Hydrology and Soil Manipulations of Iron-Rich Ditch Mesocosms Provide Little Evidence of Phosphorus Capture within the Profile

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Abstract

Agricultural drainage ditches function as first-order streams and affect nutrient management. Soil mesocosms from a ditch featuring a vertical (increasing upward) gradient in iron (Fe) and phosphorus (P) were subjected to hydraulic and soil treatments. These manipulations mimicked aspects of dredging and controlled drainage and inspected the soil release and retention of P. Treatments did not remove P from simulated groundwater. Throughput water either gained in P (lack of dredging, especially under Fe-reducing conditions) or had P concentrations indistinguishable from input water (dredging). Undredged mesocosms, when Fe-reducing, released Fe and P simultaneously. Simultaneous release of P and Fe from our Fe-reducing mesocosms indicates a mechanism whereby P capture occurs by Fe precipitation upon emergence to aerated surficial waters. Upwelling and surficial phases of ditch hydrology and the lowering of the ditch surface on dredging complicate interpretation of traditional means of describing ditch P retention and release.

Core Ideas

- Fe-based P capture occurs as Fe oxidizes upon emergence at the ditch surface.
- At our site, P capture is not based on properties of in-place soil material.
- Many common techniques assume P capture by in-place soil materials.
- At our site, P capture appears to occur simultaneous to soil formation.

In agricultural landscapes with sufficient hydraulic conductivity, open ditches transport dissolved and colloidal materials even as they provide field-scale drainage (Needelman et al., 2007a). If sufficient phosphorus (P) is exported, ditches can contribute to eutrophication (Needelman et al., 2007a), a problem worldwide (Rabalais et al., 2009). Greater understanding of P transport in ditches is needed to simultaneously provide drainage and prevent P losses (Kleinman et al., 2015).

It is important to understand how common ditch management practices such as dredging and controlled drainage affect ditch P retention and transport (Needelman et al., 2007a; Sharpley et al., 2007; Smith and Pappas 2007; Shigaki et al., 2008). Dredging removes accumulated materials to intercept rising water at greater depth and has produced, in a midwestern context, increased P release in postdredge sediments in fluvaria (Smith et al., 2006; Smith and Pappas, 2007) and decreased P concentrations in the field (Smith and Huang, 2010). Controlled drainage restricts flow to retain sediments, decreases export of dissolved constituents, and raises the water table to promote denitrification (Gilliam and Skaggs, 1986; Evans et al., 1995; Kröger et al., 2008). However, controlled drainage may promote the release of P through reductive dissolution of Fe (Sharpley et al., 2007), particularly in acidic mid-Atlantic Coastal Plain (MACP) ditches, which can feature steep gradients toward the surface of organic matter (OM), paracrystalline Fe and Al, and associated P (Vaughan et al., 2007b).

Such steep gradients (Vaughan et al., 2007b) are of interest not only for their pedology, but also for their role in their P retention and transport characteristics of the whole soil profile. Since paracrystalline oxides have substantial capacity to sorb P (Rhoton and Bigham, 2005; Richardson, 1985), typically occupy a small percentage of the Fe oxides of upland soils (Li, 2009; Elless and Rabenhorst, 1994), and their formation can be encouraged by frequent redox changes and the presence of OM (Schwertmann, 1991), can the manipulation of ditch hydrology encourage their formation and therefore add to capacity of ditches to retain P?
We conducted an experiment using soil mesocosms that, like fluvaria, allow for the examination of dredged and undredged sediments but, unlike fluvaria, do so on an intact soil profile, allow for groundwater rise and, through the manipulation of hydrology, the application of oxidizing and reducing conditions as would occur under controlled drainage. Our objectives were to quantify on intact soil profiles (i) the effect of dredging and (ii) the influence of hydrology on P retention and P release, (iii) the influence of hydrology on soil-Fe mineralogy, and (iv) the importance of ditch surficial materials to P cycling.

Materials and Methods

We manipulated soil and hydrologic states of intact drainage ditch mesocosms in a cross-factorial laboratory experiment to test effects of dredging and drainage on P cycling. The rising trajectory of input water in mesocosms reflected the rise of groundwater that occurs in ditches (Vadas et al., 2007). The mesocosm source was a drainage ditch at the University of Maryland Eastern Shore Research Farm, (38°12'22" N, 75°40'35" W), the subject of numerous previous investigations on P loss in ditch drainage (Kleiman et al., 2007; Vaughan et al., 2007a, 2007b, 2008; Shigaki et al., 2008; Church et al., 2010). Soils of fields surrounding the mesocosm source ditch are predominantly Quindocqua (fine-loamy) and Orthello (fine-silty) mixed, active, mesic Typic Endoaquents, characterized by deltactic and marine sediments overlain by ≥20 cm of loessal materials (Soil Survey Staff, 2011), and contain Mehlich-3 P concentrations roughly one order of magnitude above recommended values (Kleiman et al., 2007; Vaughan et al., 2007a; PSU, 2011). The farm had previously supported intensive chicken production for 30+ years. A pyrite-bearing layer underlies the ditch and surrounding fields at a shallow depth (<2 m; Vaughan et al., 2008).

Prior to field work in 2006, the ditch had been undredged for at least 10 yr. Since the last dredging, the ditch bottom had accumulated between 10 and 40 cm of loam- and silt-loam-textured materials. Soils in this ditch have been described as Aeric and Humaqueptic Endoaquents that lack B horizons but have accumulated significant OM and are commonly found with Fe monosulfides (Vaughan et al., 2008).

Mesocosm Collection and Handling

Cylindrical (15-cm inner diameter) mesocosms were made by driving 40-cm sections of polyvinyl chloride (PVC) pipe (sharpened at the bottom) into the ditch soil, followed by sideways excavation. Details of mesocosm extraction and the contained horizons are described elsewhere (Ruppert, 2012; Ruppert et al., 2014).

Mesocosms were air dried at the University of Maryland Research Greenhouse Complex between 27 and 33°C to allow application of paraffin between the soil and PVC to preclude bypass flow. Although drying can affect soil chemistry (Bartlett and James, 1980), make P more labile (Baldwin and Mitchell, 2000; Xu et al., 2011), or decrease P-sorption capacity (Qiu and McComb, 2002), it was imperative to curtail bypass flow. Mesocosms were fitted with geotextile fabric, acid-washed gravel, and a plastic drain screen such that soil material received adequate support on cementing of the PVC end cap (Supplemental Fig. S1). To allow simulated ground water rise, a hole was drilled through each PVC end cap and a threaded port was added, to which 0.95-cm diameter tubing was either attached (allowing water input) or detached (permitting drainage).

Simulated Groundwater

Mesocosms were periodically flooded from below with simulated groundwater created from a combination of inorganic salts (Supplemental Table S1) based on average electrolyte concentrations from shallow wells (Vadas et al., 2007) at the field source of mesocosms. One-liter Mariotte bottles provided a hydraulic head of 40 cm relative to the top of the mesocosm soil, where an outlet hole had been installed (Supplemental Fig. S1). The 40-cm head was judged to be comparable with the head in the field along some lengths of the ditch from which mesocosms were taken. This hydraulic head provided fluxes between 0.25 and 0.02 L min⁻¹, allowing the collection of 1 L of effluent from mesocosms within 1 h of the application of input water. These differences were attributed to differences in macroporosity.

Mesocosm Experiments

Experimental Design

Four soil treatments and three hydraulic treatments populated a factorial in a completely randomized design (Supplemental Table S2). Soil treatments were either “Undredged” or “Dredged.” Undredged mesocosms were collected before a dredging event, were given six replicates per treatment, and were either unmanipulated controls. “O-Addition” treatments in which 100 g of air dry surficial materials (5-cm thick) were added to the surface, or “Surficial Removal” treatments in which the upper 2 cm of surface materials were removed. Dredged mesocosms were collected after a dredging event and received two replications per treatment. The difference in performance between Dredged and Undredged mesocosms was expected to be sufficient to merit diminished replication of the Dredged treatments.

Hydrology treatments were either “Saturated” (mesocosms experienced constant saturation throughout the experiment), “Drained” (mesocosms were maintained at field capacity throughout the experiment except during periods of simulated groundwater rise), or “Alternating” (mesocosms experienced both drained and saturated conditions, Supplemental Tables S2 and S3). Benches locations were shaded from the sun in a climate-controlled greenhouse with temperatures ranging from 10°C during winter to 32°C in summer. Space restrictions precluded the use of an indoor location with more constant temperature.

Simulated Groundwater Manipulations

Prior to the start of the experiment, all mesocosms were in a freely draining but moist state. The experiment started with an initial 1-L input of water (“upwelling”) to each mesocosm from the bottom. Subsequent 1-L upwellings followed each day for 4 d. At the end of this first period of upwellings, and for the remainder of the experiment between upwellings, “Drained” treatments were freely drained and “Saturated” mesocosms
remained saturated. “Alternating” treatments were allowed to freely drain after the first, second, and fourth upwelling periods but remained saturated after the third and fifth upwelling periods. In all, five 5-d periods of upwellings occurred, in which 1 L of water was inputted to each mesocosm per day. Upwelling periods were separated by periods of hydraulic equilibration lasting at least 20 d to ensure relatively stable redox environments before each upwelling. A table illustrating the hydrology schedule is available (Supplemental Table S3, Ruppert et al., 2014). Although simulated groundwater rise was originally intended to occur regularly, complications regarding effluent water analysis resulted in irregular periods between upwelling events. This irregularity meant that effects of environmental variables within the greenhouse space (e.g., temperature, which ranged 10–32°C) and interim period length could not be separated. Throughout the experiment, distilled water was added to all mesocosms to maintain 10 cm of floodwater at the top of mesocosms under saturation, or to avoid an air-dry state among drained-state mesocosms. Since mesocosms were equilibrated with greenhouse temperatures, mineralization rates within our mesocosm soils were at times likely higher than those of soils in situ.

Measurement of Porewater Redox and pH

Two mesocosms for each Undredged treatment and one mesocosm for each Dredged treatment (see Supplemental Materials) were outfitted per horizon with a porewater sampler (macerator, Soil Moisture Corporation) to measure pH and three platinum electrodes to measure soil oxidation reduction potential relative to the standard hydrogen electrode (Supplemental Fig. S1). A portable calomel reference electrode (−244 mV relative to the standard hydrogen electrode), a multimeter, and a device providing increased internal resistance (Rabenhorst, 2009) were used to make reliable, drift-free measurements of redox.

Effluent and Soil Collection and Measurement

Effluent was collected in 1-L bottles open to air. After shaking, subsamples from each collection bottle were refrigerated at 4°C. Effluent from Undredged mesocosms in a saturated state prior to upwellings turned from clear to orange within 1 h after entering the effluent bottle, leaving an orange coating on bottle walls. These coatings were judged to consist of Fe(III) (hydr) oxides and incorporated organic acids that precipitated on reentry to the oxidizing environment outside of the mesocosms. To keep effluent constituents soluble, a small amount of HCl (similar to Zak et al., 2009) was added to effluent collection bottles for all mesocosms such that final effluent pH ~ 2 (dilution was minimal). Acidification of samples did not interfere with colorimeter absorbance. Effluent was measured for reactive P using a manually operated colorimeter (Genesis 10, Thermo Fisher Scientific Corporation) and a molybdenum blue method similar to American Public Health Association (2012).

Upon the end of the experiment, mesocosms were stored in a cold room (4°C) for 2 to 14 d before opening with a table saw. Soils were air dried prior to analysis. Horizon descriptions are in Ruppert et al. (2014). Soils were categorized as Cg, C, Ag, A, mucky A, or O on the basis of structure, OM, and clay percentage (Supplemental Materials, Supplemental Table S4). Also available in the Supplemental Materials are the oxalate extraction and oxalate-extract analysis procedures.

Data Processing and Analysis

Treatment differences were declared statistically significant at the 0.05 level. To determine if treatments affected the redox state of experimental units, redox potential (Eh) and pH values were averaged over time and over horizons (by weight) so that single values for Eh and pH were obtained per mesocosm. The effect of hydrology on Eh and pH in Dredged mesocosms could not be evaluated statistically since per-treatment replication = 1 for Eh and pH of Dredged mesocosms. Inclusion of Alternating mesocosms in the model resulted in pseudoreplication (Hurlbert, 1984); therefore, Alternating mesocosms were not included. As a result, only Saturated and Drained Undredged mesocosms were evaluated statistically for differences in pH and Eh. Unless stated otherwise, all statistical analyses were performed using the MIXED procedure of the SAS System (SAS 9.2; SAS Institute, 2008), and Tukey multiple means comparison tests were performed if the overall F-test was significant.

Effluent P data from the first 5 d of each upwelling were averaged to produce one value for effluent P per upwelling period per mesocosm. Effluent P residual plots showed increasing variance with increasing treatment means (data not shown); these data were log transformed prior to statistical analysis. Alternating mesocosms were omitted from statistical analysis of effluent P due to pseudoreplication.

For soil horizons, stepwise linear regression of oxalate-extractable P (Pox) against oxalate-extractable Fe (Feox) and Al (Alox) (to determine relative importance of Fe and Al to P sorption) and a simple linear regression of Alox versus Feox were performed using the SAS REG procedure. In scatter plots of Pox, Feox, and Alox, slope changes were observed and simple linear models were compared with change point models (see the online supplemental materials section). To estimate P sorption saturation, the degree of P saturation (DPS = 100Pox/[(Feox + Alox)]−1, molar basis) was calculated for each soil horizon using α = 1 (Beck et al., 2004). In a scatter plot, the relationship between Feox and DPS appeared to exhibit a change in correlation; an analysis of this correlation change was performed (Supplemental Materials). Whole-mesocosm Pox, Feox, and Alox were determined by weighted averaging according to horizon mass and were evaluated using the SAS MIXED procedure.

Results

Eh and pH

Among Undredged mesocosms, interactions between hydrology and soil treatments were not significant for Eh (p > 0.06) and pH (p > 0.39), and therefore main effects were evaluated. Among Undredged mesocosms, soil treatment main effects were not significant (Eh, p > 0.30; pH, p > 0.13), but hydrology was, resulting in lower pH (p < 0.0004) and higher Eh (p < 0.0001) for Drained than Saturated Undredged mesocosms (Fig. 1a and 1b). Treatments that were not evaluated statistically (Dredged and Alternating-hydrology Undredged mesocosms) behaved similarly to statistically tested treatments (Fig. 1a and 1b), per their hydraulic state. No matter the soil treatment, mesocosms in a drained state were aerobic and saturated-state mesocosms were anaerobic per the USDA NRCS Technical Standard (595–60 mV × pH, Fig. 1b) which is used to identify hydric soils and is correlated with Fe-reducing conditions (NTCHS, 2015).
Effluent Properties

For dissolved P concentrations in effluent, there was no three-way interaction of hydrology treatment, soil treatment, and upwelling ($p > 0.09$), but two-way interactions among these factors were significant. For hydrology by upwelling event, effluent dissolved P concentrations were different from and more than two times larger under saturation than under drainage (Fig. 2a). When drained, Alternating-hydrology mesocosms behaved similarly to Drained mesocosms; when saturated, Alternating mesocosms behaved similarly to Saturated mesocosms (Fig. 2a, Supplemental Table S3). For soil treatment by upwelling event, during the first upwelling, the O-Addition treatment resulted in approximately four times greater dissolved P concentration relative to the other treatments, which had similar effluent and influent P concentrations (Fig. 2b). After the first upwelling, dissolved P concentrations in effluent from Undredged treatments were more than two times higher than concentrations in effluent from the Dredged treatment (Fig. 2b). For hydrology treatment by soil treatment, Dredged Saturated mesocosms resulted in similar concentrations of effluent P as Undredged Drained mesocosms (Fig. 2c). Mean effluent P concentrations were greatest in Saturated mesocosms with O-material addition (Fig. 2c), although these concentrations may be a function of temporarily heightened P release during the first upwelling (Fig. 2b).

Dredged mesocosm effluent P was indistinguishable from input water P (Table 1). All Undredged-treatment effluent P concentrations exceeded that of input water (Table 1). This difference was five to nine times greater when Undredged mesocosms were Saturated and not Drained (Table 1).

Effluent and Surface Water Fe

Without acidification, an orange precipitate was observed on the inside of collection bottles that received effluent from Undredged mesocosms that experienced saturation prior to upwellings. With acidification, effluent from these mesocosms was orange in color, but a precipitate did not form. Evidently, Undredged mesocosms saturated prior to the start of upwellings released appreciable Fe to effluent water.

Soil Properties

Individual Horizons

Aggregate data regarding mesocosm horizons are available in Supplemental Table S4 and Ruppert et al. (2014). Phosphorus sorption capacity was Fe-dominated. Ninety-eight percent ($p < 0.01$) of the variation in soil P was explained by soil Fe.
and the addition of soil $\text{Al}_{\text{ox}}$ did not improve the model (Fig. 3a). Simple linear regression detected ($p < 0.01$) relationships between $\text{P}_{\text{ox}}$ and $\text{Al}_{\text{ox}}$ and $\text{Al}_{\text{ox}}$ and $\text{Fe}_{\text{ox}}$. In each case, fits were improved using a change point (Fig. 3a–3c). Expressed on a molar basis, the maximum observed concentration of $\text{Fe}_{\text{ox}}$ in soil horizons was 20 times greater than that of $\text{Al}_{\text{ox}}$ (Fig. 3c). The highest concentrations of $\text{P}_{\text{ox}}$, $\text{Fe}_{\text{ox}}$, and $\text{Al}_{\text{ox}}$ were in mucky A horizons, which were the dominant surface horizon of mesocosms (Fig. 3a–3c and a previous analysis in Ruppert et al., 2014). Uppermost horizons of (Undredged) control mesocosms were $2.8 \pm 1.3$ cm thick and contained $19.6 \pm 10.9$ mmol $\text{P}_{\text{ox}}$ accounting for $31\%$ of whole-mesocosm $\text{P}_{\text{ox}}$. Change points in the behavior of $\text{P}_{\text{ox}}$, $\text{Al}_{\text{ox}}$, and $\text{Fe}_{\text{ox}}$ with respect to one another occur approximately at the lowest concentrations of these analytes in mucky A horizons ($\text{Fe}_{\text{ox}} = 115$ mmol kg$^{-1}$).

The relationship between DPS and $\text{Fe}_{\text{ox}}$ exhibited two regions with divergent $R^2$ (Fig. 3d). For values of $\text{Fe}_{\text{ox}}$ characteristic of subsurface horizons ($\text{Cg}$, $\text{C}$, and $\text{Ag}$; $<36$ mmol $\text{Fe}_{\text{ox}}$ kg$^{-1}$), $\text{Fe}_{\text{ox}}$ accounts for little of the variation in DPS ($R^2 = 0.001$). For values of the $\text{Fe}_{\text{ox}}$ characteristic of surficial (mucky A and O) and

### Table 1. Mesocosm effluent phosphorus (P) means, SE, and difference ($\Delta P$) relative to input (0.48 mg P L$^{-1}$).

<table>
<thead>
<tr>
<th>Mesocosm soil treatment†</th>
<th>Mesocosm hydrology treatment‡</th>
<th>$n$</th>
<th>Drained</th>
<th>Saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>SE</td>
</tr>
<tr>
<td>Dredged</td>
<td></td>
<td>2</td>
<td>0.24</td>
<td>0.33</td>
</tr>
<tr>
<td>Undredged</td>
<td></td>
<td>6</td>
<td>0.81</td>
<td>0.19</td>
</tr>
<tr>
<td>Surficial removal</td>
<td></td>
<td>6</td>
<td>0.98</td>
<td>0.24</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>6</td>
<td>1.11</td>
<td>0.30</td>
</tr>
<tr>
<td>O-addition</td>
<td></td>
<td>6</td>
<td>1.03</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.41</td>
<td>0.98</td>
<td>+610</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.10</td>
<td>0.81</td>
<td>+546</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.64</td>
<td>0.69</td>
<td>+867</td>
</tr>
</tbody>
</table>

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
† “Dredged” mesocosms gathered after dredging, “Undredged” mesocosms gathered before dredging, “Surficial removal” indicates 2 cm of surficial materials removed, “O-addition” indicates 100 g organic material surficially added.
‡ “Drained” mesocosms drained between upwellings of simulated groundwater; “Saturated” mesocosms saturated between upwellings of simulated groundwater.
§ Student’s $t$ statistic. Statistical tests were performed on log-transformed data.
¶ NS, not significant.
near-surficial A horizons (>36 mmol Fe$_{ox}$ kg$^{-1}$), Fe$_{ox}$ accounts for a much greater share of the variation of DPS ($R^2 = 0.70$, Fig. 3d).

**Whole Mesocosms**

Undredged mesocosms contained more Fe$_{ox}$, Al$_{ox}$, and P$_{ox}$ (52.2, 13.2, and 18.4 mmol kg$^{-1}$, respectively) than Dredged mesocosms (6.4, 2.9, and 4.3 mmol kg$^{-1}$, respectively); however, no difference in DPS was detected ($p > 0.01$). Among Undredged mesocosms, Saturated mesocosms contained 30% less Fe$_{ox}$ ($p < 0.01$), 9% less Al$_{ox}$ ($p < 0.03$), and 30% less P$_{ox}$ ($p < 0.01$) than the other two hydrologic treatments (Table 2). The Surfacial Removal treatment diminished Fe$_{ox}$ ($p < 0.01$) and Al$_{ox}$ ($p < 0.01$) relative to the soil control (Table 2) but did not affect P$_{ox}$ ($p > 0.08$).

**Discussion**

**The Effect of Dredging in Mesocosms vs. the Field**

In the field, dredging removed accumulated P- and Fe-rich material at the surface of the ditch (see above section). Such removals simultaneously lower the elevation of the soil surface and place dredged soils in more frequent contact with groundwater. Consequently, dredged soils will experience saturation more frequently than undredged soils, indicating that reduction in effluent P concentrations due only to dredging, as observed in our experiment (Fig. 2b), may not occur in the field, because dredged ditch soils will become more frequently saturated, and Dredged Saturated mesocosms in our study released as much P as Drained Undredged mesocosms (Fig. 2c).

Our finding that dredging lowered effluent P relative to the control when hydrology was held constant is consistent with Smith and Huang (2010) and Shiagi et al. (2008). Disrupted materials from dredged and undredged ditches from the same site where our intact soil mesocosms were taken were compared for their P-release potential by Shiagi et al. (2008). After 48 h, fluvaria water was less concentrated in P (by an order of magnitude) using materials from a dredged ditch versus materials from an adjacent undredged ditch (Shiagi et al., 2008). Fluvaria studies likely preserve aerobic conditions throughout the sediment profile, unlike ditches in the field, and should be viewed as insightful into the P sorption potential of aerobic sediments, not the functioning of the whole soil profile, which functions differently according to aeration state antecedent to groundwater rise (Fig. 1a, 1b, 2a, and 2c).

In a field study of Midwestern collection ditches, Smith and Huang (2010) observed decreased P exports in dredged ditch reaches versus undredged reaches for up to 1 yr after dredging (similar to Shiagi et al., 2008, and the present study; Fig. 2b). Midwestern collection ditches are different from the primary ditch from which our mesocosms were taken. Midwestern collection ditches are secondary ditches that primarily drain tile, function and behave much like streams (featuring near-constant to constant flow, whether recently dredged or not), and likely are neither as acidic nor dominated by Fe as the coastal plain soils of this study. Nevertheless, it makes intuitive sense that removal of high-P materials would lower ditch free water P concentrations, as observed in Smith and Huang (2010), Shiagi et al. (2008), and here (Fig. 2b).

In contrast, Smith et al. (2006) and Smith and Pappas (2007) observed (in fluvaria) increased P release from Midwest collection ditch sediments after dredging relative to sediments collected before dredging. These results are considered to apply only in the short term by Smith and Huang (2010), who cite the oxidation, sediment introductions, and colonization of plants, algae, and bacterial biofilms as mechanisms whereby P release may be curtailed or P sorption may occur longer term in dredged versus undredged materials. Because the work of Smith and Huang (2010), Smith and Pappas (2007), and Smith et al. (2006) occurred in the context of collection ditches in the Midwest, their findings may not apply in our context.

Despite the difference in average effluent P in Dredged mesocosms between Drained and Saturated hydrologies (Fig. 2b and 2c), these effluent P values were indistinguishable from the P in input water (Table 1). Our minimal statistical power associated with Dredged mesocosms ($n = 2$ per hydrology level, Supplemental Material) is clearly a factor. Trends in these data (Table 1) point to the possibility that dredged, Fe-oxidizing soils might capture P at the level of P in our input water, and that dredged Fe-reducing soils would not. However even if the effect of dredging on an aerated soil is real, aeration-associated attenuation of P in dredged ditches may be of little practical consequence, since aeration becomes less frequent under dredging. Regardless of the effect of dredging on P, dredging of high-Fe ditch soils may be recommended to avoid Fe-related oxidation of OM (Van Bodegom et al., 2005) and accompanying nitrogen release (Emsens et al., 2016).

**Effects of Hydrology**

P Release from Saturated Mesocosms vs. Controlled Drainage

Saturation prompted the release of P (Fig. 2a and 2c) and Fe among Undredged mesocosms, and Saturated mesocosms contained less soil P and Fe than other hydrology treatments at

**Table 2** Whole-mesocosm response of Undredged mesocosms to hydraulic and soil treatments.

<table>
<thead>
<tr>
<th>Parameter†‡ §</th>
<th>Hydraulic treatment†‡</th>
<th>Soil treatment¶</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drained</td>
<td>Saturated</td>
<td>Alternating</td>
</tr>
<tr>
<td></td>
<td>mmol kg$^{-1}$</td>
<td>mmol kg$^{-1}$</td>
<td>mmol kg$^{-1}$</td>
</tr>
<tr>
<td>Fe$_{ox}$</td>
<td>57.0 ± 3.1a¶</td>
<td>41.1 ± 3.1b</td>
<td>58.0 ± 3.1a</td>
</tr>
<tr>
<td>Al$_{ox}$</td>
<td>13.3 ± 0.5ab</td>
<td>12.2 ± 0.5a</td>
<td>14.0 ± 0.5b</td>
</tr>
<tr>
<td>P$_{ox}$</td>
<td>20.3 ± 1.2a</td>
<td>14.6 ± 1.2b</td>
<td>20.3 ± 1.2a</td>
</tr>
<tr>
<td>Surfacial removal</td>
<td>Control</td>
<td>O-addition</td>
<td></td>
</tr>
<tr>
<td>Fe$_{ox}$</td>
<td>44.4 ± 3.1a</td>
<td>59.0 ± 3.0b</td>
<td>52.7 ± 3.1ab</td>
</tr>
<tr>
<td>Al$_{ox}$</td>
<td>11.9 ± 0.5a</td>
<td>14.0 ± 0.5b</td>
<td>13.5 ± 0.5ab</td>
</tr>
<tr>
<td>DPS</td>
<td>27.6 ± 0.9a</td>
<td>22.5 ± 0.8b</td>
<td>25.4 ± 0.6ab</td>
</tr>
</tbody>
</table>

†“Drained” mesocosms were drained after each upwelling event; “Saturated” mesocosms were held saturated throughout the experiment; “Alternating” mesocosms were drained or remained saturated cyclically.

‡ Oxalate-extractable iron, aluminum, and phosphorus. DPS, degree of phosphorus saturation ($= 100P_{ox}(\text{Fe}_{ox} + \text{Al}_{ox})^{-1}$).

§ Within means, rows followed by the same letter are not significantly different according to Tukey’s adjusted means comparison tests. Uncertainties are standard error.

¶ “Surfacial removal” mesocosms had 2 cm of surficial materials removed; “O-addition” mesocosms had 100 g organic material surficially added.
the end of the experiment (Table 2). Upwellings preceded by saturation always resulted in Fe-reducing conditions and higher effluent P than upwellings preceded by a drained state, in which whole mesocosms were always Fe oxidizing (Fig. 1a, 1b, 2a, and 2c). This observation is consistent with Amata et al. (1998), who recorded heightened ditch P concentrations resulting from controlled drainage, and it justifies the concern of Needelman et al. (2007b) and Sharples et al. (2007) that reductive dissolution of Fe could release P from saturated ditch soils.

However, our heightened values for effluent P from Undredged saturated-state mesocosms should not be used to extrapolate to ditches under controlled drainage in the field. In some field settings, ditches (Evans et al., 1995) and tile (Nash et al., 2015) under controlled drainage have had P loads and losses diminished. This might be accomplished in at least two ways that are not captured by our mesocosms: (i) under controlled drainage, mass flow would be minimal, unlike in our experiment in which mass flow (upwellings) occurred deliberately; (ii) Undredged mesocosms experiencing Fe-reducing conditions before upwellings released P and Fe simultaneously, thereby providing a mechanism of P capture. Phosphorus capture in diffusion-dominated soils, as with controlled drainage, has been recorded in fens (Zak et al., 2004) and fen mesocosms (Zak et al., 2010) at the boundary between aerobic and anaerobic soil zones, with reductions (in aerated zones) in porewater P of up to two orders of magnitude recorded (Zak et al., 2004). Although saturated conditions clearly solubilize P, the solubilization of Fe and the lack of flow under controlled drainage may mitigate P concentrations in aerated waters and soil zones.

**P Transport and the Pedology of Field Soils under Unrestricted Drainage**

The simultaneous release of Fe and P by Fe-reducing Undredged mesocosms also indicates a mechanism whereby P concentrations can be mollified when drainage is not restricted. In our mesocosms, the capture of mesocosm effluent precluded Fe settlement on the soil surface. In natural systems, however, the oxidation of Fe, which can occur in seconds or minutes (Davison and Seed, 1983), provides a mechanism to capture P within ditches. This is consistent with the observation of increased surficial Fe and P near outlets of primary ditches (Vaughan et al., 2007b; Ruppert, 2012).

The surficial capture of P by emergent Fe is a mechanism of P capture that occurs outside of the soil profile. The inability of any of our mesocosm treatments to capture P from input water (Table 1) indicates such a mechanism. We conclude that the soil profile is not the locus of P sorption when hydrology is unrestricted (freely flowing vs. controlled). Instead, the lack of soil treatment effect (Table 1) and high P and Fe that occur among (surficial) mucky A horizons (Fig. 3a) point to the surficial capture of P by oxidized Fe.

The surficial capture of P allows for subsurface P storage as surficial materials are buried. But as the surface of the ditch ascends and prior surfaces become buried, they too become Fe and P donors as the zone of Fe oxidation and P capture moves upward. The burial of previously surface-captured P and Fe and subsequent release are consistent with (i) the observation of gradients of Fe and P toward the surface by Vaughan et al. (2007b), (ii) the close correlation of Fe and P in horizons of Undredged soil mesocosms (Fig. 3a), and (iii) the lack of correlation between Fe and DPS that occurs for (surficial) C, Cg, and Ag horizons versus a clear correlation between DPS and Fe for (surficial) A and mucky A horizons (Fig. 3d).

Although our data indicate profile storage and release of P and a mechanism for surficial P capture, it is possible that some within-profile capture of P occurred to which our experimental units were insensitive. Because our experimental units were air dried in a greenhouse prior to the application of wax to preclude bypass flow, P may have been made sufficiently labile (Baldwin and Mitchell, 2000; Xu et al., 2011) in our mesocosms that any in-profile P sorption was masked by higher P release. As a result, although we have clearly observed a mechanism for the surficial capture of P, we cannot conclude that within-profile P capture does not occur. If it does, however, it is likely a small effect. Under Fe-reducing conditions, the active loss of Fe toward the surface with rising groundwater exports P-sorbing potential to the surface. Under aerobic conditions, the remaining Fe in the profile is still likely saturated or near-saturated with P. Our measurements of DPS have average minimum values of ~22.5 (Fig. 3d) for subsurface horizons of low Al and Fe (Fig. 3a and 3b), and therefore low P-capture potential. Values of DPS > 23 to 25 are commonly provided as evidence for likely P desorption (Beauchemin and Simard, 1999). Therefore, if P capture does occur within the soil profile, it likely occurs in horizons of minimal P-sorbing capacity.

That P capture is likely a surficial process in the ditch system from which our mesocosms were collected should prompt skepticism regarding the application of commonly used nutrient management techniques at our and similar field sites. Batch studies, fluvia, the use of DPS, and even our use of mesocosms assume that P release and capture occur because of in-place soil materials. Some of these techniques cannot (fluvia) or often do not (batch studies) explore redox-based controls. Whereas P release is certainly a matter of in-place soil materials, P capture in our high-Fe soil context would appear to be concurrent with pedological formation, with location (redox state) and the Fe:P ratio of emergent porewater (similar to Zak et al., 2010, 2004) as soil-forming factors.

**Mineralogy**

The purpose of our Alternating hydrology treatment was to prompt improved P capture by increasing the percentage of paracrystalline Fe oxides. It is clear, however, that the Alternating treatment did not distinguish itself in terms of Fe, Al, or P (Table 2), nor in effluent P (Fig. 2a and 2c). This is either (i) because most Fe entering the ditch does so through emerging porewater, and quickly oxidizing Fe in natural water is known to produce paracrystalline Fe (Schwertmann, 1991, 1993), especially in the context of drainage (Schwertmann, 1966; Needelman et al., 2007b) and high concentrations of P, OM, and other anions (Schwertmann, 1991; Petrovic and Kastalan-Macan, 1996; Gerke, 2010); or (ii) because crystalline Fe oxides, originally resident in the ditch soil or eroded into the ditch, become paracrystalline over repeated redox cycles. It is possible that the Alternating treatment could not develop further paracrystalline Fe because Fe present in the Undredged mesocosms, as extracted, was already in paracrystalline form. Any crystalline Fe present in the mesocosms would most likely be below horizons containing high OM, therefore C horizons (which are of low Fe content; Supplemental Table S4).
Management Implications

The importance of surficial processes to P capture in our ditch system indicates that the linear geometry and minimal surface area characterizing many ditches may not maximize P-storage capacity. Alternative ditch designs, not necessarily for the purpose of retaining P, have been proposed (Evans et al., 2007; Powell et al., 2007a, 2007b).

Emergent porewater chemistry that likely controls P capture in our ditch may not contain sufficient Fe to avoid eutrophication. In ditches where this is the case, exogenous materials (Penn et al., 2007; Martínez-Rodríguez et al., 2010; Ippolito et al., 2011; Bryant et al., 2012; McGrath et al., 2013) would be needed to mollify efficiency lags in P capture.

It is possible that P release rates recorded in this experiment surpass release rates in the field. The drying of mesocosms (preparing mesocosms for wax application to preclude bypass flow) and higher temperatures than encountered in the field (greenhouse setting) could be expected to induce the release of P (Baldwin and Mitchell, 2000; Qiu and McComb, 2002; Xu et al., 2011).

Further Steps

The high Fe content of the mesocosm source ditch likely occurs because of a near-surface layer of pyrite that underlies our field site (Vaughan et al., 2008). The high Fe and sulfur concentrations that result (Vaughan et al., 2008) allow the retention of Fe to occur under aerobic (Fe oxides) or anaerobic (Fe monosulfides) conditions. The similarity of ditches at our site to other locations in the MACP has not been determined, but high-Fe and -sulfur parent materials are widespread (Fanning, 2006). The fact that many studies of MACP ditches originate at our field site (Kleiman et al., 2007; Vaughan et al., 2007a, 2007b, 2008; Shigaki et al., 2008; Church et al., 2010; Ruppert et al., 2014) indicates a need to characterize additional sites to determine how representative the results of this and the above studies may be. Studies to measure emergent porewater Fe:P are also merited.

Conclusions

Our experiment featured soils from a ditch high in Fe. Treatments (soil and hydrologic) did not capture P from input water. Mesocosms taken from the ditch after dredging featured throughput water with P contents indistinguishable from input water; mesocosms taken from the ditch before dredging released P to throughput water, especially when redox conditions were Fe reducing. Iron-reducing conditions not only released P but also Fe, indicating a mechanism whereby P capture may occur outside the soil environment. The capture of P outside the soil environment should prompt the rethinking of techniques used to understand P capture in ditches. Whereas dredging removes materials prone to P release, the simultaneous lowering of the profile will induce more frequent saturation, potentially limiting the P-related benefits of dredging. Rates of P release recorded in our experiment may overstate P release in the field because our mesocosm soils were, at times, subject to lower moisture contents and higher temperatures than in the field.

Supplemental Material

To shorten the Materials and Methods section, some content has been placed in an online Supplemental Materials section, with