b) of different sulfate treatments (the data of labile S was shown  
321 by the mean values of all sampling times during the 45-days incubation period  $\pm$  SD,  $n=6$ ). The  
322 horizontal dashed line indicates SWI. Control:  $970$   $\mu\text{M}$ ; group B: low sulfate,  $1,770$   $\mu\text{M}$ ; group  
323 A: high sulfate,  $2,600$   $\mu\text{M}$ .

325 The labile S (Figure.3b) profiles exhibited a similar trend, increasing with depth in  
326 all three groups. Interestingly, lower concentrations of labile S in surface sediments  
327 were found in group A, except at day 20 (Figure.S4). The average concentrations of  
328 labile S within the depths from SWI to -3 cm in group A were lower than those in the

329 Control and group B (Figure.3b). However, that trend was reversed below -4 cm. The  
330 concentration of labile S in group A remained at a higher level in the deep sediment  
331 (below -3 to -4 cm) throughout the incubation period (Figure.S4). The average  
332 concentrations of labile S in group A from -4 to -10 cm were significantly higher than  
333 those in group B and the Control (one-way ANOVA,  $p<0.05$ ).

### 334 *3.3. Vertical distribution of SRP in sediment-water profiles*

335 Soluble reactive P (SRP) concentrations in the overlying water were significantly  
336 higher in the groups with the increasing sulfate concentration (one-way ANOVA,  
337  $p<0.05$ ) and the average values followed the order: group A>group B>Control (Figure.  
338 4 and Figure. S3). After the 30th day of incubation, the concentration of SRP in the pore  
339 water of sulfate addition groups (group A and B) was higher than the Control. On the  
340 45th day of incubation, the average concentrations of SRP in pore water from SWI to -  
341 8 cm in group A and group B were 52.3% and 48.6% higher than the Control. However  
342 below -8 cm, no evident difference in concentrations of SRP was observed during 45-  
343 days incubation between the three groups (RSD=1.06 % in three groups).



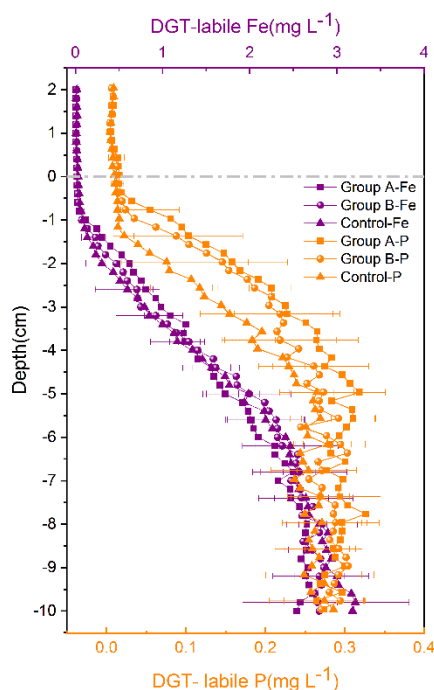
344

345 Figure 4. Changes of SRP (Soluble Reactive P) in the sediment-water profiles from the three  
 346 treatment groups during the 45-days incubation period (data shown by mean  $\pm$  SD,  $n = 2$ ). The  
 347 horizontal dashed line indicates the SWI. Control: 970  $\mu\text{M}$ ; group B: low sulfate, 1,770  $\mu\text{M}$ ;  
 348 group A: high sulfate, 2,600  $\mu\text{M}$ .

#### 349 3.4. Vertical distribution of DGT-labile Fe and P in sediment-water profile

350 The concentrations of labile Fe and P from the overlying water to the surface  
 351 sediments (SWI to -1cm) remained at relatively low values and increased until -10 cm  
 352 sediment depth (Figure.5, Figure.S5 and Figure.S6). There was no significant  
 353 difference for labile Fe and labile P between different sampling time (most of  $P > 0.05$ ,  
 354 the specific  $P$  values were listed in Table S2 and Table S3). Below -1cm, the  
 355 concentrations of labile Fe were varied from 0.24 to 2.71  $\text{mg L}^{-1}$  in group A, 0.13 to  
 356 2.82  $\text{mg L}^{-1}$  in group B and 0.10 to 3.21  $\text{mg L}^{-1}$  in the Control group, respectively.  
 357 However, the concentrations of labile P were ranged between 0.01 to 0.33  $\text{mg L}^{-1}$  in  
 358 group A, 0.03 to 0.30  $\text{mg L}^{-1}$  in group B and 0.01 to 0.28  $\text{mg L}^{-1}$  in the Control.

359 Statistically significant positive correlations between labile Fe and labile P in sediment  
360 were determined for each treatment ( $p < 0.001$ ) (Fig.S7).



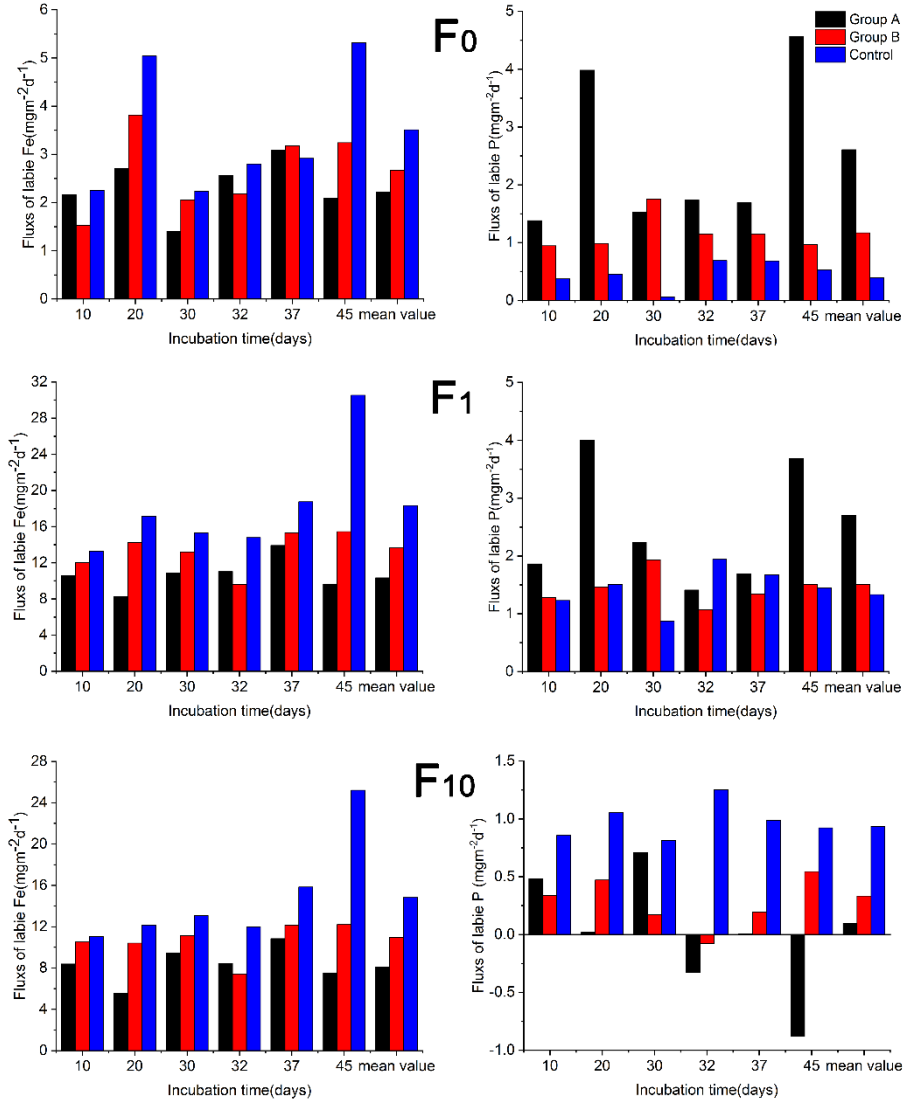
361  
362 Figure 5. Effects of the sulfate addition on the one-dimensional vertical distribution of DGT-  
363 labile P and DGT-labile Fe in water-sediments profiles (data shown by the mean values of all  
364 sampling times during the 45-days incubation period  $\pm$  SD,  $n=6$ ). The horizontal dashed line  
365 indicates the sediment-water interface (SWI). Control: 970  $\mu\text{M}$ ; group B: low sulfate, 1,770  
366  $\mu\text{M}$ ; group A: high sulfate, 2,600  $\mu\text{M}$ .

### 367 3.5. Apparent diffusive flux of $\text{PO}_4^{3-}$ and $\text{Fe(II)}$

368 The apparent diffusive fluxes of the target elements were calculated at SWI ( $F_0$ ) and  
369 1 cm below the SWI ( $F_1$ ) based on Fick's first law (Figure. 6). The apparent fluxes of  
370  $\text{PO}_4^{3-}$  and  $\text{Fe(II)}$  in the three groups across the SWI were all positive (effluxes) and  
371 ranged between 0.06 to 4.56  $\text{mgm}^{-2}\text{d}^{-1}$  and 1.41 to 5.32  $\text{mgm}^{-2}\text{d}^{-1}$ , respectively. The  
372 mean flux of  $\text{PO}_4^{3-}$  from the surface layer of sediment to water ( $F_0$ ) showed an  
373 increasing trend with the increase of sulfate in overlying water. The mean  $F_0$  of  $\text{PO}_4^{3-}$

374 in group A and group B were 5.5 and 1.9 times higher than that in the Control (0.40  
375  $\text{mgm}^{-2}\text{d}^{-1}$ ), respectively. The mean  $F_0$  of Fe(II) was lowest in group A (2.22  $\text{mgm}^{-2}\text{d}^{-1}$ )  
376 compared to that in group B (2.67  $\text{mgm}^{-2}\text{d}^{-1}$ ) and the Control (3.51  $\text{mgm}^{-2}\text{d}^{-1}$ ). The  
377 values of  $F_1$  in three groups were also positive and the fluxes of  $\text{PO}_4^{3-}$  and Fe(II) from  
378 deep sediment to surface sediment ranged between 0.88 to 4.00  $\text{mgm}^{-2}\text{d}^{-1}$  and 8.24 to  
379 30.53  $\text{mgm}^{-2}\text{d}^{-1}$ . Increasing sulfate in overlying water elevated the mean values of the  
380 flux of  $\text{PO}_4^{3-}$  from deep sediment to surface sediment ( $F_1$ ) with order of group A>group  
381 B>Control, whereas an opposite trend was observed for Fe(II).

382 The net flux ( $F_{10}$ ) of  $\text{PO}_4^{3-}$  and Fe(II) in the surface sediment was calculated by  
383 using the equation:  $F_{10}=F_1-F_0$ . The  $F_{10}$  of  $\text{PO}_4^{3-}$  and Fe(II) were all positive, except for  
384  $F_{10}$  of P in group A (highly variable, from 0.88 to -0.48  $\text{mgm}^{-2}\text{d}^{-1}$ ). The mean values of  
385  $F_{10}$  decreased with the increased sulfate in the overlying water. The retention  
386 efficiencies (defined by the quotient of  $F_1$  and  $F_{10}$ ) of P, diffused from deep to surface  
387 sediments in the Control group was about 70.1% and obviously higher than those in the  
388 group A and group B groups (3.6% and 22.1%, respectively). The retention efficiencies  
389 of Fe(II) were 78.5%, 80.4% and 80.8% in group A, group B and C, respectively.



390

391 Figure. 6 the apparent diffusive fluxes of  $\text{PO}_4^{3-}$  and  $\text{Fe}^{2+}$  in different treatments. The label  $F_0$   
 392 represents the diffusive flux of  $\text{PO}_4^{3-}$  and  $\text{Fe}^{2+}$  from surface sediments to water.  $F_1$  represents the  
 393 diffusive flux of  $\text{PO}_4^{3-}$  and  $\text{Fe}^{2+}$  from deep to surface sediments.  $F_{10}$  ( $F_{10}=F_1-F_0$ ) is net flux of  
 394  $\text{PO}_4^{3-}$  and  $\text{Fe}^{2+}$  in surface sediment. The mean flux of each group represents the average flux  
 395 during the 45-days incubation period. The mean values of fluxes given here were calculated

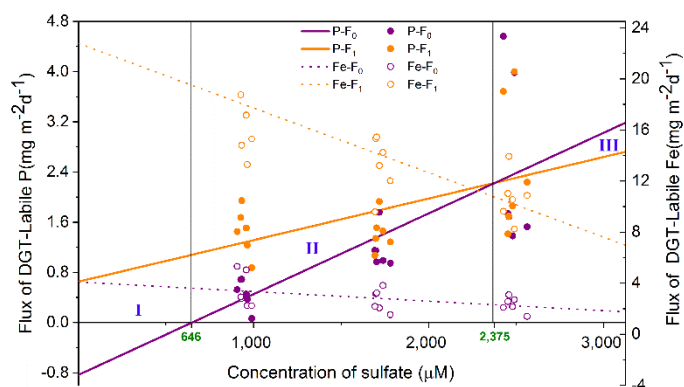
396 according to the following equation: 
$$\bar{F} = \frac{\sum_{i=1}^6 (F_i \times t_i)}{\sum_{i=1}^6 t_i}$$

397 Where  $\bar{F}$  is the average flux during the 45-days incubation ( $\text{mg m}^{-2} \text{d}^{-1}$ ),  $F_i$  is the flux on  
 398 the  $i^{\text{th}}$  sampling day ( $\text{mgm}^{-2} \text{d}^{-1}$ ),  $t_i$  is the time interval from the  $(i-1)^{\text{th}}$  sampling day to the  $i^{\text{th}}$   
 399 sampling day (day). Control:  $970 \mu\text{M}$ ; group B: low sulfate,  $1,770 \mu\text{M}$ ; group A: high sulfate,  
 400  $2,600 \mu\text{M}$ .

401 3.6. Relationship between sulfate concentration and internal P release

402 Based on the fluxes of labile Fe and P at six sampling times across the SWI ( $F_0$ ) and  
403 1 cm below the SWI ( $F_1$ ), we constructed the diagram for sulfate (Figure. 7). The fluxes  
404 of labile P from deep to surface sediments ( $F_1$ ) were all positive. Furthermore, a 100  
405  $\mu\text{M}$  increase of sulfate in overlying water, compared to the concentration of sulfate in  
406 the Control group, would induce a  $0.128 \text{ mgm}^{-2}\text{d}^{-1}$  increase of P flux from surface  
407 sediment to the overlying water (Figure. S8).

408 When the concentrations of sulfate were less than  $646 \mu\text{M}$  (Part I in the diagram),  
409 the flux of labile P across the SWI was negative. When the concentration increased  
410 from  $646$  to  $2,375 \mu\text{M}$  (Part II), the difference between  $F_1$  and  $F_0$  of labile P gradually  
411 reduced to zero. When the concentration of sulfate further increased to more than  $2,375$   
412  $\mu\text{M}$  (Part III),  $F_0$  of labile P was larger than  $F_1$ . The flux of labile Fe at two depths, over  
413 the whole concentration range of sulfate ( $0$  to  $3,000 \mu\text{M}$ ), were all positive and  $F_0$  was  
414 always less than  $F_1$ . In addition, the difference between  $F_0$  and  $F_1$  of labile Fe  
415 continuously decreased with the increase of sulfate in overlying water.



416

417 Figure. 7. The functional relation between the apparent diffusive fluxes of  $\text{PO}_4^{3-}(\text{Fe}^{2+})$  and  
418 sulfate in overlying water within a concentration range of  $0$ - $3,000 \mu\text{M}$ . The label  $F_0$  represents

419 the diffusive flux of  $\text{PO}_4^{3-}$  and  $\text{Fe}^{2+}$  from surface sediment to overlying water and  $F_1$  represents  
420 the diffusive flux from deep to surface sediments.

## 421 **4. Discussion**

### 422 *4.1. Effects of sulfate elevation on the internal P release*

423 It has been reported that elevated sulfate concentrations in freshwaters systems with  
424 intermediate concentrations of sulfate ( $>100 \mu\text{M}$ ), greatly promoted the release of  
425 internal P under anoxic conditions (Caraco et al. 1989, 1993, Chen et al. 2016a). As for  
426 under oxic conditions, Zak et al. (2006) found that increasing sulfate affected the  
427 mobilization of P in a lowland freshwater river polluted by mining activities with  
428 extremely high concentrations of sulfate (2,600-7,800  $\mu\text{M}$ ). Those concentrations of  
429 sulfate are typical of the concentration range ( $\sim 3,000$ -30,000  $\mu\text{M}$ ) of salt waters (Caraco  
430 et al. 1989). Here, we additionally found that sulfate with modest concentrations (970-  
431 2,600  $\mu\text{M}$ ) promoted release of P under oxic conditions across the SWI.

432 A higher concentration of SRP in the overlying water was observed with an increase  
433 in sulfate (Figure. 4 and Figure. S3). At the end of experiment, the mean concentrations  
434 of SRP in sediment pore water from the SWI to -8 cm were 52.3% and 48.6% greater  
435 in the group A and group B, respectively, when compared to the Control group (Figure.  
436 4). In addition, P fluxes at the SWI were all positive, which suggested that P was  
437 released from surface sediments to the water column (Figure.6). P fluxes from deep to  
438 surface sediments (Figure.6) were also positive ( $F_1$  of P  $>0$ ) and larger than the  
439 corresponding fluxes from surface sediment to water, indicating that P released from

440 the oxic surface sediment mainly originated from deeper sediment. Compared with our  
441 results under oxic conditions, the maximum concentration of SRP in overlying water  
442 under anoxic environments was one order of magnitude higher and the released P was  
443 mainly from surface sediments (Chen et al. 2016a, Han et al. 2015). These results  
444 demonstrated that redox conditions clearly influenced the mechanisms of sulfate-  
445 promoted release of internal P.

#### 446 *4.2. Mechanisms of sulfate-promoted release of internal P*

447 The process of sulfate-promoted internal P release is closely linked to the reduction  
448 of sulfate in sediments (Caraco et al. 1989, Roden and Edmonds 1997, Rozan et al.  
449 2002, Zak et al. 2006). Higher concentrations of labile S below -3cm (Figure. 3b) were  
450 observed in group A, which can be mainly attributed to the increase of sulfate in  
451 overlying water triggering more sulfate penetration and reduction in the deep sediment.  
452 The fluxes of P from deep to surface sediments increased along with the increase of  
453 sulfate in water column (Figure. 6). This result agreed well with the previous report that  
454 P mobilization is ultimately dependent on the concentration of S(-II) (Zhao et al. 2019).  
455 Usually, the source of sulfide is mainly controlled by the reduction of sulfate (Motelica-  
456 Heino et al. 2003), which, in freshwater sediments, is regulated by many factors, such  
457 as dissolved oxygen, organic matter and concentration of sulfate (Leonov and  
458 Chicherina 2008). Here, below the depth of -1 cm, oxygen was exhausted (Figure. 2a)  
459 and ORP values decreased to <100 mV (Figure. 2c) in all three groups, which suggested  
460 that deep sediment became anoxic and conditions were suitable for sulfate reduction.

461 The rate of sulfate reduction has been reported as a diffusion-limited, first-order rate  
462 process and dependent on initial sulfate concentration (Loh et al. 2013). In our study,  
463 increasing concentrations of sulfate in the overlying water led to higher concentrations  
464 of sulfate in the pore water (Figure. 3a), which may have accounted for the enhanced  
465 activity of sulfate reduction in the deeper, anoxic layers of sediment.

466 In addition to influencing sulfate reduction in the sediments, higher concentrations  
467 of sulfate in the overlying water will also influence the dynamics of Fe(II) in the  
468 sediment (Figure. 6). The positive correlations ( $p < 0.001$ ) between labile Fe(II) and  
469 labile P (Figure.S7) in each treatment that suggested coincident distributions of labile  
470 Fe and labile P existed in the sediment. These coincident distributions with depth should  
471 be a result of the reduction of the P-bearing Fe(III)(oxyhydr)oxides (Ding et al. 2012,  
472 Xu et al. 2012). The reduction of Fe(III)(oxyhydr)oxides in sediments to Fe(II), is a  
473 basic pattern for the P mobilization from sediment to water (Christophoridis and  
474 Fytianos 2006). The Fe(II) produced can be maintained in the deep sediment through  
475 the formation as iron sulfide coupled with sulfate reduction (Roden and Edmonds 1997).  
476 For instance, even under sulfate concentrations limited to 200  $\mu\text{M}$ , sulfide-mediated  
477 chemical iron reduction (SCIR) in freshwater systems is a dominate pathway of iron  
478 reduction (Hansel et al. 2015). The reduced Fe(II) could precipitate as sulfides via SCIR  
479 or directly react with S(-II) in the pore water other than getting back into pore water  
480 (Kwon et al. 2014, Lehtoranta et al. 2009). These coincide with our observations that  
481 the concentration range of labile Fe (Figure. 5) and fluxes of labile Fe from deep

482 sediment to surface sediment (Figure. 6) were both decreased in high sulfate system  
483 (group A) under a higher concentration of S(-II). Thus, the upward diffusive fluxes of  
484 Fe(II) from deep to surface sediments in high sulfate systems were reduced by enhanced  
485 sulfate reduction. This resulted in less Fe(II) and sulfide diffusing to the surface  
486 oxidized layer as Fe(II) precipitation as sulfides occurred in the deep sediments.  
487 Therefore, fewer reducing substances would consume oxygen already present in  
488 sediment in High sulfate systems, supporting the observation that a better-oxidized  
489 condition existed in surface sediments and that higher DO concentrations across the  
490 SWI were found in group A and group B systems compared to the Control (Figure. 2a).

491 In this study, the oxygen penetration depth (OPD) varied from 0.48 to 0.78 cm  
492 (Figure.2b), suggesting that an oxidized layer existed in the surface sediment. Under  
493 natural conditions, a thin oxidized layer may exist in surficial sediment in shallow  
494 waters, where it can easily be further oxygenated by hydrodynamic disturbance  
495 (Chatelain and Guizien 2010). Oxic conditions are important for iron to maintain its  
496 oxidized state, which, in turn, correlates with P retention in sediments (Mortimer 1942).  
497 The OPD regulates the thickness of the oxic layer (Wang et al. 2014), a higher thickness  
498 decreasing the P release from sediment to overlying water (McManus et al. 1997).  
499 However, a higher concentration of SRP released from surface sediment to water was  
500 observed in the High sulfate (group A) system (Figure. 4 and Figure. 6). These results  
501 suggested that even the deeper OPD of around several millimeters might not be enough  
502 to retain the excessive P released from sediment to water induced by elevated sulfate.

503 Most of the upward diffused Fe(II) in each group (retention efficiencies of Fe(II)  
504 varied from 78.5% to 80.8%) was oxidized and retained in surface sediment (Figure. 6)  
505 as the oxidation of Fe(II) by oxygen is a rapid process (Chen et al. 2015). Lower fluxes  
506 of Fe(II) from deep to surface sediment in the higher sulfate level systems resulted in a  
507 lower P-retaining capacity in surface sediments. The decreased ratio of labile Fe to P in  
508 sediment associated with higher sulfate also suggested higher sulfate lowered the P  
509 retaining capacity (Figure. S7). Therefore, the fluxes of Fe(II), rather than oxygen, were  
510 responsible for the larger release of P in more concentrated sulfate systems.

#### 511 *4.3. Concentration effect of sulfate on internal P release*

512 In this study, we found that increasing sulfate could promote internal P release in  
513 eutrophic waters and have the potential to switch sediments between P source and sink,  
514 if factors other than sulfate concentration are not considered (Figure.7). **The control of**  
515 **P and sulfate concentration in water were both necessary.** Thus, it is important to  
516 quantify the effects of sulfate concentration on internal P release under oxic conditions  
517 across the SWI in any given freshwater system.

518 That the fluxes of P from deep to surface sediments were all positive ( $F_1$  of  $P > 0$ )  
519 suggesting that, in some eutrophic waters, P release from deep sediments might be  
520 inevitable. When concentrations of sulfate were lower than 646  $\mu\text{M}$ , well-oxidized  
521 conditions across the SWI would be effective for sediment retention of P ( $F_0$  of  $P < 0$ ).  
522 However, at sulfate levels  $> 646 \mu\text{M}$ , a 100  $\mu\text{M}$  increase of sulfate in overlying water  
523 would result in a  $0.128 \text{ mgm}^{-2}\text{d}^{-1}$  increase in P flux from the sediment to the water

524 column. In this case, just maintaining a thin oxidized layer (<1 cm) in surface sediment  
525 would not be sufficient to control internal P release, as enhanced sulfate reduction  
526 limited the Fe(II) release from deep to surface sediments. Once sulfate increased to  
527 more than 2,375  $\mu\text{M}$ , the retention capacity for P in the oxidized layer would be  
528 exhausted and surface sediment would become another source of P to be released to  
529 overlying water. Furthermore, increasing concentrations of sulfate, would gradually  
530 reduce the upward diffusion of Fe(II) from the deep sediment, decreasing the  
531 production of new adsorption sites for P in surface sediments.

#### 532 *4.4. Environmental implications*

533 Previous studies reporting that sulfate could induce the release of P from sediment  
534 mainly focused on anoxic conditions (Caraco et al. 1993, Chen et al. 2016a, Han et al.  
535 2015, Roden and Edmonds 1997). However, a thin oxidized layer usually exists in  
536 surficial sediments in shallow waters and anoxic conditions might not persist during  
537 most seasons except over the algal bloom period. In this study, we found that, under  
538 oxic conditions across the SWI with modest concentrations of sulfate in eutrophic  
539 freshwater, increasing sulfate levels could also promote the release of P from the  
540 sediment. The release of internal P induced by sulfate under oxic conditions across the  
541 SWI was one magnitude less than in anoxic environments. However, as cyanobacteria  
542 have a higher affinity for P, situations with these low concentrations and continuously-  
543 released phosphorus from sediment may still contribute to eutrophication and even  
544 production of algal blooms (Prentice et al. 2015). **Sediments served as a source for the**

545 P supply in the water column used by cyanobacteria, and such a process was activated  
546 greatly by the higher concentration of sulfate, which pumped up more P from the  
547 sediments. More importantly, the intensity of P release was directly influenced by the  
548 concentration of sulfate in overlying water and the flux of Fe(II) was the primary factor  
549 responsible for P retention. Therefore, as oxygen penetration depth in natural sediments  
550 is limited, just improving or maintaining the oxygen level in bottom water may alone  
551 be insufficient ~~to control internal P release in a high sulfate ecosystem~~. Technologies  
552 aim to increase the depth of oxygen penetration in sediment, suppress the sulfate  
553 reduction, or provide new adsorption sites in sediment would be promising for the  
554 control internal P release in a high sulfate ecosystem.

## 555 5. Conclusions

556 This study investigated the effect of increasing sulfate in shallow waters on internal  
557 P release under oxic conditions across the SWI. Higher concentrations of sulfate  
558 increased the concentration of SRP in both overlying and pore waters. In addition,  
559 higher concentrations of sulfate in overlying water induced a significant increase of  
560 labile S(-II) in deep sediment, indicating that enhanced sulfate penetration and  
561 reduction occurred in deeper layers of sediment. The fluxes of labile Fe and P from  
562 deep to surface sediments were positive and greater than the corresponding fluxes from  
563 surface sediment to water column, suggesting that reduction of P-bearing  
564 Fe(III)(oxyhydr)oxides in deep sediment acted as a major source for internal P release  
565 under oxic conditions across the SWI. Lower fluxes of Fe(II) from deep to surface

566 sediments were found in the High sulfate experimental system, resulting in less re-  
567 oxidized Fe(III) in surface sediments. However, induced by the elevated sulfate, more  
568 P released from deep sediment to surface sediment inevitably resulted in an increase in  
569 the flux of P across the SWI. The results indicated that the influence of sulfate on  
570 internal P released depended largely on the concentrations of sulfate. When the  
571 concentration of sulfate was larger than ca. 646  $\mu\text{M}$ , a 100  $\mu\text{M}$  increase of sulfate  
572 induced a 0.128  $\text{mgm}^{-2}\text{d}^{-1}$  increase of P flux from surface sediment to water column.  
573 Therefore, sulfate concentrations should be considered and controlled for the  
574 management of eutrophic waters.

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