Phosphorus release from the drying and reflooding of diverse shallow sediments

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Acknowledgements

We are grateful to Henning S. Jensen and colleagues at the University of Southern Denmark for valuable advice on sequential phosphorus extraction techniques. Thanks to David Weed, Jen Pham, Laura Podzikowski, David Kinsman, Steve Robbins, Brandon Kovnat, Rob Davis, Paige Howell, David Costello, and Megan Lowenberg for lab and field support. Allen Burton and his lab at the University of Michigan provided protocols and logistical support for measuring acid volatile sulfides in sediments. Early drafts of this manuscript were improved by comments from Alan Steinman and R. Jan Stevenson. This research was funded by National Science Foundation Division of Environmental Biology grants 0743402, 0423627, 0910008 and 1027253.

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Abstract

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

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

Introduction

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

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

Sediment-water P exchange is controlled by several distinct biogeochemical processes, including sorption-desorption, co-precipitation, biotic assimilation, and organic matter mineralization (Boström et al. 1988), as well as physical transport processes including diffusion and advection (Wetzel 2001). A longstanding paradigm, developed through research on lake sediments, is that phosphate (PO_4^{3-}) sorption to a “cap” of oxidized iron (Fe) minerals at the sediment-water interface is the primary mechanism of sediment P retention, preventing PO_4^{3-} dissolved in pore water from entering overlying water (Mortimer 1941; Mortimer 1942). When oxygen is depleted at the sediment-water interface, microbial Fe reduction leads to PO_4^{3-} desorption and potential release into surface waters (Marsden 1989). Conversely, when flooded sediments are drained or dried, exposure to oxygen may increase PO_4^{3-} sorption as formerly reduced Fe is oxidized (De Groot and Fabre 1993). Drying influences this sorption-desorption not only by exposing redox-sensitive metals to oxygen, but also by changing their mineral forms (Twinch 1987; Baldwin and Mitchell 2000; Qiu and McComb 2002).

At times, the structure of Fe minerals may supersede their redox status in determining PO_4^{3-} sorption capacity (Baldwin 1996; Loeb et al. 2008). Across soils and sediments from diverse ecosystems and hydrologic regimes, one of the strongest predictors of sediment PO_4^{3-} sorption is consistently the amount of poorly crystalline Fe and/or aluminum (Al) oxides and oxyhydroxides (Shukla et al. 1971; Williams et al. 1971; Richardson 1985; Darke and Walbridge 2000). Flooding dry soils usually causes an increase in poorly crystalline Fe and Al oxides (Sah and Mikkelsen 1989; Darke and Walbridge 2000; Zhang et al. 2003), whereas drying flooded sediments usually decreases these amorphous forms (Twinch 1987; Baldwin 1996; Qiu and McComb 2002; de Vicente et al. 2010). Thus, sediment drying may have counteracting effects on sediment PO_4^{3-} sorption by simultaneously oxidizing reduced Fe minerals (increasing sorption capacity) and increasing their crystallinity (decreasing sorption capacity).

Although Fe mineral sorption is often the dominant form of P retention in soils and sediments, other processes involving sulfur, calcareous minerals, and organic matter also control sediment-water P exchange (Boström et al. 1988; Hupfer and Lewandowski 2008). Free sulfide (hereafter H_2S) reacts with Fe to form insoluble Fe sulfide minerals (FeS_x), effectively inactivating Fe binding sites and diminishing PO_4^{3-} sorption capacity (Roden and Edmonds 1997). The Fe-PO_4^{3-} sorption capacity can be reconstituted by FeS_x oxidation when sediments dry (Smolders et al. 2006b; Dieter et al. 2015). In calcareous sediments, PO_4^{3-} can co-precipitate with or sorb to calcium carbonate ($CaCO_3$) minerals, retaining large amounts of P (Hamilton et al. 2009). These calcareous minerals tend to precipitate from alkaline waters with a rise in pH and/or temperature, and to dissolve under acidic conditions (Boström et al. 1988). Finally, organic matter often contains the largest pool of P in shallow aquatic sediments (e.g., Dunne et al. 2007). The release of P from organic matter occurs mainly by microbial mineralization, which is stimulated when anoxic sediments are drained and exposed to oxygen (Baldwin and Mitchell 2000; Dieter et al. 2015). Other organic P transformation pathways, like abiotic hydrolysis by minerals, have been identified in laboratory studies, although their magnitude and importance in ecosystems remain largely unknown (Baldwin 2013).

Despite our understanding that complex biogeochemical processes control sediment P retention and release (Richardson 1985; Boström et al. 1988), the net effect of sediment drying and re-flooding on P flux remains difficult to predict. In part this is because few studies have conducted comparative experiments on sediments with widely varying characteristics. We conducted laboratory experiments to test the effects of sediment drying and re-flooding on sediment-water P exchange using sediments from 16 shallow freshwater ecosystems of diverse biogeochemistry. We hypothesized that the direction and magnitude of sediment-water P exchange in response to experimental drying and re-flooding would be affected by biogeochemical characteristics (Figure 1). We predicted that 1) sediments with high total Fe and/or FeS_x would release less P after drying and re-flooding than when continuously flooded due to oxidation of reduced Fe; 2) primarily organic sediments would release more P when dried and re-flooded than continuously flooded due to enhanced mineralization rates, and 3) in calcareous sediments, $CaCO_3$-associated P would increase during drying due to loss of porewater carbon dioxide and consequent pH increases, unless simultaneous oxidation processes produced sufficient acid to exceed the sediment's buffering capacity (Figure 1). These predictions are not mutually exclusive and more than one of them may be important in some sediments.

Methods

Overview of Experimental Design

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

To test for effects on sediment-water P exchange, we measured soluble reactive phosphorus (SRP) in pore and surface waters through time. We considered sediment P to have been "retained" when it was maintained in solid forms, including through sorption, co-precipitation, and covalent bonding (i.e., in organic material), and to have been "released" when dissolved, reactive PO_4^{3-} was measured in either pore or surface water.

Sediment Sampling

We collected sediments under 0.5-1 m of water (Eckman grab, 10-20 cm depth) on two dates (June and September 2009) and experiments were conducted in two groups of eight sediments each. Within 24 hours of sampling, we sieved (2 mm) and homogenized the wet sediments. Homogenization was necessary for replicated experimental treatments because sediments from shallow water bodies are inherently variable over small spatial scales. Homogenization was done carefully and quickly to minimize exposure to oxygen. We sub-sampled homogenized material for a suite of chemical characterizations including sequential P extraction. We stored sieved sediment in sealed buckets at 4°C for up to 6 days prior to establishment of microcosms.

Experimental Methods

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

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

Measuring Response to Hydrologic Treatment

We assessed sediment-water P exchange and related processes by sampling surface and pore waters for SRP, sulfate (SO_4^{2-}), nitrate (NO_3^-), and reduced iron (Fe(II)) during the re-flooding phase. We sampled surface water by filtering (0.45 μm cellulose-acetate filter with a glass fiber pre-filter, Steriltech) 30 mL of water from the top of the water column, which was mixed by the aerator. We sampled 10 mL of sediment pore water through a nominal pore size of ~0.2 μm installed at the vertical midpoint of the sediment column prior to adding homogenized sediment to experimental units (Rhizon; Rhizosphere Research Products, Wageningen, The Netherlands). We replaced the volume sampled with low nutrient filtered lake water. After 9-11 weeks of flooding, we recorded sediment heights to calculate bulk density and siphoned off surface water for water chemistry analysis.

Laboratory Analyses

We measured SRP concentrations in surface and pore water samples using the molybdate blue colorimetric method (Murphy and Riley 1962), and NO_3^- and SO_4^{2-} using membrane-suppression ion chromatography. We measured Fe(II) using a modified ferrozine assay (Lovley and Phillips 1987). Organic matter, total phosphorus (Total P), total iron (Total Fe), total carbonate ($CaCO_3$), acid volatile sulfides (AVS), Ox-Fe, and sequentially extracted P binding fractions were measured in homogenized moist sediment prior to the experimental treatments. We used acid ammonium oxalate to measure oxalate-extractable Fe (Ox-Fe), an indicator of poorly crystalline iron minerals (McKeague and Day 1966; Walbridge et al. 1991) and analyzed organic matter as loss on ignition. We extracted Total P and Total Fe as in Andersen (1975) and quantified $CaCO_3$ by acidifying in a sealed container, measuring CO_2 produced using a pressure transducer. We measured Fe in Ox-Fe and Total Fe extracts using flame atomic absorption spectrophotometry. We froze moist sediment for AVS analysis (US EPA Method 821-R-91-100) by acidifying sediment samples with HCl to convert AVS to H_2S, which was then trapped as sulfide (S^{2-}) in an alkaline solution (0.5 M NaOH) and measured colorimetrically after reaction with a mixed diamine reagent (H_2SO_4, N,N-dimethyl-p-phenylenediamine oxalate, and ferric chloride hexahydrate) (Allen et al. 1991). Analytical sulfide standards were prepared from a stock solution standardized versus thiosulfate.

Sequential Extraction of P Binding Fractions

We used a sequential extraction procedure (Paludan and Jensen 1995) to measure operationally defined sediment P binding fractions (Pettersson et al. 1988). The first step used de-oxygenated de-ionized water to extract loosely bound P (H_2O~P). Next, bicarbonate-buffered dithionite (0.11 M) extracted PO_4^{3-} bound to redox-sensitive oxidized iron minerals (BD~P) and some non-reactive (mostly organic) P (BD~DNRP) (Reitzel et al. 2006). This step also may extract some apatite-bound P in calcareous sediment (Reitzel 2005). The third step used sodium hydroxide (0.1 M NaOH) to extract PO_4^{3-} bound to redox-insensitive Al and Fe oxides that undergo anionic exchange with hydroxide (NaOH~SRP) and non-reactive organic and inorganic P (pyro- and polyphosphates). Non-reactive P extracted by NaOH was acidified to separate out precipitating humic acid associated P (HA~P) from other non-reactive P molecules (NaOH~DNRP). After NaOH extraction, HCl (0.5 M) extracted acid-soluble P, mostly bound to apatite and other calcareous minerals (HCl~P). Residual P in the sediment pellet following the preceding chemical treatments was presumed to be bound in highly recalcitrant organic matter or crystalline mineral substances, and was extracted by combustion followed by boiling for 10 min in 1 M HCl (Res~P). Reactive P in each fraction was detected colorimetrically, and non-reactive P was measured as the difference between reactive P and colorimetrically detected P following persulfate digestion (total P). We did not detect any non-reactive H_2O~P or BD~P, so results are not reported for those fractions. As an indicator of all organic P fractions, we summed the NaOH~DNRP and HA~P fractions and called this fraction Organic~P. Although the operationally defined measured NaOH~DNRP and HA~P fractions may not entirely be composed of covalently bonded organic P molecules, past research has shown them to be mostly composed of organic P, and thus we use them as indicators of, rather than direct measures of, sediment organic P (Reitzel et al. 2006).

Statistical Analyses

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

To detect P and Fe concentration differences between hydrologic treatments among sediments, we used reduced maximum likelihood mixed-effects models with hydrologic treatment (Trt), sediment (SedType), and the interaction between them (Trt x SedType) as fixed effects and each individual microcosm as a random effect to account for repeated measures through time. We used likelihood ratio tests to assess the significance of including microcosm as a random effect by comparing two models, identical in all terms except the random effect, revealing whether inclusion of this term produced a model with significantly more likelihood (Pinheiro and Bates 2004). To test effects on NO_3^- and SO_4^{2-} concentrations, we used linear models with Trt, SedType, and the Trt x SedType interactions as fixed effects.

To identify which sediments responded to hydrologic treatment and the direction of the response we tested for significant differences between Dry and Reference treatments within each of the 16 sediments. For each water chemistry response variable (SRP, Fe(II), SO_4^{2-} and NO_3^-), we averaged values across replicate microcosms (n = 3) and through time during the re-flooding phase (sampling frequency varied for dissolved species and by sediment). We then used 16 individual analysis of variance (ANOVA) tests with Trt as a fixed factor to test for differences between Dry and Reference within each sediment. We detected significance at $\alpha = 0.05$ with the Benjamini and Hochberg (1995) correction for multiple comparisons. This correction minimizes the risk of making Type II Errors by controlling the false discovery rate, rather than the family wise error rate (Verhoeven et al. 2005).

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

To test whether or not our results supported our hypotheses of how drying influences sediment P retention mechanisms (Figure 1, Table 2), we compared stepwise regression-generated “best” models to univariate hypothesis-based models with indicators of four sediment properties which we predict to be important: organic P (organic matter, organic~P, NaOH~DNRP, HA~P), iron-bound P (Total Fe, Ox-Fe, BD~SRP, Fe:P ratio), oxidizable FeS_x (AVS), and $CaCO_3$-associated P (Total $CaCO_3$, HCl~SRP) as predictors (Table 2). Within each set of measured indicators of the four sediment properties, the model with the lowest Akaike Information Criterion (AIC) was selected as a candidate “hypothesis” model for calculation of AIC weights. Thus, a set of five candidate models for each of the two response variables (surface water and pore water Dry-Reference SRP) included one model for each of the four sediment hypotheses, and one stepwise regression-selected “best” model. We used AIC to assign weights to each model that predict the probability that, given our data, each individual model is the best within the group of models (Burnham and Anderson 2004).

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

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

Results

Sediment Chemistry

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

Effects of Hydrologic Treatment on Water Chemistry

The effect of hydrologic treatment on sediment-water P exchange significantly varied among the 16 sediments, both in terms of magnitude of P release and direction of response (Table 4). Both hydrologic treatment and sediment identity interacted to affect pore and surface water SRP, pore and surface water SO_4^{2-}, pore water Fe(II), and surface water NO_3^- ($p < 0.001$) after re-flooding.

Sediment-Water P Exchange

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

Significant differences in SRP between hydrologic treatments in pore water were not always accompanied by significant differences in surface water of the same sediment, and vice versa (Figure 3; Table 4). In seven of the 16 sediments, average pore water SRP was greater in Dry than Reference treatments, whereas in two sediments, pore water SRP was higher in the Reference than Dry treatments (Figure 3; Table 4). Average surface water SRP was higher in Dry than Reference treatments of six sediments, and no sediments had significantly higher surface water SRP in the Reference than Dry treatments. In several sediments, hydrologic treatment had no effect on SRP concentrations in pore water and/or surface water (Figure 3; Table 4). Average SRP concentrations were generally much higher in pore water than surface water (mean ± std error: 439 ± 40 and 15 ± 1.8 μg P L^{-1}, respectively; Table 4).

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

Indicators of Phosphorus Flux Processes: Fe(II), SO_4^{2-}, and NO_3^-

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

In the case of SO_4^{2-} and NO_3^-, the direction of response to hydrologic treatment was consistent across sediments. Concentrations were either higher in Dry than Reference sediments or not significantly different between hydrologic treatments; Reference sediments never released more SO_4^{2-} or NO_3^- than Dry sediments (Figure 3). In most cases (9 out of 16 sediments), surface water NO_3^- was significantly higher in Dry than Reference treatments (Figure 3). In pore waters, NO_3^- was uniformly very low (usually below our detection limit of ~0.01 mg N L^{-1}) with no significant differences between treatments (data not shown). Sulfate differences were especially pronounced in pore water, in which nine of the 16 sediments had significantly greater SO_4^{2-} in Dry than Reference pore waters, and the magnitude of these differences was often high (Figure 3).

Relationships between Sediment Chemistry and Dissolved P Dynamics

To investigate how sediment biogeochemical properties influenced P release in response to hydrologic treatment, we tested relationships between post-reflooding SRP and sediment variables. In pore waters, stepwise forward regression identified Total Fe and H_2O~SRP as the best predictors of P release, and Akaike weights indicated a 98% probability that of the five candidate models compared, this is the best model (Table 5). Total Fe was negatively related and H_2O~SRP was positively related to drying-induced P release detected in porewater (Figure 5). These directional relationships support our hypotheses of how drying influences sediment P biogeochemistry (Figure 1, Table 2). The univariate model predicting porewater Dry-Reference SRP from Total Fe (negative relationship) was also statistically significant ($p<0.05$), but much less supported than the stepwise model ($\omega_i = 1\%$, Table 5).

Mobilization of P from sediments to pore waters provides information on sediment P biogeochemistry, but P that crosses the sediment-water interface and enters surface waters has the potential to cause eutrophication. The univariate model with AVS was the best model predicting drying-induced P release to surface waters, and there was a 64% probability that of the four candidate models compared, the data best supported this model. The negative relationship with AVS indicates that sediments with high AVS tended to release less P to surface waters when dried and re-flooded compared to when continuously flooded (Figure 5). There was also a significant negative relationship between total sediment $CaCO_3$ and surface water P release (Figure 5) with an 18% probability that this was the "best" of the four models compared (Table 5). Both of these relationships, although statistically significant, were relatively weak ($R^2= 0.41$ and 0.26, respectively). In our sixteen sediments, AVS and $CaCO_3$ were significantly positively correlated (Pearson's $r = 0.70$, $p = 0.002$). We hypothesized a negative relationship between surface water Dry-Reference SRP and AVS, but hypothesized no relationship with $CaCO_3$ (Tables 1, 5). When AVS is held constant, the relationship between surface water P release and $CaCO_3$ is not statistically significant (partial correlation, $p = 0.7745$), providing more evidence for a causal effect of AVS than $CaCO_3$.

Discussion

In diverse sediments, the effect of experimental drying and re-flooding on sediment-water P exchange varied in both direction and magnitude. Of the experimentally dried sediments that differed significantly from continuously flooded sediments, most released more P to surface and/or pore waters when dried and re-flooded than when continuously flooded. Sediment-water P exchange is controlled by many interacting processes, including redox-driven Fe-PO_4^{3-} sorption, biotic uptake and mineralization, and pH-driven carbonate co-precipitation, all of which are influenced in complex ways by drying and re-flooding (Boström et al. 1988; Hupfer and Lewandowski 2008). The percentage of observed variance in drying-induced P flux explained by our linear models was relatively low, suggesting that the comprehensive suite of geochemical characteristics that we measured did not fully represent controls on sediment-water P flux.

Across sediments, drying-induced P flux to surface waters was related to different sediment characteristics than P flux to interstitial pore waters, demonstrating that mobilization of P from solid forms in sediment to dissolved PO_4^{3-} in pore waters is controlled by a different (although not necessarily mutually exclusive) set of factors than transport of dissolved PO_4^{3-} across the sediment-water interface into surface waters. P mobilization is governed by a suite of chemical and biotic processes, but transport of mobilized P across the sediment-water interface is driven by physical processes including diffusion, turbulence, and advection (Wetzel 2001). Physical transport processes may be enhanced by biotic activities including bioturbation (Mermillod-Blondin and Rosenberg 2006).

The negative relationship between drying-induced P release to pore waters and sediment Fe supports the hypothesis that drying improves P retention by creating Fe(III) sorption sites for PO_4^{3-} (De Groot & Fabre 1993; Smolders et al. 2006a; Smolders et al. 2006b). This result was especially pronounced in sediment from SM, which contained the most Fe by all measures and was one of only two sediments in which significantly more P was released to pore waters in continuously flooded Reference than Dry treatments. Despite the known importance of Fe mineral structure in controlling sediment PO_4^{3-} sorption (Baldwin 1996; Baldwin and Mitchell 2000; Loeb et al. 2008), sediment Total Fe predicted P flux response more strongly than Ox-Fe, suggesting the importance of redox-driven sorption/desorption processes in this short-term drying experiment.

Although sediment Fe content was the best predictor of P release to pore water, relationships between P release to surface water and Fe indicator variables were only marginally significant ($p > 0.06$). Instead, sediment AVS was the best predictor of drying-induced P release to surface water, and P release was also significantly related to $CaCO_3$. The negative relationship between AVS and drying-induced P release to surface waters supports the hypothesis that drying increases sediment PO_4^{3-} sorption by oxidizing FeS_x in sediments, creating Fe(III) sorption sites. Significantly higher SO_4^{2-} in surface and pore waters of many Dry treatment sediments compared to their corresponding Reference treatments further indicates that FeS_x oxidation during drying led to improved sediment P retention in high AVS sediments. Lower P release response to drying in high AVS sediments may also be due to the fact that sediments high in AVS will contain less easily mobilized Fe-associated PO_4^{3-} as much of the available Fe may be “saturated” through binding with S (Lamers et al. 1998, Smolders et al. 2006b).

The role of sulfur in sediment P release in flooded ecosystems has long been known (Caraco et al. 1989). In anoxic sediments, SO_4^{2-} is microbially reduced to H_2S, and reacts with Fe to form insoluble FeS_x minerals, decreasing Fe-PO_4^{3-} sorption and leading to PO_4^{3-} release to surface waters (Roden and Edmonds 1997; Lucassen et al. 2004; Smolders et al. 2006b). Understanding these redox-driven processes has led to the suggestion that some wetlands could benefit from temporary drying that oxidizes FeS_x minerals and re-creates Fe sorption sites (Lucassen et al. 2004; Smolders et al. 2006b). However, when temporarily drying sediments, potential acidification must be taken into account. Although most soils are well-buffered and floodwaters contain sufficient alkalinity to prevent acidification, FeS_x oxidation can lower sediment pH, causing dissolution of calcareous minerals and any PO_4^{3-} associated with them, as well as acidification that may threaten other ecosystem functions (Lucassen et al. 2004).

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

Although we did not hypothesize that H_2O~P would respond differently to drying and re-flooding than to continuous flooding, there was a significant positive relationship between drying-induced P release to pore waters and sediment H_2O~P. The H_2O~P fraction typically represents a small proportion of total sediment P, but it is the most reactive fraction. Previous studies have demonstrated that water-soluble P can explain soil-water P flux in a variety of settings, including intact cores from pasture land under a gradient of use intensity (Pant and Reddy 2003) and in incubations of diverse agricultural soils (Hooda et al. 2000, Tang et al. 2016). This operationally defined fraction is assumed to measure inorganic PO_4^{3-} that is "loosely sorbed" to sediments (Paludan and Jensen 1995), but the precise chemical nature of the H_2O~P fraction is unknown. The H_2O~P fraction may also include PO_4^{3-} that is released from microbial biomass due to physiological stress from osmotic pressure put on microbial cells when they are suddenly surrounded by solute-free water (Turner and Haygarth 2001; Schimel et al. 2007). The mechanism by which drying and re-flooding would influence the H_2O~P fraction differentially than continuous flooding remains unclear, and likely involves chemical and biological processes not captured by our bulk geochemical measurements.

Our results suggest that something about the drying and re-flooding process "unlocks" the H_2O~P fraction of sediment P, allowing it to be rapidly mobilized to pore waters when sediments are re-flooded. Future research elucidating the precise chemical and biological nature of this and other operationally defined P fractions is needed to improve our ability to predict responses of sediment P to drying and re-flooding.

Several studies have used sediment Fe:P molar ratios as predictors of an ecosystem's propensity to release P into surface waters, identifying critical thresholds of 8.3-10, below which P release is expected (Jensen et al. 1992; Geurts et al. 2008; Zak et al. 2010; Forsmann and Kjaergaard 2014). In our study, sediment molar Fe:P ranged from 3.5 to 37. Mean surface water SRP reached high concentrations (>10 μg L^{-1}) upon re-flooding only in sediments with molar Fe:P ratios less than ~6. However, some sediments below this "threshold" did not release P into surface waters (P18, TM, P10, LF), and this pattern was similar with molar OxFe:P ratios and post-treatment porewater Fe:SRP ratios. In systems with oxygenated surface waters, pore water Fe:PO_4^{3-} ratios are more effective predictors of sediment P release than sediment Fe:P ratios (Geurts et al. 2008). In part this is because sediment total Fe sometimes includes Fe that is bound to S and therefore unavailable to sorb PO_4^{3-}. Overall, low sediment Fe:P ratios may be useful in identifying ecosystems that may be vulnerable to P release from Fe-bound forms, but do not necessarily indicate whether P will be released from or retained in sediments.

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

The two sediments that displayed large, sustained P release during re-flooding after drying (FCTC, WG) were collected from ecosystems with a history of higher P loading than the other sediments. FCTC sediments were collected from historically drained agricultural land that was recently re-flooded as part of a wetland restoration (Kinsman-Costello et al. 2014) and WG sediments were collected from riparian areas of hypereutrophic Wintergreen Lake (Manny et al. 1994). The high sediment H_2O~P in WG may indicate that it is at or near saturation in regards to P sorption (Hooda et al. 2000) and likely reflects the legacy of P inputs and eutrophication in Wintergreen Lake which has a long history of heavy waterfowl use (Manny et al. 1994). The sustained increase and high surface water SRP concentrations in these two sediments, despite constant aeration, suggests that sediments such as these are likely to release P to surface waters when dried and re-flooded regardless of whether their overlying waters are oxic or anoxic. It also emphasizes that reactive forms of sediment P, rather than total sediment P or Fe:P ratio, determine the propensity of sediments to release P into surface waters, as these two sediments did not contain the highest total P concentrations among sediments tested. Phosphorus released from sediments such as these could cause considerable eutrophication in an aquatic ecosystem with a shallow water column.

Conclusion

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

Overall, this experiment demonstrates that sediment-water P exchange following drying and re-flooding is a highly variable phenomenon that is subject to multiple controls, and that wetland water level fluctuations may lead to substantial sediment P release, particularly in sediments with relatively high fractions of easily mobilized water-extractable PO_4^{3-}. Sediment P release in response to drying and reflooding may limit the ability of natural, restored, and constructed wetlands and streams to provide important ecosystem services. Within ecosystems, eutrophication resulting from sediment P release may degrade wetland habitat quality and ecosystem health. Along landscape flow paths, sediment P release may cause aquatic ecosystems to act as sources, rather than sinks, for P, potentially contributing to harmful eutrophication in vulnerable downstream ecosystems.

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

Site Name	**Abbrev.**	**UTM Easting**[a]	**UTM Northing**	**Cond. (µS cm^{-1})**[b]	**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

[a] Universal Transverse Mercator Zone 16

[b] Conductivity corrected to 25 °C

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

Table 2 Hypothesized effects of four main sediment properties on amount of phosphate (PO_4^{3-}) released from sediments to pore and surface waters after drying and re-flooding, and lists of measured variables that are potential predictors of each sediment property of interest. Variables are defined in Table 4 and the main text. Measured indicator variables were used to test hypothesized effects of hydrologic change on PO_4^{3-} release using a model comparisons approach with AIC.

Sediment Property	Measured Indicator Variables	Hypothesized effect on 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 FeS_x	AVS	negative
$CaCO_3$-associated P	Total $CaCO_3$, HCl~SRP	no net effect

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 ($CaCO_3$) are reported as per gram dry weight of sediment.

Sediment	Total P (μg g^{-1})	Organic Matter[b] (%)	Total Fe (mg g^{-1})	Fe:P Molar ratio	Ox-Fe (mg g^{-1})	AVS (μmol g^{-1})	$CaCO_3$ (mg g^{-1})	Bulk Density (g cm^{-3})	Dry Soil Moisture[c] (%)
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

[a] Abbreviations defined in Table 1.

[b] Measured as loss on ignition

[c] 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 (α = 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 ± standard error.

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

[a] *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 (ω_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	Δ AIC$_c$	ω_i
PW SRP							
	Organic P	Org. Matter	negative	0.01	0.68	14.50	<0.01
	Iron-Bound P	*Total Fe*	*negative*	*0.34*	*0.02*	*9.46*	*0.01*
	Oxidizable FeS_x	AVS	negative	0.23	0.06	11.15	<0.01
	$CaCO_3$-Associated P	Total $CaCO_3$	negative	0.15	0.14	12.46	<0.01
	Stepwise Model	**Total Fe, H_2O~SRP**	**negative, positive**	**0.68**	***<0.01***	**0.00**	**0.98**
SW SRP							
	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
	Oxidizable FeS_x, Stepwise Model	**AVS**	**negative**	**0.41**	***<0.01***	**0.00**	**0.64**
	$CaCO_3$-Associated P	*Total $CaCO_3$*	*negative*	*0.26*	*0.04*	*2.54*	*0.18*

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^{-2} d^{-1})
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[a]	Michigan, USA	Experimental drying and re-flooding homogenized wetland sediment	0 - 16

[a] 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), SO_4^{2-} (C, D), Fe(II) (E), and 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.