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## Phosphorus release from the drying and reflooding of diverse shallow sediments

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18 **Abstract**

19           Phosphorus (P) retention is an important ecosystem service provided by sediments and soils. However,  
20 when shallow aquatic sediments and poorly drained soils dry and re-flood, they can be a source, rather than a sink,  
21 of P. Using experimental drying and re-flooding in the laboratory, we assessed the resultant sediment-water P  
22 exchange in a biogeochemically diverse set of sediments from 16 sites in Michigan. The direction and magnitude of  
23 P exchange to pore waters and surface waters upon re-flooding varied among sediments. Different sediment  
24 properties were related to P release to pore water than to P release to overlying surface water, suggesting that  
25 different processes control two phases of sediment P release: mobilization from solid to dissolved forms in the  
26 sediment pore water; and movement of dissolved P from pore water into overlying surface water. We observed  
27 especially high P release in dried and re-flooded sediments with high amounts of loosely sorbed phosphate,  
28 suggesting that drained sediments with a legacy of high P loads will be most likely to release P and experience  
29 internal eutrophication when re-flooded. The differential responses of sediments suggest that aquatic ecosystem  
30 restoration and management for nutrient removal must be evaluated with site-specific knowledge of sediment and  
31 soil biogeochemistry.

32 **Key Words:** water level fluctuations, wetland restoration, sediment, soil, phosphorus, iron

33

## 34 **Introduction**

35           Phosphorus (P) pollution continues to drive the cultural eutrophication of aquatic ecosystems, especially  
36 within and downstream of agricultural and urban areas (Carpenter et al. 1998). Shallow aquatic ecosystems can  
37 retain P, preventing its movement to sensitive downstream water bodies (Reddy and DeLaune 2008). For this  
38 reason, wetlands and streams are often constructed, restored, and/or managed to mitigate P pollution (Kadlec and  
39 Wallace 2009). The most permanent mechanism of wetland P removal is storage and burial in sediments (Johnston  
40 1991), yet the capacity of sediments to retain P is variable (Richardson 1985). At times, sediments can be sources of  
41 P (Richardson 1985; Coveney et al. 2002; Dunne et al. 2012), particularly in restored areas with a legacy of P  
42 addition (McLauchlan 2006).

43           Many shallow aquatic ecosystems, including wetlands, experience seasonal and inter-annual water level  
44 fluctuations, which may be exacerbated or attenuated by human actions such as water withdrawals, engineered land  
45 drainage, and controlled re-flooding of historically drained areas (Ardón et al. 2010; Steinman and Ogdahl 2011;  
46 Kinsman-Costello et al. 2014). When soils or sediments are dried and re-flooded, they often release a pulse of  
47 inorganic nutrients, a phenomenon sometimes referred to as the “Birch effect” (Birch 1960; Baldwin and Mitchell  
48 2000; Wilson and Baldwin 2008). Increases in drought conditions and extreme precipitation events in the United  
49 States should lead to more frequent sediment drying and re-flooding events (Pryor et al. 2014). Shallow ecosystems  
50 are especially sensitive to hydrologic change because relatively small changes in water level may inundate or expose  
51 large areas of sediment, strongly affecting biogeochemical processes due to consequent changes in redox potential  
52 and moisture. Sediments usually represent a large pool of P (e.g., Dunne et al. 2007), and sediment-water exchange  
53 can control available P in shallow overlying water columns.

54           Sediment-water P exchange is controlled by several distinct biogeochemical processes, including sorption-  
55 desorption, co-precipitation, biotic assimilation, and organic matter mineralization (Boström et al. 1988), as well as  
56 physical transport processes including diffusion and advection (Wetzel 2001). A longstanding paradigm, developed  
57 through research on lake sediments, is that phosphate ( $\text{PO}_4^{3-}$ ) sorption to a “cap” of oxidized iron (Fe) minerals at  
58 the sediment-water interface is the primary mechanism of sediment P retention, preventing  $\text{PO}_4^{3-}$  dissolved in pore  
59 water from entering overlying water (Mortimer 1941; Mortimer 1942). When oxygen is depleted at the sediment-  
60 water interface, microbial Fe reduction leads to  $\text{PO}_4^{3-}$  desorption and potential release into surface waters (Marsden  
61 1989). Conversely, when flooded sediments are drained or dried, exposure to oxygen may increase  $\text{PO}_4^{3-}$  sorption as

62 formerly reduced Fe is oxidized (De Groot and Fabre 1993). Drying influences this sorption-desorption not only by  
63 exposing redox-sensitive metals to oxygen, but also by changing their mineral forms (Twinch 1987; Baldwin and  
64 Mitchell 2000; Qiu and McComb 2002).

65         At times, the structure of Fe minerals may supersede their redox status in determining  $\text{PO}_4^{3-}$  sorption  
66 capacity (Baldwin 1996; Loeb et al. 2008). Across soils and sediments from diverse ecosystems and hydrologic  
67 regimes, one of the strongest predictors of sediment  $\text{PO}_4^{3-}$  sorption is consistently the amount of poorly crystalline  
68 Fe and/or aluminum (Al) oxides and oxyhydroxides (Shukla et al. 1971; Williams et al. 1971; Richardson 1985;  
69 Darke and Walbridge 2000). Flooding dry soils usually causes an increase in poorly crystalline Fe and Al oxides  
70 (Sah and Mikkelsen 1989; Darke and Walbridge 2000; Zhang et al. 2003), whereas drying flooded sediments  
71 usually decreases these amorphous forms (Twinch 1987; Baldwin 1996; Qiu and McComb 2002; de Vicente et al.  
72 2010). Thus, sediment drying may have counteracting effects on sediment  $\text{PO}_4^{3-}$  sorption by simultaneously  
73 oxidizing reduced Fe minerals (increasing sorption capacity) and increasing their crystallinity (decreasing sorption  
74 capacity).

75         Although Fe mineral sorption is often the dominant form of P retention in soils and sediments, other  
76 processes involving sulfur, calcareous minerals, and organic matter also control sediment-water P exchange  
77 (Boström et al. 1988; Hupfer and Lewandowski 2008). Free sulfide (hereafter  $\text{H}_2\text{S}$ ) reacts with Fe to form insoluble  
78 Fe sulfide minerals ( $\text{FeS}_x$ ), effectively inactivating Fe binding sites and diminishing  $\text{PO}_4^{3-}$  sorption capacity (Roden  
79 and Edmonds 1997). The Fe- $\text{PO}_4^{3-}$  sorption capacity can be reconstituted by  $\text{FeS}_x$  oxidation when sediments dry  
80 (Smolders et al. 2006b; Dieter et al. 2015). In calcareous sediments,  $\text{PO}_4^{3-}$  can co-precipitate with or sorb to calcium  
81 carbonate ( $\text{CaCO}_3$ ) minerals, retaining large amounts of P (Hamilton et al. 2009). These calcareous minerals tend to  
82 precipitate from alkaline waters with a rise in pH and/or temperature, and to dissolve under acidic conditions  
83 (Boström et al. 1988). Finally, organic matter often contains the largest pool of P in shallow aquatic sediments (e.g.,  
84 Dunne et al. 2007). The release of P from organic matter occurs mainly by microbial mineralization, which is  
85 stimulated when anoxic sediments are drained and exposed to oxygen (Baldwin and Mitchell 2000; Dieter et al.  
86 2015). Other organic P transformation pathways, like abiotic hydrolysis by minerals, have been identified in  
87 laboratory studies, although their magnitude and importance in ecosystems remain largely unknown (Baldwin 2013).

88         Despite our understanding that complex biogeochemical processes control sediment P retention and release  
89 (Richardson 1985; Boström et al. 1988), the net effect of sediment drying and re-flooding on P flux remains difficult

90 to predict. In part this is because few studies have conducted comparative experiments on sediments with widely  
91 varying characteristics. We conducted laboratory experiments to test the effects of sediment drying and re-flooding  
92 on sediment-water P exchange using sediments from 16 shallow freshwater ecosystems of diverse biogeochemistry.  
93 We hypothesized that the direction and magnitude of sediment-water P exchange in response to experimental drying  
94 and re-flooding would be affected by biogeochemical characteristics (Figure 1). We predicted that 1) sediments with  
95 high total Fe and/or  $\text{FeS}_x$  would release less P after drying and re-flooding than when continuously flooded due to  
96 oxidation of reduced Fe; 2) primarily organic sediments would release more P when dried and re-flooded than  
97 continuously flooded due to enhanced mineralization rates, and 3) in calcareous sediments,  $\text{CaCO}_3$ -associated P  
98 would increase during drying due to loss of porewater carbon dioxide and consequent pH increases, unless  
99 simultaneous oxidation processes produced sufficient acid to exceed the sediment's buffering capacity (Figure 1).  
100 These predictions are not mutually exclusive and more than one of them may be important in some sediments.

## 101 **Methods**

### 102 *Overview of Experimental Design*

103 We collected sediment from 16 shallow freshwater ecosystems in southwest Michigan near Michigan State  
104 University's W.K. Kellogg Biological Station, choosing sites that spanned a gradient of groundwater influence to  
105 maximize biogeochemical diversity (Table 1). Sediment samples were not intended to represent the specific sites  
106 from which they were sampled, but rather to provide a diversity of biogeochemical characteristics for comparative  
107 purposes. The sediments were distributed into microcosms with overlying low-nutrient water columns. We subjected  
108 microcosms to one of two hydrologic treatments: temporary drying followed by re-flooding ("Dry") or continuous  
109 flooding ("Reference"). For each of the 16 sediments, each treatment was replicated three times, for a total of 96  
110 experimental units.

111 To test for effects on sediment-water P exchange, we measured soluble reactive phosphorus (SRP) in pore  
112 and surface waters through time. We considered sediment P to have been "retained" when it was maintained in solid  
113 forms, including through sorption, co-precipitation, and covalent bonding (i.e., in organic material), and to have  
114 been "released" when dissolved, reactive  $\text{PO}_4^{3-}$  was measured in either pore or surface water.

### 115 *Sediment Sampling*

116 We collected sediments under 0.5-1 m of water (Eckman grab, 10-20 cm depth) on two dates (June and  
117 September 2009) and experiments were conducted in two groups of eight sediments each. Within 24 hours of

118 sampling, we sieved (2 mm) and homogenized the wet sediments. Homogenization was necessary for replicated  
119 experimental treatments because sediments from shallow water bodies are inherently variable over small spatial  
120 scales. Homogenization was done carefully and quickly to minimize exposure to oxygen. We sub-sampled  
121 homogenized material for a suite of chemical characterizations including sequential P extraction. We stored sieved  
122 sediment in sealed buckets at 4°C for up to 6 days prior to establishment of microcosms.

### 123 *Experimental Methods*

124 The hydrologic manipulation had three phases: equilibration, drying, and re-flooding. Sediments were  
125 distributed into microcosms (clear acrylic tubing, 46 cm tall, 7.3 cm diameter) to a height of 15 cm. Within four  
126 days, we initiated the equilibration phase by carefully adding one liter of filtered (Whatman GF/F, 0.7  $\mu$  m) lake  
127 water (Lower Crooked Lake, MI, Supplemental Table 1). We used overlying water from a single source for all  
128 microcosms to isolate effects of sediment differences on sediment-water P flux from surface water chemistry effects.  
129 We allowed sediments to equilibrate with overlying water for 2-5 weeks, during which oxygen in the overlying  
130 water was kept close to atmospheric equilibrium using aquarium bubblers to mimic an oxygenated productive water  
131 column. After observing that SRP concentrations in overlying water changed relatively little after the first 2 weeks  
132 of equilibration, a shorter equilibration phase was used for the second set of incubations.

133 After equilibration, we imposed hydrologic treatments (drying phase). For each sediment, we removed  
134 surface water from three of the six microcosms, placing them in a forced-air drying oven set at 30 °C for 4-5 weeks  
135 (Dry microcosms). The other three replicates remained flooded as during the equilibration phase (Reference  
136 microcosms). Sediments contained variable levels (1-44%) of soil moisture (determined gravimetrically) at the end  
137 of the drying phase due to initial textural differences. To begin the re-flooding phase, we carefully removed surface  
138 water from Reference microcosms and replaced it with fresh low-nutrient filtered lake water. Sediment in the Dry  
139 microcosms was rewetted with 100-300 mL of de-ionized water to replace moisture lost to evaporation, and  
140 subsequently re-flooded with one liter of low-nutrient filtered lake water.

### 141 *Measuring Response to Hydrologic Treatment*

142 We assessed sediment-water P exchange and related processes by sampling surface and pore waters for  
143 SRP, sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), and reduced iron (Fe(II)) during the re-flooding phase. We sampled surface  
144 water by filtering (0.45  $\mu$  m cellulose-acetate filter with a glass fiber pre-filter, Steriltech) 30 mL of water from the  
145 top of the water column, which was mixed by the aerator. We sampled 10 mL of sediment pore water through a

146 nominal pore size of  $\sim 0.2 \mu\text{m}$  installed at the vertical midpoint of the sediment column prior to adding homogenized  
147 sediment to experimental units (Rhizon; Rhizosphere Research Products, Wageningen, The Netherlands). We  
148 replaced the volume sampled with low nutrient filtered lake water. After 9-11 weeks of flooding, we recorded  
149 sediment heights to calculate bulk density and siphoned off surface water for water chemistry analysis.

#### 150 *Laboratory Analyses*

151 We measured SRP concentrations in surface and pore water samples using the molybdate blue colorimetric  
152 method (Murphy and Riley 1962), and  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  using membrane-suppression ion chromatography. We  
153 measured Fe(II) using a modified ferrozine assay (Lovley and Phillips 1987). Organic matter, total phosphorus  
154 (Total P), total iron (Total Fe), total carbonate ( $\text{CaCO}_3$ ), acid volatile sulfides (AVS), Ox-Fe, and sequentially  
155 extracted P binding fractions were measured in homogenized moist sediment prior to the experimental treatments.  
156 We used acid ammonium oxalate to measure oxalate-extractable Fe (Ox-Fe), an indicator of poorly crystalline iron  
157 minerals (McKeague and Day 1966; Walbridge et al. 1991) and analyzed organic matter as loss on ignition. We  
158 extracted Total P and Total Fe as in Andersen (1975) and quantified  $\text{CaCO}_3$  by acidifying in a sealed container,  
159 measuring  $\text{CO}_2$  produced using a pressure transducer. We measured Fe in Ox-Fe and Total Fe extracts using flame  
160 atomic absorption spectrophotometry. We froze moist sediment for AVS analysis (US EPA Method 821-R-91-100)  
161 by acidifying sediment samples with HCl to convert AVS to  $\text{H}_2\text{S}$ , which was then trapped as sulfide ( $\text{S}^{2-}$ ) in an  
162 alkaline solution (0.5 M NaOH) and measured colorimetrically after reaction with a mixed diamine reagent ( $\text{H}_2\text{SO}_4$ ,  
163 N,N-dimethyl-p-phenylenediamine oxalate, and ferric chloride hexahydrate) (Allen et al. 1991). Analytical sulfide  
164 standards were prepared from a stock solution standardized versus thiosulfate.

#### 165 *Sequential Extraction of P Binding Fractions*

166 We used a sequential extraction procedure (Paludan and Jensen 1995) to measure operationally defined  
167 sediment P binding fractions (Pettersson et al. 1988). The first step used de-oxygenated de-ionized water to extract  
168 loosely bound P ( $\text{H}_2\text{O}\sim\text{P}$ ). Next, bicarbonate-buffered dithionite (0.11 M) extracted  $\text{PO}_4^{3-}$  bound to redox-sensitive  
169 oxidized iron minerals (BD $\sim$ P) and some non-reactive (mostly organic) P (BD $\sim$ DNRP) (Reitzel et al. 2006). This  
170 step also may extract some apatite-bound P in calcareous sediment (Reitzel 2005). The third step used sodium  
171 hydroxide (0.1 M NaOH) to extract  $\text{PO}_4^{3-}$  bound to redox-insensitive Al and Fe oxides that undergo anionic  
172 exchange with hydroxide (NaOH $\sim$ SRP) and non-reactive organic and inorganic P (pyro- and polyphosphates). Non-  
173 reactive P extracted by NaOH was acidified to separate out precipitating humic acid associated P (HA $\sim$ P) from other



174 non-reactive P molecules (NaOH~DNRP). After NaOH extraction, HCl (0.5 M) extracted acid-soluble P, mostly  
175 bound to apatite and other calcareous minerals (HCl~P). Residual P in the sediment pellet following the preceding  
176 chemical treatments was presumed to be bound in highly recalcitrant organic matter or crystalline mineral  
177 substances, and was extracted by combustion followed by boiling for 10 min in 1 M HCl (Res~P). Reactive P in  
178 each fraction was detected colorimetrically, and non-reactive P was measured as the difference between reactive P  
179 and colorimetrically detected P following persulfate digestion (total P). We did not detect any non-reactive H<sub>2</sub>O~P  
180 or BD~P, so results are not reported for those fractions. As an indicator of all organic P fractions, we summed the  
181 NaOH~DNRP and HA~P fractions and called this fraction Organic~P. Although the operationally defined measured  
182 NaOH~DNRP and HA~P fractions may not entirely be composed of covalently bonded organic P molecules, past  
183 research has shown them to be mostly composed of organic P, and thus we use them as indicators of, rather than  
184 direct measures of, sediment organic P (Reitzel et al. 2006).

#### 185 *Statistical Analyses*

186 We calculated initial P flux rates between the sediment and overlying water over the first 30 days after re-  
187 flooding, using the slope calculated by linear regression analysis of SRP concentration with time (days after re-  
188 flooding). If the slope was not significantly different from zero ( $\alpha = 0.05$ ), the flux rate was deemed to be zero.  
189 Because of logistical constraints on the frequency of porewater sampling, we obtained insufficient numbers of  
190 samples to calculate meaningful flux rates between sediments and pore water.

191 To detect P and Fe concentration differences between hydrologic treatments among sediments, we used  
192 reduced maximum likelihood mixed-effects models with hydrologic treatment (Trt), sediment (SedType), and the  
193 interaction between them (Trt x SedType) as fixed effects and each individual microcosm as a random effect to  
194 account for repeated measures through time. We used likelihood ratio tests to assess the significance of including  
195 microcosm as a random effect by comparing two models, identical in all terms except the random effect, revealing  
196 whether inclusion of this term produced a model with significantly more likelihood (Pinheiro and Bates 2004). To  
197 test effects on NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations, we used linear models with Trt, SedType, and the Trt x SedType  
198 interactions as fixed effects.

199 To identify which sediments responded to hydrologic treatment and the direction of the response we tested  
200 for significant differences between Dry and Reference treatments within each of the 16 sediments. For each water  
201 chemistry response variable (SRP, Fe(II), SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>), we averaged values across replicate microcosms (n = 3)

202 and through time during the re-flooding phase (sampling frequency varied for dissolved species and by sediment).  
203 We then used 16 individual analysis of variance (ANOVA) tests with Trt as a fixed factor to test for differences  
204 between Dry and Reference within each sediment. We detected significance at  $\alpha = 0.05$  with the Benjamini and  
205 Hochberg (1995) correction for multiple comparisons. This correction minimizes the risk of making Type II Errors  
206 by controlling the false discovery rate, rather than the family wise error rate (Verhoeven et al. 2005).

207 To obtain a single value reflecting how sediment-water P exchange responded to drying in each of the 16  
208 sediment types, we calculated the difference in average re-flooding phase P concentration between hydrologic  
209 treatments (Dry-Reference). To investigate the role of sediment biogeochemistry, we used this index as a response  
210 variable predicted from sediment characteristics in linear models. For each response (pore and surface water SRP),  
211 we used stepwise forward regression analysis to identify sediment variables that best predicted water chemistry  
212 responses. To avoid the influence of multicollinearity among predictors in models, variables with a variance  
213 inflation factor of greater than two were not incorporated into the models (Graham 2003). We chose predictor  
214 variables from all sediment variables measured, including absolute values of sequentially extracted P-binding  
215 fractions. To best meet linear model assumptions of equal variance and normality, pore water Dry-Reference SRP  
216 values were left untransformed, and surface water Dry-Reference SRP values were natural  $\log(x+\text{min value})$ -  
217 transformed.

218 To test whether or not our results supported our hypotheses of how drying influences sediment P retention  
219 mechanisms (Figure 1, Table 2), we compared stepwise regression-generated “best” models to univariate  
220 hypothesis-based models with indicators of four sediment properties which we predict to be important: organic P  
221 (organic matter, organic~P, NaOH~DNRP, HA~P), iron-bound P (Total Fe, Ox-Fe, BD~SRP, Fe:P ratio), oxidizable  
222  $\text{FeS}_x$  (AVS), and  $\text{CaCO}_3$ -associated P (Total  $\text{CaCO}_3$ , HCl~SRP) as predictors (Table 2). Within each set of  
223 measured indicators of the four sediment properties, the model with the lowest Akaike Information Criterion (AIC)  
224 was selected as a candidate “hypothesis” model for calculation of AIC weights. Thus, a set of five candidate models  
225 for each of the two response variables (surface water and pore water Dry-Reference SRP) included one model for  
226 each of the four sediment hypotheses, and one stepwise regression-selected “best” model. We used AIC to assign  
227 weights to each model that predict the probability that, given our data, each individual model is the best within the  
228 group of models (Burnham and Anderson 2004).

229 For all chemical analyses, values lower than detection limit were replaced with zeros prior to analysis.

230 Unless otherwise stated, sediment percent organic matter was arcsine-square root transformed, and all other  
231 variables were natural log-transformed. All statistical analyses were completed in R version 2.13.2 (Team 2011).

## 232 **Results**

### 233 *Sediment Chemistry*

234 The sediments used to investigate effects of drying on sediment-water P exchange represented a broad  
235 range of biogeochemical characteristics (Table 3). Sediment total P was significantly positively correlated with  
236 sediment organic matter, Total Fe, Ox-Fe, and all sequentially extracted P binding fractions (See Web Appendix,  
237 Table SI2). Molar ratios of sediment Fe:P ranged from 3.5 - 37, with a mean of 10. Sediment P binding fractions,  
238 both as absolute and relative amounts, showed substantial variability among sediments (Figure 2).

### 239 *Effects of Hydrologic Treatment on Water Chemistry*

240 The effect of hydrologic treatment on sediment-water P exchange significantly varied among the 16  
241 sediments, both in terms of magnitude of P release and direction of response (Table 4). Both hydrologic treatment  
242 and sediment identity interacted to affect pore and surface water SRP, pore and surface water  $\text{SO}_4^{2-}$ , pore water  
243 Fe(II), and surface water  $\text{NO}_3^-$  ( $p < 0.001$ ) after re-flooding.

### 244 *Sediment-Water P Exchange*

245 The highest total amounts of sediment P release to surface water were observed in Dry sediments (Figure 3;  
246 Table 4). Initial (first 30 days) P flux rates were generally low to moderate, even when total P release over the  
247 course of the experiment was high, although some flux rates were quite high (Table SI3). Of the 14 initial P flux  
248 rates that were significantly different from zero (seven Dry and seven Reference, Table SI3), flux rates ranged from  
249  $-0.3$  to  $16.5 \text{ mg P m}^{-2} \text{ d}^{-1}$  in Dry treatments and from  $-0.2$  to  $0.4 \text{ mg P m}^{-2} \text{ d}^{-1}$  in continuously flooded Reference  
250 microcosms. Negative flux rates indicate initial loss of SRP from the water column into sediments. We measured the  
251 highest flux rates in Dry sediments from sites FCTC ( $2.9 \text{ mg P m}^{-2} \text{ d}^{-1}$ ) and WG ( $16.5 \text{ mg P m}^{-2} \text{ d}^{-1}$ ). Initial P flux  
252 rates were generally poor predictors of final SRP concentration, reflecting the inconsistency of P flux patterns  
253 through time among sediments (Figure SI 1).

254 Significant differences in SRP between hydrologic treatments in pore water were not always accompanied  
255 by significant differences in surface water of the same sediment, and vice versa (Figure 3; Table 4). In seven of the  
256 16 sediments, average pore water SRP was greater in Dry than Reference treatments, whereas in two sediments,  
257 pore water SRP was higher in the Reference than Dry treatments (Figure 3; Table 4). Average surface water SRP

258 was higher in Dry than Reference treatments of six sediments, and no sediments had significantly higher surface  
259 water SRP in the Reference than Dry treatments. In several sediments, hydrologic treatment had no effect on SRP  
260 concentrations in pore water and/or surface water (Figure 3; Table 4). Average SRP concentrations were generally  
261 much higher in pore water than surface water (mean  $\pm$  std error:  $439 \pm 40$  and  $15 \pm 1.8 \mu\text{g P L}^{-1}$ , respectively; Table  
262 4).

263 Patterns of change in SRP concentrations were highly variable among treatments (Figure SI 1). In surface  
264 water, SRP concentrations were usually low ( $<10 \mu\text{g L}^{-1}$ ), although higher concentrations were observed on some  
265 sampling days. Only two sediments (FCTC and WG) showed a sustained increase in SRP concentration in surface  
266 water without re-uptake by sediments (Figure 4). In both cases, Dry sediments released significantly more SRP than  
267 the Reference sediments, and final SRP concentrations were substantial ( $340 \pm 25$  and  $71 \pm 10 \mu\text{g P L}^{-1}$ ,  
268 respectively; Figure 4).

#### 269 *Indicators of Phosphorus Flux Processes: Fe(II), $\text{SO}_4^{2-}$ , and $\text{NO}_3^-$*

270 Pore water dissolved Fe(II) was significantly different between treatments in only five of the 16 sediments  
271 (Figure 3), and pore water Fe(II) response mirrored SRP response in three sediments (EM, JH & SM). In two  
272 sediment types the Dry treatments had significantly more pore water dissolved Fe(II) than their Reference  
273 counterparts, whereas three sediments contained higher Fe(II) in Reference than Dry sediments (Figure 3).

274 In the case of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , the direction of response to hydrologic treatment was consistent across  
275 sediments. Concentrations were either higher in Dry than Reference sediments or not significantly different between  
276 hydrologic treatments; Reference sediments never released more  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  than Dry sediments (Figure 3). In  
277 most cases (9 out of 16 sediments), surface water  $\text{NO}_3^-$  was significantly higher in Dry than Reference treatments  
278 (Figure 3). In pore waters,  $\text{NO}_3^-$  was uniformly very low (usually below our detection limit of  $\sim 0.01 \text{ mg N L}^{-1}$ ) with  
279 no significant differences between treatments (data not shown). Sulfate differences were especially pronounced in  
280 pore water, in which nine of the 16 sediments had significantly greater  $\text{SO}_4^{2-}$  in Dry than Reference pore waters, and  
281 the magnitude of these differences was often high (Figure 3).

#### 282 *Relationships between Sediment Chemistry and Dissolved P Dynamics*

283 To investigate how sediment biogeochemical properties influenced P release in response to hydrologic  
284 treatment, we tested relationships between post-reflooding SRP and sediment variables. In pore waters, stepwise  
285 forward regression identified Total Fe and  $\text{H}_2\text{O}\text{-SRP}$  as the best predictors of P release, and Akaike weights

286 indicated a 98% probability that of the five candidate models compared, this is the best model (Table 5). Total Fe  
287 was negatively related and H<sub>2</sub>O~SRP was positively related to drying-induced P release detected in porewater  
288 (Figure 5). These directional relationships support our hypotheses of how drying influences sediment P  
289 biogeochemistry (Figure 1, Table 2). The univariate model predicting porewater Dry-Reference SRP from Total Fe  
290 (negative relationship) was also statistically significant ( $p < 0.05$ ), but much less supported than the stepwise model ( $\omega_i = 1\%$ , Table 5).

292 Mobilization of P from sediments to pore waters provides information on sediment P biogeochemistry, but  
293 P that crosses the sediment-water interface and enters surface waters has the potential to cause eutrophication. The  
294 univariate model with AVS was the best model predicting drying-induced P release to surface waters, and there was  
295 a 64% probability that of the four candidate models compared, the data best supported this model. The negative  
296 relationship with AVS indicates that sediments with high AVS tended to release less P to surface waters when dried  
297 and re-flooded compared to when continuously flooded (Figure 5). There was also a significant negative relationship  
298 between total sediment CaCO<sub>3</sub> and surface water P release (Figure 5) with an 18% probability that this was the  
299 “best” of the four models compared (Table 5). Both of these relationships, although statistically significant, were  
300 relatively weak ( $R^2 = 0.41$  and  $0.26$ , respectively). In our sixteen sediments, AVS and CaCO<sub>3</sub> were significantly  
301 positively correlated (Pearson’s  $r = 0.70$ ,  $p = 0.002$ ). We hypothesized a negative relationship between surface water  
302 Dry-Reference SRP and AVS, but hypothesized no relationship with CaCO<sub>3</sub> (Tables 1, 5). When AVS is held  
303 constant, the relationship between surface water P release and CaCO<sub>3</sub> is not statistically significant (partial  
304 correlation,  $p = 0.7745$ ), providing more evidence for a causal effect of AVS than CaCO<sub>3</sub>.

### 305 Discussion

306 In diverse sediments, the effect of experimental drying and re-flooding on sediment-water P exchange  
307 varied in both direction and magnitude. Of the experimentally dried sediments that differed significantly from  
308 continuously flooded sediments, most released more P to surface and/or pore waters when dried and re-flooded than  
309 when continuously flooded. Sediment-water P exchange is controlled by many interacting processes, including  
310 redox-driven Fe-PO<sub>4</sub><sup>3-</sup> sorption, biotic uptake and mineralization, and pH-driven carbonate co-precipitation, all of  
311 which are influenced in complex ways by drying and re-flooding (Boström et al. 1988; Hupfer and Lewandowski  
312 2008). The percentage of observed variance in drying-induced P flux explained by our linear models was relatively  
313 low, suggesting that the comprehensive suite of geochemical characteristics that we measured did not fully represent

314 controls on sediment-water P flux.

315           Across sediments, drying-induced P flux to surface waters was related to different sediment characteristics  
316 than P flux to interstitial pore waters, demonstrating that mobilization of P from solid forms in sediment to dissolved  
317  $\text{PO}_4^{3-}$  in pore waters is controlled by a different (although not necessarily mutually exclusive) set of factors than  
318 transport of dissolved  $\text{PO}_4^{3-}$  across the sediment-water interface into surface waters. P mobilization is governed by a  
319 suite of chemical and biotic processes, but transport of mobilized P across the sediment-water interface is driven by  
320 physical processes including diffusion, turbulence, and advection (Wetzel 2001). Physical transport processes may  
321 be enhanced by biotic activities including bioturbation (Mermillod-Blondin and Rosenberg 2006).

322           The negative relationship between drying-induced P release to pore waters and sediment Fe supports the  
323 hypothesis that drying improves P retention by creating Fe(III) sorption sites for  $\text{PO}_4^{3-}$  (De Groot & Fabre 1993;  
324 Smolders et al. 2006a; Smolders et al. 2006b). This result was especially pronounced in sediment from SM, which  
325 contained the most Fe by all measures and was one of only two sediments in which significantly more P was  
326 released to pore waters in continuously flooded Reference than Dry treatments. Despite the known importance of Fe  
327 mineral structure in controlling sediment  $\text{PO}_4^{3-}$  sorption (Baldwin 1996; Baldwin and Mitchell 2000; Loeb et al.  
328 2008), sediment Total Fe predicted P flux response more strongly than Ox-Fe, suggesting the importance of redox-  
329 driven sorption/desorption processes in this short-term drying experiment.

330           Although sediment Fe content was the best predictor of P release to pore water, relationships between P  
331 release to surface water and Fe indicator variables were only marginally significant ( $p > 0.06$ ). Instead, sediment  
332 AVS was the best predictor of drying-induced P release to surface water, and P release was also significantly related  
333 to  $\text{CaCO}_3$ . The negative relationship between AVS and drying-induced P release to surface waters supports the  
334 hypothesis that drying increases sediment  $\text{PO}_4^{3-}$  sorption by oxidizing  $\text{FeS}_x$  in sediments, creating Fe(III) sorption  
335 sites. Significantly higher  $\text{SO}_4^{2-}$  in surface and pore waters of many Dry treatment sediments compared to their  
336 corresponding Reference treatments further indicates that  $\text{FeS}_x$  oxidation during drying led to improved sediment P  
337 retention in high AVS sediments. Lower P release response to drying in high AVS sediments may also be due to the  
338 fact that sediments high in AVS will contain less easily mobilized Fe-associated  $\text{PO}_4^{3-}$  as much of the available Fe  
339 may be “saturated” through binding with S (Lamers et al. 1998, Smolders et al. 2006b).

340           The role of sulfur in sediment P release in flooded ecosystems has long been known (Caraco et al. 1989). In  
341 anoxic sediments,  $\text{SO}_4^{2-}$  is microbially reduced to  $\text{H}_2\text{S}$ , and reacts with Fe to form insoluble  $\text{FeS}_x$  minerals,

342 decreasing Fe- $\text{PO}_4^{3-}$  sorption and leading to  $\text{PO}_4^{3-}$  release to surface waters (Roden and Edmonds 1997; Lucassen et  
343 al. 2004; Smolders et al. 2006b). Understanding these redox-driven processes has led to the suggestion that some  
344 wetlands could benefit from temporary drying that oxidizes  $\text{FeS}_x$  minerals and re-creates Fe sorption sites (Lucassen  
345 et al. 2004; Smolders et al. 2006b). However, when temporarily drying sediments, potential acidification must be  
346 taken into account. Although most soils are well-buffered and floodwaters contain sufficient alkalinity to prevent  
347 acidification,  $\text{FeS}_x$  oxidation can lower sediment pH, causing dissolution of calcareous minerals and any  $\text{PO}_4^{3-}$   
348 associated with them, as well as acidification that may threaten other ecosystem functions (Lucassen et al. 2004).

349         Based on other studies showing P release upon re-flooding of dried sediments (Qiu and McComb 1994;  
350 Olila et al. 1997; Corstanje and Reddy 2004), we hypothesized that organic P would be mineralized during dry  
351 phases and/or released due to microbial cell lysis upon re-flooding. However, we observed no significant  
352 relationships between indicators of organic P and P release in our sediments, suggesting that if these processes  
353 occurred they were either obscured by interactions with processes controlled by other sediment characteristics or  
354 were not reflected in our operationally defined indicators of organic P. Our indicators of organic P collectively  
355 reflect a chemically diverse fraction of P-containing molecules (Baldwin 2013), and more refined quantification of  
356 different forms of non-reactive P may shed more light on mechanisms of organic P mobilization and release in  
357 response to drying and re-flooding.

358         Although we did not hypothesize that  $\text{H}_2\text{O}\sim\text{P}$  would respond differently to drying and re-flooding than to  
359 continuous flooding, there was a significant positive relationship between drying-induced P release to pore waters  
360 and sediment  $\text{H}_2\text{O}\sim\text{P}$ . The  $\text{H}_2\text{O}\sim\text{P}$  fraction typically represents a small proportion of total sediment P, but it is the  
361 most reactive fraction. Previous studies have demonstrated that water-soluble P can explain soil-water P flux in a  
362 variety of settings, including intact cores from pasture land under a gradient of use intensity (Pant and Reddy 2003)  
363 and in incubations of diverse agricultural soils (Hooda et al. 2000, Tang et al. 2016). This operationally defined  
364 fraction is assumed to measure inorganic  $\text{PO}_4^{3-}$  that is “loosely sorbed” to sediments (Paludan and Jensen 1995), but  
365 the precise chemical nature of the  $\text{H}_2\text{O}\sim\text{P}$  fraction is unknown. The  $\text{H}_2\text{O}\sim\text{P}$  fraction may also include  $\text{PO}_4^{3-}$  that is  
366 released from microbial biomass due to physiological stress from osmotic pressure put on microbial cells when they  
367 are suddenly surrounded by solute-free water (Turner and Haygarth 2001; Schimel et al. 2007). The mechanism by  
368 which drying and re-flooding would influence the  $\text{H}_2\text{O}\sim\text{P}$  fraction differentially than continuous flooding remains  
369 unclear, and likely involves chemical and biological processes not captured by our bulk geochemical measurements.

370 Our results suggest that something about the drying and re-flooding process “unlocks” the H<sub>2</sub>O~P fraction of  
371 sediment P, allowing it to be rapidly mobilized to pore waters when sediments are re-flooded. Future research  
372 elucidating the precise chemical and biological nature of this and other operationally defined P fractions is needed to  
373 improve our ability to predict responses of sediment P to drying and re-flooding.

374 Several studies have used sediment Fe:P molar ratios as predictors of an ecosystem’s propensity to release  
375 P into surface waters, identifying critical thresholds of 8.3-10, below which P release is expected (Jensen et al. 1992;  
376 Geurts et al. 2008; Zak et al. 2010; Forsmann and Kjaergaard 2014). In our study, sediment molar Fe:P ranged from  
377 3.5 to 37. Mean surface water SRP reached high concentrations ( $>10 \mu\text{g L}^{-1}$ ) upon re-flooding only in sediments  
378 with molar Fe:P ratios less than ~6. However, some sediments below this “threshold” did not release P into surface  
379 waters (P18, TM, P10, LF), and this pattern was similar with molar OxFe:P ratios and post-treatment porewater  
380 Fe:SRP ratios. In systems with oxygenated surface waters, pore water Fe:PO<sub>4</sub><sup>3-</sup> ratios are more effective predictors  
381 of sediment P release than sediment Fe:P ratios (Geurts et al. 2008). In part this is because sediment total Fe  
382 sometimes includes Fe that is bound to S and therefore unavailable to sorb PO<sub>4</sub><sup>3-</sup>. Overall, low sediment Fe:P ratios  
383 may be useful in identifying ecosystems that may be vulnerable to P release from Fe-bound forms, but do not  
384 necessarily indicate whether P will be released from or retained in sediments.

385 Regardless of the mechanism of P release, we detected initial P release rates that were within the range of  
386 previously published values (Table 6). Most of our sample sites, although located in a largely agricultural landscape,  
387 are only moderately impacted by agricultural P inputs due to the dominance of soil and groundwater flow paths  
388 rather than overland runoff. Despite this lack of overt P impact, we measured moderate to high P release rates in  
389 seven of the experimentally dried and re-flooded sediments. Our highest observed release rates were on par with  
390 published results from flooded agricultural soils and lands with strong legacies of P inputs (Table 6; Olila et al.  
391 1997; Corstanje and Reddy 2004; Bostic and White 2007; Tang et al. 2016).

392 The two sediments that displayed large, sustained P release during re-flooding after drying (FCTC, WG)  
393 were collected from ecosystems with a history of higher P loading than the other sediments. FCTC sediments were  
394 collected from historically drained agricultural land that was recently re-flooded as part of a wetland restoration  
395 (Kinsman-Costello et al. 2014) and WG sediments were collected from riparian areas of hypereutrophic Wintergreen  
396 Lake (Manny et al. 1994). The high sediment H<sub>2</sub>O~P in WG may indicate that it is at or near saturation in regards to  
397 P sorption (Hooda et al. 2000) and likely reflects the legacy of P inputs and eutrophication in Wintergreen Lake



398 which has a long history of heavy waterfowl use (Manny et al. 1994). The sustained increase and high surface water  
399 SRP concentrations in these two sediments, despite constant aeration, suggests that sediments such as these are  
400 likely to release P to surface waters when dried and re-flooded regardless of whether their overlying waters are oxic  
401 or anoxic. It also emphasizes that reactive forms of sediment P, rather than total sediment P or Fe:P ratio, determine  
402 the propensity of sediments to release P into surface waters, as these two sediments did not contain the highest total  
403 P concentrations among sediments tested. Phosphorus released from sediments such as these could cause  
404 considerable eutrophication in an aquatic ecosystem with a shallow water column.

#### 405 *Conclusion*

406 Restoration of natural hydrology can involve temporary drying of long-flooded sediments, or flooding of  
407 long-drained sediments, with substantial P release and potential eutrophication issues upon re-flooding. However,  
408 not all sediments in this study showed P release after drying and re-flooding. To better predict the response of  
409 sediment-water P exchange to hydrologic alterations, the biogeochemical characteristics of wetland sediments must  
410 be evaluated on a site-specific basis. In particular, easily mobilized and reactive sediment P fractions should be  
411 considered especially likely to be released following a drying and re-flooding event. Future research will benefit  
412 from incorporating more sophisticated measures of P chemistry (e.g.,  $^{31}\text{P}$  NMR to elucidate non-reactive P forms)  
413 and direct measures of microbial processes (e.g., microbial biomass P). Ultimately, our ability to predict aquatic  
414 sediment response to drying and re-flooding events is limited by the techniques available to measure the multiple  
415 complex microbial and geochemical processes that influence the reactivity, transformation, and transport of P.

416 Overall, this experiment demonstrates that sediment-water P exchange following drying and re-flooding is  
417 a highly variable phenomenon that is subject to multiple controls, and that wetland water level fluctuations may lead  
418 to substantial sediment P release, particularly in sediments with relatively high fractions of easily mobilized water-  
419 extractable  $\text{PO}_4^{3-}$ . Sediment P release in response to drying and reflooding may limit the ability of natural, restored,  
420 and constructed wetlands and streams to provide important ecosystem services. Within ecosystems, eutrophication  
421 resulting from sediment P release may degrade wetland habitat quality and ecosystem health. Along landscape flow  
422 paths, sediment P release may cause aquatic ecosystems to act as sources, rather than sinks, for P, potentially  
423 contributing to harmful eutrophication in vulnerable downstream ecosystems.

424

425 **References**

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568

569 **Table 1** Sampling site information. All sediments were collected in water of 0.5 - 1 m depth. Percent groundwater  
 570 influence (GW) was calculated from average magnesium ( $Mg^{2+}$ ) concentrations measured in surface waters  
 571 (Whitmire and Hamilton 2005) using a mixing model assuming groundwater and precipitation represent the only  
 572 inputs of dissolved  $Mg^{2+}$  to the ecosystems and assuming  $Mg^{2+}$  concentrations of  $0.05 \text{ mg L}^{-1}$  for precipitation  
 573 (1979-2002 NADP/NTN 2003) and  $23 \text{ mg L}^{-1}$  for groundwater (Kalamazoo County mean).

Site Name	Abbrev.	UTM Easting <sup>a</sup>	UTM Northing	Cond. ( $\mu\text{S cm}^{-1}$ ) <sup>b</sup>	GW (%)
Lux Arbor Pond 9*	P9	0626419	4703237	33	3
Lux Arbor Pond 10*	P10	0626455	4703201	39	5
Lux Arbor Pond 18*	P18	0626637	4704091	57	13
Lux Arbor Pond 6*	P6	0625855	4703265	77	18
Fort Custer Area 2 Wetland*	FCTC	0641163	4687408	291	37
Lux Arbor Pond 23*	P23	0627091	4705624	239	57
Osprey Bay*	OB	0626837	4703733	298	57
Turkey Marsh*	TM	0631750	4696366	353	75
Eagle Marsh	EM	0638009	4687350	341	79
Sheriff's Marsh	SM	0637557	4695693	400	81
Wintergreen Lake	WG	0632473	4695097	343	84
Jackson Hole	JH	0635460	4685882	376	90
Whitford Lake	WL	0635404	4685816	382	92
Brook Lodge Marsh	BL	0634585	4690718	455	92
Loosestrife Fen	LF	0634931	4691989	396	92
Douglas Lake	DL	0634596	4690688	382	94

574 <sup>a</sup>Universal Transverse Mercator Zone 16

575 <sup>b</sup>Conductivity corrected to 25 °C

576 \*Sampling sites that likely were not continuously flooded over the past 10 years (S. Hamilton, personal  
 577 observations)

578

579 **Table 2** Hypothesized effects of four main sediment properties on amount of phosphate ( $\text{PO}_4^{3-}$ ) released from  
 580 sediments to pore and surface waters after drying and re-flooding, and lists of measured variables that are potential  
 581 predictors of each sediment property of interest. Variables are defined in Table 4 and the main text. Measured  
 582 indicator variables were used to test hypothesized effects of hydrologic change on  $\text{PO}_4^{3-}$  release using a model  
 583 comparisons approach with AIC.

Sediment Property	Measured Indicator Variables	Hypothesized effect on $\text{PO}_4^{3-}$ release
Organic P	Organic Matter, Organic~P, NaOH~DNRP, HA~P	positive
Iron-bound P	Total Fe, Ox-Fe, BD~SRP, Fe:P	negative
Oxidizable $\text{FeS}_x$	AVS	negative
$\text{CaCO}_3$ -associated P	Total $\text{CaCO}_3$ , HCl~SRP	no net effect

584



**Table 3** Biogeochemical characteristics of 16 experimental wetland sediments measured prior to hydrologic regime manipulation, in order of sediment total phosphorus (Total P). Total P, total iron (Total Fe), oxalate-extractable iron (Ox-Fe), acid volatile sulfides (AVS) and total calcium carbonate (CaCO<sub>3</sub>) are reported as per gram dry weight of sediment.

Sediment	Total P ( $\mu\text{g g}^{-1}$ )	Organic Matter <sup>b</sup> (%)	Total Fe ( $\text{mg g}^{-1}$ )	Fe:P Molar ratio	Ox-Fe ( $\text{mg g}^{-1}$ )	AVS ( $\mu\text{mol g}^{-1}$ )	CaCO <sub>3</sub> ( $\text{mg g}^{-1}$ )	Bulk Density ( $\text{g cm}^{-3}$ )	Dry Soil Moisture <sup>c</sup> (%)
WL	28	1	1.87	37.1	0.5	0.91	9	1.33	3
JH	105	5	3.66	19.3	0.46	1	5	0.82	8
EM	130	4	3.89	16.6	1.8	1.5	62	0.99	10
OB	167	8	1.6	5.3	0.3	0.17	4	0.52	9
P6	177	6	3.43	10.7	1.3	1.5	12	0.63	3
P23	366	19	4.09	6.2	0.69	0.22	4	0.29	21
BL	443	18	11.84	14.8	0.16	4.6	396	0.20	32
TM	459	15	4.54	5.5	0.69	1.7	265	0.41	19
P18	512	24	4.69	5.1	1.6	0.27	12	0.21	14
DL	523	55	9.44	10	4.3	2.4	190	0.08	50
WG	528	24	3.37	3.5	0.7	0.37	3	0.30	27
P10	537	17	4.98	5.2	2	0.13	12	0.26	9
P9	556	21	3.99	4	1	0.48	7	0.41	8
LF	773	40	4.96	3.6	1.3	0.82	9	0.24	38
FCTC	1440	80	11.88	4.6	8.6	0.21	2	0.16	50
SM	1910	30	36.88	10.7	40.1	7.5	23	0.23	22

<sup>a</sup>Abbreviations defined in Table 1.

<sup>b</sup>Measured as loss on ignition

<sup>c</sup>Moisture content of sediment after experimental desiccation, prior to re-flooding

**Table 4** Sediment P flux response to drying and re-flooding (Dry) or continuously flooded (Ref) treatments. SRP concentrations in pore waters (PW) and surface waters (SW) were averaged through time and among cores within hydrologic treatment and sediment. Significant differences between mean PW and SW SRP concentrations in Dry and Ref treatments were tested using an F test on means within microcosms through time ( $F_{1,4}$ ). P values in bold represent significance after Benjamini & Hochberg's (1995) correction for multiple comparisons ( $\alpha = 0.05$ ). Final SW SRP is the SRP concentration measured on the final day of the re-flooding phase, averaged across cores within treatment and sediment ( $n=3$  unless otherwise noted). Data are mean  $\pm$  standard error.

Sediment	Mean PW SRP ( $\mu\text{g P L}^{-1}$ )			Mean SW SRP ( $\mu\text{g P L}^{-1}$ )			Final SW SRP ( $\mu\text{g P L}^{-1}$ )	
	Dry	Ref	<i>p</i>	Dry	Ref.	<i>p</i>	Dry	Ref
BL	12 $\pm$ 4	34 $\pm$ 18	0.070	1 $\pm$ 0	1 $\pm$ 0	0.369	0 $\pm$ 0	4 $\pm$ 3
DL	21 $\pm$ 6	2 $\pm$ 1	<b>0.001</b>	1 $\pm$ 0	2 $\pm$ 1	0.059	1 $\pm$ 1	0 $\pm$ 0
EM	39 $\pm$ 3	101 $\pm$ 11	<b>0.001</b>	1 $\pm$ 0	1 $\pm$ 0	<b>0.001</b>	2 $\pm$ 1	1 $\pm$ 0
FCTC	571 $\pm$ 121	496 $\pm$ 134	0.653	56 $\pm$ 7	3 $\pm$ 2	<b>0.002</b>	71 $\pm$ 10	17 $\pm$ 16
JH	371 $\pm$ 51	49 $\pm$ 7	<b>0.002</b>	3 $\pm$ 1	1 $\pm$ 0	<b>0.005</b>	1 $\pm$ 0	1 $\pm$ 0
LF	15 $\pm$ 8	30 $\pm$ 12	0.288	1 $\pm$ 0	1 $\pm$ 0	0.149	2 $\pm$ 0	1 $\pm$ 0
OB	773 $\pm$ 92	201 $\pm$ 40	<b>0.013</b>	30 $\pm$ 7	1 $\pm$ 0	<b>0.001</b>	33 $\pm$ 29	1 $\pm$ 0
P10	126 $\pm$ 11	47 $\pm$ 8	<b>0.011</b>	2 $\pm$ 0	1 $\pm$ 0	0.399	1 $\pm$ 0	2 $\pm$ 1
P18	276 $\pm$ 78	71 $\pm$ 12	0.144	5 $\pm$ 1	1 $\pm$ 0	0.026	14 $\pm$ 6	2 $\pm$ 0
P23	221 $\pm$ 54	124 $\pm$ 21	0.466	3 $\pm$ 1	1 $\pm$ 0	0.054	1 $\pm$ 0	1 $\pm$ 0
P6	294 $\pm$ 32	40 $\pm$ 9	<b>&lt;0.001</b>	2 $\pm$ 0	1 $\pm$ 0	<b>0.010</b>	2 $\pm$ 1	1 $\pm$ 0
P9	275 $\pm$ 57	100 $\pm$ 23	<b>0.017</b>	15 $\pm$ 2	1 $\pm$ 0	0.035	21 <sup>a</sup>	1 $\pm$ 1
SM	183 $\pm$ 26	1080 $\pm$ 124	<b>0.006</b>	4 $\pm$ 1	7 $\pm$ 1	0.049	1 $\pm$ 0	5 $\pm$ 2
TM	10 $\pm$ 3	18 $\pm$ 4	0.086	2 $\pm$ 1	1 $\pm$ 0	0.303	0 $\pm$ 0	0 $\pm$ 0
WL	139 $\pm$ 13	27 $\pm$ 8	0.058	1 $\pm$ 0	1 $\pm$ 0	0.606	1 $\pm$ 1	1 $\pm$ 0
WG	3877 $\pm$ 332	2076 $\pm$ 154	<b>&lt;0.001</b>	294 $\pm$ 25	7 $\pm$ 1	<b>&lt;0.001</b>	340 $\pm$ 25	1 $\pm$ 0

<sup>a</sup>  $n = 1$  because of core leakage

**Table 5** Comparison of linear models predicting sediment SRP release in response to drying and re-flooding from sediment characteristics. Sediment-water microcosms containing 16 diverse sediments were subjected to drying and re-flooding (Dry) or continuous flooding (Reference). Average post-reflooding SRP concentrations in Reference treatments were subtracted from the Dry treatment of the same sediment (“Dry-Reference SRP”). Univariate models predicting Dry-Reference SRP from indicator variables were compared using AIC, and the “best” model within each set of sediment property indicators was selected for model comparison. A single “best” model was identified by selecting parameters from all measured sediment variables using stepwise forward selection and included as a candidate model (in boldface). Candidate models were compared by calculating Akaike weights ( $\omega_i$ ). Predictor variables were natural-log or arcsine square root transformed, PW Dry-Reference SRP response was left untransformed, and SW Dry-Reference SRP response was natural log+4 transformed. Models that were not identified as the “best” model, but were significant at  $p < 0.05$  are italicized.

Sediment Property	Predictor(s)	Direction	$R^2$	$p$ -value	$\Delta AIC_c$	$\omega_i$
<u>PW SRP</u>						
Organic P	Org. Matter	negative	0.01	0.68	14.50	<0.01
<i>Iron-Bound P</i>	<i>Total Fe</i>	<i>negative</i>	<i>0.34</i>	<i>0.02</i>	<i>9.46</i>	<i>0.01</i>
Oxidizable FeS <sub>x</sub>	AVS	negative	0.23	0.06	11.15	<0.01
CaCO <sub>3</sub> -Associated P	Total CaCO <sub>3</sub>	negative	0.15	0.14	12.46	<0.01
<b>Stepwise Model</b>	<b>Total Fe, H<sub>2</sub>O~SRP</b>	<b>negative, positive</b>	<b>0.68</b>	<b>&lt;0.01</b>	<b>0.00</b>	<b>0.98</b>
<u>SW SRP</u>						
Organic P	Organic~P	positive	0.04	0.43	5.87	0.03
Iron-Bound P	Fe:P	negative	0.24	0.06	2.98	0.14
<b>Oxidizable FeS<sub>x</sub>, Stepwise Model</b>	<b>AVS</b>	<b>negative</b>	<b>0.41</b>	<b>&lt;0.01</b>	<b>0.00</b>	<b>0.64</b>
<i>CaCO<sub>3</sub>-Associated P</i>	<i>Total CaCO<sub>3</sub></i>	<i>negative</i>	<i>0.26</i>	<i>0.04</i>	<i>2.54</i>	<i>0.18</i>

**Table 6** Selected published P release rate values for re-flooded sediments or soils.

Source	Location	Study Description	P release rate range (mg P m <sup>-2</sup> d <sup>-1</sup> )
Bostic & White 2007	Florida, USA	Re-flooding marsh sediment intact cores	-3.68 - 43
Corstanje & Reddy 2004	Florida, USA	Re-flooding marsh sediment intact cores	0.7 - 109
Olila et.al. 1997	Florida, USA	Re-flooding marsh sediment intact cores	7.6 - 334.2
Qiu & McComb 1994	Perth, Australia	Air drying and re-flooding littoral lake sediments intact cores	37
Zak et al. 2010	Germany and Poland	Re-flooding historically drained fen sediment intact cores	0.1 - 52.3
Banach et al. 2009	Poland	Re-flooding floodplain sediment monoliths	7.4 - 9.9
Tang et al. 2016	Netherlands	Flooding agricultural soils	0.01-1.28
Steinman et al. (unpublished)	Michigan, USA	Re-flooding intact cores along moisture gradient from upland to 1 m deep	0.4 - 37.9
This study <sup>a</sup>	Michigan, USA	Experimental drying and re-flooding homogenized wetland sediment	0 - 16

<sup>a</sup> Measurements of flux from homogenized sediments in sediment-water microcosms, for comparison with published studies from intact sediment cores.

## Figure Legends

**Figure 1.** Conceptual diagram illustrating hypothesized biogeochemical effects of experimental sediment drying and re-flooding on phosphorus retention mechanisms. In this diagram, “~P” indicates P binding, such as sorption, co-precipitation, or covalent bonding, that retains P in association with the sediments.

**Figure 2** Absolute concentrations (A) and percentages (B) of operationally defined phosphorus binding fractions in the 16 sediments used in the experimental drying and re-flooding. Absolute values are as per gram dry weight of sediment. Sediment abbreviations are defined in Table 1.

**Figure 3** Mean concentrations of SRP (A, B),  $\text{SO}_4^{2-}$  (C, D), Fe(II) (E), and  $\text{NO}_3^-$ -N (F) in temporarily dried (Dry) sediments plotted against continuously flooded controls (Reference) in sediment pore waters (PW: A, C, E) and in overlying surface waters (SW: B, D, F) of microcosms containing 16 biogeochemically diverse sediments, compared to 1:1 lines. Note that both axes in panels A through E are plotted on log scales, and the differences in scale between panels. Solid black circles denote statistically significant differences between the two hydrologic treatments, and hollow circles denote no significant difference ( $p < 0.05$ ,  $F_{1,4}$ ). Sediment points lying above the 1:1 line had higher average concentration in Dry treatments than Reference ones.

**Figure 4** Post-re-flooding SRP concentrations in surface waters overlying dried and re-flooded (circles) and continuously flooded (triangles) sediments for the only two of 16 experimental sediments that showed consistently and strongly elevated SRP concentrations in surface waters after re-flooding. Each data point is an average of three replicate experimental microcosms, with standard error bars.

**Figure 5** Relationships between drying-induced P flux and sediment characteristics in 16 sediments subjected to hydrologic manipulation. Drying-induced P flux (“P release”) is measured as the difference between average soluble reactive phosphate (P) in pore (a, b) or surface (c, d) waters in dried then re-flooded (Dry) treatments compared to that in continuously flooded (Ref) reference sediments of the same sediment (Dry minus Ref). Solid black circles denote statistically significant differences between hydrologic treatments based on Benjamini & Hochberg’s (1995) correction for multiple comparisons, and hollow circles denote no significant difference. Solid line is based on least-squares linear regression model. To best meet linear model assumptions of equal variance and normality of errors, Dry-Ref pore water P release was left untransformed, Dry-Ref surface water P release was  $\ln+4$  transformed, and sediment predictors were log-transformed.